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TITANIUM - 1966

Lectures Given at a Norair Symposium,
March 28-29, 1966

DEFENSE METALS INFORMATION CENTER

BATTELLE MEMORIAL INSTITUTE

COLUMBUS, OHIO 43201

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FORWARD

On March 28-29, 1966, the Norair Division of the Northrop Corporation sponsored a Titanium Symposium in the Hawthorne Memorial Center at Hawthorne, California. The primary objective of the symposium was to provide technical personnel of diversified disciplines with a working knowledge of titanium technology. The papers were designed to be of value to a nonmetallurgical technical audience as well as enlightening to those familiar with titanium technology. The format developed by Norair in conjunction with DMIC followed a logical sequence of talks covering metallurgy, manufacturing technology, and design of titanium parts for aircraft and aerospace applications.

The secondary purpose of the symposium was delineated by Dr. R. L. Jones, Director, Research and Technology at Norair, in the symposium summation. Dr. Jones called for a greater use of the interdisciplinary approach in aerospace design. Essentially the interdisciplinary approach calls for utilization of all required support technologies (materials, manufacturing, quality control, etc.) early in the conceptional design state rather than piecemeal after the design has been formalized.

Because of the renewed and current widespread interest in titanium, the Defense Metals Information Center, in cooperation with Norair, has reproduced in this memorandum the thirteen lectures that were delivered at that symposium. This was done in the belief by DMIC that, for those new to titanium, this collection of papers offers a fairly simple yet comprehensive picture of titanium technology as it exists today. DMIC also believes that many of those who are already familiar with titanium can profit from a review of the recent developments which have occurred, particularly in the areas of corrosion behavior, forging, extrusion, forming, joining, and design, and which are summarized herein.

In assembling these various manuscripts for publication, DMIC gratefully acknowledges the assistance of Dr. E. B. Mikus, Chief of Materials Research at Norair, who organized the symposium and acted as Symposium Chairman, and of B. G. Calfin, Metallics Research Branch at Norair, who served as Symposium Coordinator. DMIC is also grateful to the Northrop Corporation as well as to the individual lecturers and authors for their permission to publish these papers. A list of the individual contributors to this symposium is given below.

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TITANIUM - YESTERDAY, TODAY, AND TOMORROW

J. G. Louvier*

What is the status of titanium today? One does not have to read the technical metal journals to find out. One has only to read the comics, and let "Dick Tracy" inform one of titanium, the titanium space coupe and the titanium trade with Moon Valley. Titanium has become a comic strip by-word. What better criteria could be found to establish titanium as one of today's prime space age materials. However, do not be misled by this current popularity of titanium; it is not a newly discovered element. A brief review of the history and evolution of this metal appears warranted prior to expounding on its current status and future potential.

HISTORY

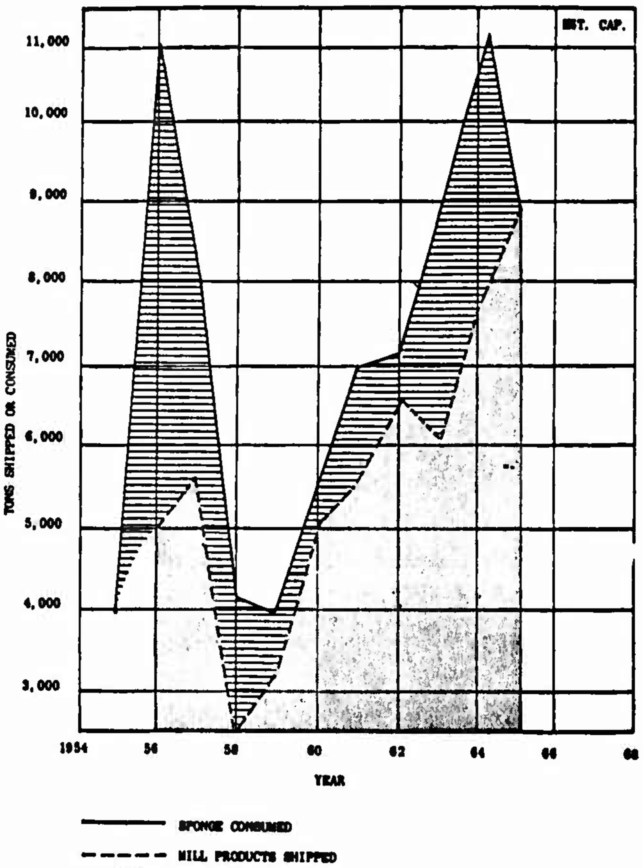
Titanium was first discovered in 1790, approximately 175 years ago, as a constituent in black sand, ilmenite, by an English clergyman and amateur alchemist, William Gregory. He called the element menachanite after the town Menachan near where it was discovered. However, it was an Austrian, M. H. Klaproth, who in 1795 discovered the identical element while analyzing rutile and gave the element its present name of titanium, after twelve Greek mythical gods known as the Titans, the earliest giants of the earth.

Many minerals contain titanium, but only two are of prime commercial importance, ilmenite and rutile - the very minerals in which titanium was first discovered. Ilmenite is a combined iron-titanium oxide of varied composition, while rutile is titanium dioxide, richer in titanium than ilmenite but generally diluted with other minerals. The important sources of ore in North America are the Lake Allord district of eastern Quebec; Lake Sanford, New York; Iron Mountain, Wyoming; and Pablo Beach, Florida. Titanium ores are also abundant, of course, in other areas of the world. In fact, titanium ranks ninth among the elements in abundance in the earth's crust, being exceeded only by oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. Thus, titanium, far from being a rare element, is actually quite an abundant one. The difficulties encountered in processing the titanium ores into metal have kept titanium classified for so long as a rare metal.

Not until over a century after its discovery was the element titanium isolated from the compounds it so readily forms with such elements as oxygen, nitrogen, and carbon. Some have likened titanium to a "streetwalker" because it will pick up anything and everything. In 1910, M. A. Hunter in a General Electric Laboratory succeeded in obtaining the first metallic titanium by the chlorination of the titanium oxide ore and the subsequent reduction of the titanium tetrachloride with sodium in an air-tight steel container. Titanium remained a laboratory curiosity, however; until 1946 when Dr. William J. Kroll, under the auspices of the Bureau of Mines, proved that titanium metal could be produced on a pilot-plant scale using a process he had been developing for a number of years involving the reduction of titanium tetrachloride with molten magnesium. The product from this process is in a cinder-like form and is referred to as sponge. Du Pont advanced the Kroll process to a commercial scale and became the first producer of metallic titanium or titanium sponge for general sale in September of 1948.

PRODUCTION

The production of titanium was enthusiastically promoted by the government after World War II. As presented graphically in Figure 1, titanium production increased steadily, as did the number of producers, until the peak year of 1957. At this time, Defense Department curtailment of aircraft construction contracts and government subsidy resulted in a reduction of titanium production from 100 percent capacity to 6 percent capacity within a 6-month period. Correspondingly, the number of producers dropped from a high of 25 to 6. This recession did not alter the continuing steady decrease in titanium prices.



W.W.WINKLER, Reference 1 (Modified)

FIGURE 1. ANNUAL SPONGE CONSUMPTION AND MILL PRODUCT SHIPMENTS

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The titanium industry survived largely on its own merit from this depression period. Production and use of mill products increased steadily from this period until they recovered and eventually surpassed the peak of 1957 while continuing the reduction in product costs. Sponge costing approximately \$5 per pound in 1953 was being sold for \$1.25 per pound in 1965. Percentage reductions in mill products were comparable, decreasing from \$25 to \$50 per pound to \$6 to \$18 per pound depending on the product. The shipments of mill products for 1966 are expected to exceed 10,000 tons. This quantity will be the result of the efforts of two U. S. sponge producers, supplemented by 16 percent import, principally from Japan, and six mill products producers. The impetus for this ever-rising production rate has been attributed to a combination of improved technology, reduced cost, and increased application.

APPLICATION

Practically all of the titanium produced is being used for defense requirements with civilian application increasing with decreasing cost.

The largest current usage of titanium and titanium alloys as shown in Table 1 is in civilian and military jet engines, accounting for 40 percent of the total production. Titanium has been used in almost every jet engine that has been built. Jet engine components fabricated of titanium are compressor wheels, hubs, shafts, spacers, and blades.

TABLE 1. CONSUMPTION OF TITANIUM BY APPLICATION, 1963 to 1965

Application	Percent of Total Titanium Shipped in Year Specified 1965	1964	1963
Jet Engines (Includes Small Percent Civilian)	40	24	25
Aircraft Frames (Includes Small Percent Civilian)	30	46	36
Missile and Spacecraft	15	21	32
Civilian	10	8	6
Miscellaneous (Navy Vessels, Ordnance, Hardward, Experimental	5	1	1

Aircraft frames, including fire walls, access doors, stiffeners, doublers, cowlings, and rip stoppers run a close second to jet engines in titanium usage, requiring 30 percent of the total production. In fact, in 1964, the percentage consumption values for jet engines and airframes were approximately reversed, with airframes accounting for maximum usage.

Missile and space vehicle application, a leader in 1963, is currently third in titanium usage at 15 percent of the total production. Rocket motor cases, oxidizer and fuel tanks, rocket engine nozzles, nozzle extensions, pressure vessels and engine skirts, as well as frames and skins are typical missle and space vehicle components fabricated of titanium.

Civilian usage of titanium attained an all-time high in 1965, requiring 10 percent of the total production. This 10 percent was consumed in valves and pumps for corrosive chemicals; in wire cloth, screens, and filter presses for filtering equipment; in anodizing racks for electroplating; and in heat exchangers, condensers, and tank linings where corrosion may be a problem.

MATERIAL CHARACTERISTICS

The reasons for the increasing usage and application of titanium and titanium alloys are obvious upon consideration of the material properties versus the requirements of the aerospace, ordnance, and chemical industries, the prime users. The characteristics of titanium so essential to these industries and to their future progress are numerous and are shown in Table 2 in comparison to 7075 aluminum and 4130 steel.

TABLE 2. COMPARISON OF SOME BASIC PROPERTIES OF Ti-6Al-4V TITANIUM, 7075 ALUMINUM AND 4130 STEEL

Property	Titanium (6Al-4V)	Aluminum (7075)	Steel (4130)
Density (lbs/in.^{3})	0.161	0.100	0.283
Elastic Modulus (psi x 10^6)	16.5	10.5	29.5
Melting Temperature (degrees F)	3020	1180	2795
Coefficient of Linear Expansion (10^{-6} in./in./F)	5.5	12.5	6.5
Thermal Conductivity (Btu/hr/ft^2/F/Ft)	4	75	26
Yield Strength Heat Treated (Typical ksi)	155	70	160
Strength to Weight Ratio (10^3 inch)	963	700	565
Elastic Modulus to Weight Ratio (10^6 inch)	102	105	104

The density of titanium (0.161 lbs/in^3) is about midway between that of aluminum (0.100 lbs/in.^{3}) and steel (0.286 lbs/in.^{3}) justifiably classifying the material as a light weight metal. This low density in conjunction with the high strengths attainable results in exceptionally high strength to weight ratios, approximately double that of steel having an equivalent strength. Strengths can be obtained ranging from 40,000 psi for commercially pure titanium to 200,000 psi for certain alloyed grades. The creep strength is superior to other light weight metals, with some titanium alloys retaining useful strength for short periods at temperatures up to 800 F.

The tensile modulus of elasticity, an indication of stiffness, ranges from approximately 15 to 18 x 10^6 psi, and is considerably higher than that of aluminum alloys (10.5 x 10^6 psi) but is only about 1/2 that of steels (29.5 x 10^6 psi). However, again upon consideration of the low density, the elastic modulus to weight ratio is comparable to that of the steel alloy.

The coefficients of expansion and thermal conductivity of titanium alloys are much lower than that of either aluminum or steel alloys.

The corrosion resistance of titanium is phenomenal, being virtually immune to attack by salt water, marine and industrial atmospheres, and oxidizing solutions or acids. This excellent corrosion resistance is due largely to a thin tenacious oxide film which forms on the surface of titanium. However, titanium can be attacked by strong reducing acids, and certain alloys are susceptible to aqueous environmental cracking and hot salt-stress corrosion cracking.

Probably one of the most important properties of titanium, and the least emphasized or acknowledged is its ability to alloy readily with most metals and many of the non-metals. This ability enables adjustment of the material characteristics to meet explicit requirements, affording extreme versatility. The alloys are usually designated by the chemical symbol and the percent of the major alloying element additions such as: Ti-6Al-4V, Ti-5Al-2.5Sn, etc. An exception is commercially pure titanium in which CP titanium is usually used preceded by the minimum yield strength in ksi of the specific alloy grade, i.e., 40 CP titanium, 70 CP titanium. Specific types and quantities of alloying additions affect the phases present in the structure of the metal. This is manifested by three types of structures by which the alloys are classified:

(1) Alpha - single phase, not heat treatable. Exemplary alloys are CP titanium and Ti-5Al-2.5Sn.

(2) Alpha-beta - two phase, heat treatable, the extent of heat treatment proportional to the ammount of beta, or second phase present. Ti-6Al-4V and Ti-6Al-6V-2Sn are typical alloys.

(3) Beta - single phase at room temperature, heat treatable to higher strengths than the other alloys, but not stable, particularly on extended exposure above 600 F. Only one commercial alloy, Ti-13V-11Cr-3Al.

ALLOYS

In 1954 only 6 alloy grades of titanium were produced, with this number increasingly consistently with the passing years, to attain 19 by 1959 and 30 by 1965. However, 85 percent of the mill products shipped in 1965 were composed of only three grades: Ti-6Al-4V, Ti-5Al-2.5Sn, and unalloyed. Of these three grades, Ti-6Al-4V accounted for 60 percent of the production, with the remaining 25 percent being divided about equally between unalloyed and and Ti-5Al-2.5Sn. As shown in Table 3, this percent usage by alloy grades has followed this pattern with little deviation for a number of years. However, the trend toward the use of higher strength titanium alloys is now evident and is shown schematically in Figure 2. A total of 8 grades, 3 unalloyed and the alloy grades Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, Ti-6Al-4V, Ti-6Al-6V-2Sn, and Ti-13V-11Cr-3Al, are used for about 90 percent of the applications. The material characteristics of these grades are described below and summarized in Table 4.

TABLE 3. TITANIUM SHIPMENTS BY ALLOY GRADE, 1960 to 1964

ALLOY GRADE	PERCENT OF TOTAL TITANIUM SHIPPED IN SPECIFIED YEAR		
	1964	1962	1960
6Al-4V	60	65	60
5Al-2.5Sn	12	9	7
UNALLOYED, 3 GRADES	13	13	19
OTHER	15	13	14

The three unalloyed grades having minimum tensile yield strengths of 40 ksi, 55 ksi, and 70 ksi are actually alloys of titanium with oxygen. These commercially pure grades are all alpha phase and cannot be heat treated. These grades afford the maximum formability, possessing the greatest ductility, as well as the best corrosion resistance and weldability. They also, of course, comprise the grades with the least strength. The unalloyed grades are available in all forms, including seamless tubing.

The Ti-5Al-2.5Sn grade is also a non-heat-treatable all alpha alloy, but possesses moderate strength, approximately 35 percent greater than the strength attainable in the 70 ksi unalloyed grade. Creep resistance is superior since a high percentage of its room-temperature strength is maintained at temperatures to 800 F. Formability is only fair to good, but it is one of the most weldable alloys. Ti-5Al-2.5Sn is more susceptible to hot salt-stress corrosion than any of the other commercial alloys. The alloy is readily available in all forms except tubing.

The Ti-8Al-1Mo-1V alloy is one that is termed a near alpha or super alpha alloy; the beta content for this alpha-beta alloy being too low to be of any practical value for heat treatment. However, its strength in the annealed condition is higher than for any other alpha alloy with corresponding superiority in creep resistance. The alloy is subject to an ordering reaction (a systematic repetition of the atomic structure) when exposed to temperatures in the range of 900 F to 1300 F and slowly cooled. Strength is increased slightly at the expense of reduced fracture toughness. However, fracture toughness after special annealing treatments, (e.g., duplex annealing, which eliminates the order structure), is higher in proportion to its strength than that for any other alloy. The formability of the alloy is only fair, but weldability is good. Unfortunately, the alloy is one of the more susceptible to aqueous environmental cracking and to hot salt-stress corrosion.

The Ti-6Al-4V grade and its stronger modification Ti-6Al-6V-2Sn are both alpha-beta alloys and, therefore, are heat treatable. The Ti-6Al-6V-2Sn alloy is heat treatable to higher strengths (180,000 minimum ultimate) than any other alpha-beta alloy. Weldability of Ti-6Al-6V-2Sn is considered poor and also somewhat inferior to Ti-6Al-4V. Formability of both alloys is fair in the annealed

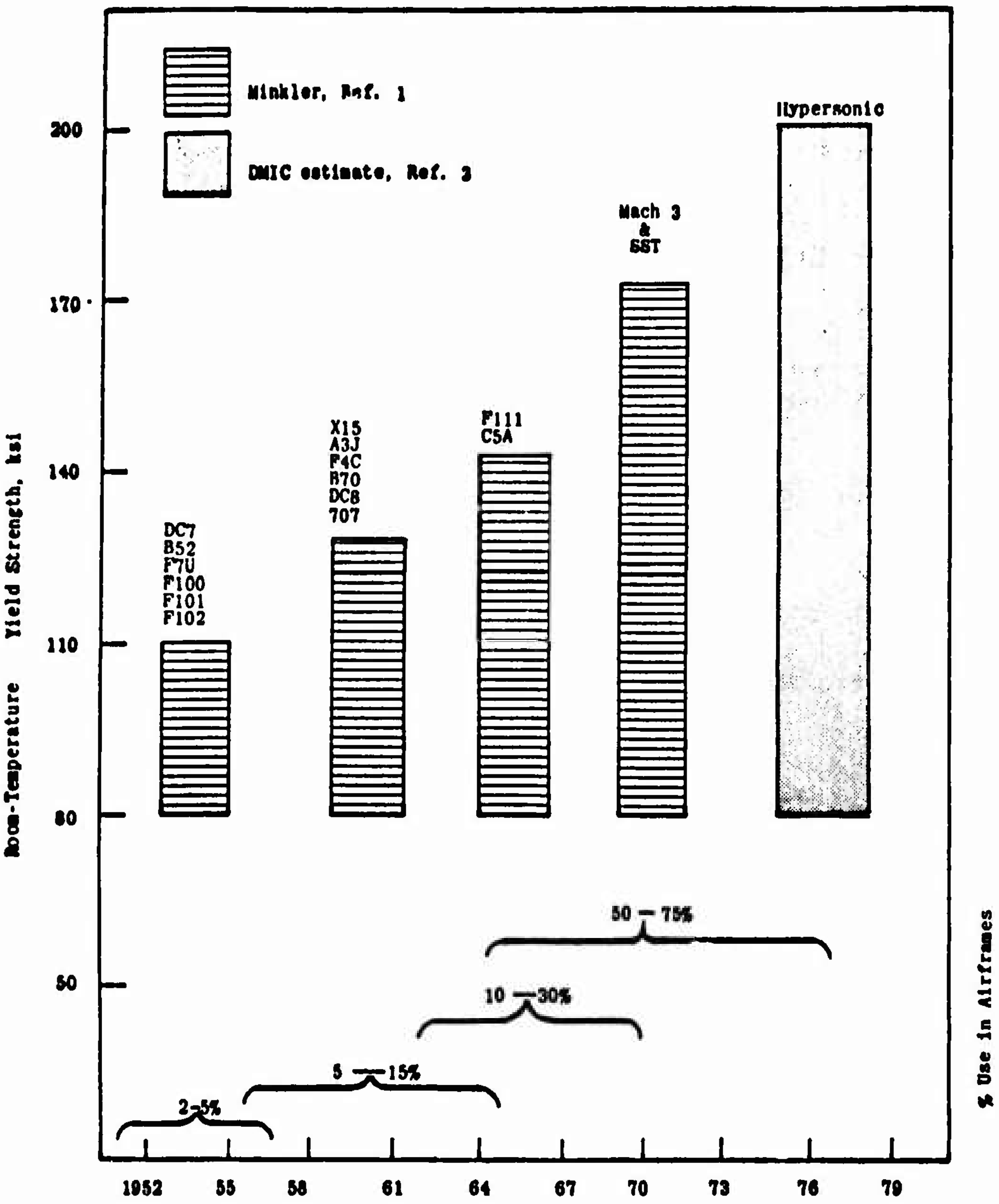

FIGURE 2. RANGE OF TITANIUM AND TITANIUM-ALLOY YIELD STRENGTHS AND PERCENT USED IN AIRFRAME VERSUS TIME

or solution-treated conditions, with Ti-6Al-4V considered the superior of the two alloys in this respect. Ti-6Al-4V is available in all forms except tubing, while Ti-6Al-6V-2Sn is available primarily in heavy sections such as plate, forgings, and extrusions. Ti-6Al-6V-2Sn sheet stock is being produced in limited quantities, and usage is expanding.

Ti-13V-11Cr-3Al is the only commercial all beta alloy. This alloy can be heat-treated to the highest strengths (over 200,000 psi ultimate) of any commercial titanium alloy. However, the heat-treated alloy has limited stability on prolonged exposures above 600 F, but it does retain a high percentage of its room-temperature strength at temperatures up to 800 F. This grade can be formed readily before aging. The alloy is weldable, but the welds tend to embrittle after aging and, therefore, the weldability is limited. Fracture toughness is considerably inferior to other alloys and the alloy is also susceptible to hot salt-stress corrosion. The alloy is available in all forms except tubing and with extrusions being in limited supply.

Other alloys in considerable use, but to a lesser extent than those described above, are Ti-8Mn, Ti-4Al-3Mo-1V, Ti-7Al-4Mo, and Ti-7Al-2Cb-1Ta among others.

FORECAST

The titanium used in making these alloys is still produced by essentially the same procedure perfected in the late 1940's by Dr. W. J. Kroll. The process, however, has reached its economic limit and further reduction in titanium raw metal or sponge cost depends on the development of a more efficient process. Although recognized as not being an easy task, the industry is already attempting to improve the situation.

TABLE 4. SUMMARY OF MATERIAL CHARACTERISTICS OF PREDOMINENT COMMERCIAL ALLOYS

ALLOY	TYPE	HEAT TREATABILITY	ULTIMATE STRENGTH TYP. ksi	WELDABILITY	FORMABILITY	COMPARATIVE ELEV. TEMP. LEVEL F FOR GOOD STRENGTH
Unalloyed	Alpha	None	60-95	Excellent	Excellent	400
5Al-2.5Sn	Alpha	None	130	Excellent	Good	800
8Al-1Mo-1V	Near or super alpha	Not practical Has structural ordering	140 155	Good	Fair, Slightly less than 6Al-4V	900
6Al-4V	Alpha-Beta	Fair	Ann. 140 H.T. 165	Ann. Good H.T. Fair	Fair (Ann. or ST)	750
6Al-6V-2Sn	Alpha-Beta	Good	Ann. 155 H.T. 180	Poor	Fair	750
13V-11Cr-3Al	Beta	Excellent	Ann. 140 H.T. 190	Ann. Good H.T. Questionable, embrittles on aging	Good (Ann. or ST)	600 (unstable above)

New mills are being developed tailored specifically to the requirements of the titanium industry in order to attain increased production of more products with superior quality. One major producer has already initiated a continuous strip rolling mill incorporating a continuous vacuum annealing furnace capable of producing strip up to 52 inches wide by 0.010 to 0.080 inch thick. The maximum circumscribing circle size (overall size) attainable in extrusions has recently been expanded from 7 to 9 inches, with a further increase in size to be expected as larger extrusion presses are utilized. Along with this increase in circle size, the maximum extrudable length has been extended from 25-30 feet to 40-50 feet, depending on the cross-sectional area. Castings are not widely used and the availability is very limited. However, recent developlments may change this status for the better.

A low-temperature (400 F) salt bath descaling process has been developed for removing tenacious high-temperature oxide scale. Research is being performed to further reduce the descaling temperature and improve the process. Coatings which inhibit scaling during elevated-temperature exposure in air, and that may even serve the dual purpose of acting as a lubricant during hot forming, are being investigated intensively. Their development would alleviate considerably the difficult descaling requirements.

Improved production or fabrication technology results in lowered cost with increasing application, particularly by civilian users. The civilian market is expected to increase in 1966 by as much as 50 percent. New programs in hydrospace (deep submergence vehicles), desalination, and hardware are also expected to exert their influence. The greatest potential for titanium application is again considered to be in airframe structures, with the total titanium production, as mentioned previously, expected to exceed 10,000 tons in 1966.

In conjunction with improved manufacturing technology, research is being constantly conducted to develop new alloys or treatments in order to remedy any adverse or undesirable characteristics, as well as to enhance or achieve essential properties that may have been either inadequate or lacking. Higher strength alloys will be available in the near future with strength-to-weight ratios increased from approximately 995 x 10^3 to 1400 x 10^3 and with improved elevated-temperature stability so as to extend structural application from 900 F to the 1100 to 1200 F range.

New alloys are being developed to afford increased resistance to hot salt cracking, notably the modification of the Ti-7Al-2Cb-1Ta alloy to Ti-6Al-2Cb-1Ta-0.8Mo and the new high-strength alloy Ti-2Al-4Mo-4Zr. The addition of 4Zr to the Ti-6Al-6V-2Sn alloy results in significant strength and ductility improvements, while the modification of Ti-5Al-2.5Sn alloy with 2.5V and 1.3Cb affords markedly improved cryogenic properties down to -423 F. Various thermal treatments are also being investigated and developed which may alter the characteristics of specific alloys sufficiently to make them satisfactory with regard to their heretofore unacceptable properties such as fracture toughness, hot salt-stress cracking, or aqueous environmental cracking.

With the titanium producer and researcher making obvious all-out efforts to meet the requirements of the designer and consumer, and the consumer, and the designer and consumer applying to the fullest extent those characteristics of titanium which are so desirable, titanium should truly become the Titan, after whom the metal was so aptly named, of the space age materials.

REFERENCES

The following references were used in addition to the technical sales literature published by the Titanium Metals Corporation of America.

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BASIC TITANIUM METALLURGY

Dr. E. L. Harmon*

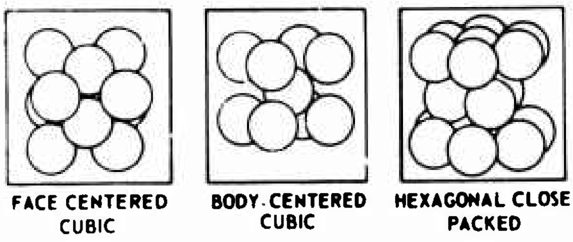
In order to present a reasonably representative introduction to basic metallurgy in the short time allotted, we will only be able to cover selected high spots of the subject matter.

Some of the more important characteristics of metals and alloys in general will be described, with particular reference to titanium.

Let us consider the solidification of a metal from the melt. Usually several nuclei will start to solidify simultaneously as a molten metal is cooled. A given solid nucleus, or crystallite, will grow until it bumps into another crystallite which is growing from a different direction. When the metal has completely solidified, it will contain numerous crystallites, called grains, which are contiguous with one another. Within each grain all of the atoms will be arranged in a regular lattice-like array. This geometric pattern that the atoms tend to form when a metal solidifies is known as its crystal structure or crystal lattice. The three most important types for metals are:

(1) Face-centered cubic
(2) Body-centered cubic
(3) Hexagonal close-packed.

These are illustrated in Figure 1.



THREE COMMON TYPES OF CRYSTAL STRUCTURE WITH SPHERES REPRESENTING ATOMS

FIGURE 1.

The term face-centered cubic arises from the fact that atoms are located at the corners of a cube and also at the center of each of the faces of the cube. Similarly, in the body-centered cubic crystal structure atoms are located at the corners of a cube and also one atom is located right in the center of the cube. The atoms in the hexagonal close-packed crystal structure are located at each of the corners of the hexagon. In addition, there is an atom in the center of the top face, one in the center of the bottom face, and three atoms within the hexagon located halfway between the top and bottom faces. There are pronounced differences between the hexagonal close-packed structure and both the body-centered cubic and face-centered structures. A cube, whether it is body-centered cubic or face-centered cubic, appears the same whether you are looking at it from one of the four sides or the top or bottom face. The appearance and the behavior of a hexagon, however, are highly orientation dependent. Crystallography of metals is a very complicated subject, and it is not the intent to go into detail here. The important points to remember are two: first, there are important differences in the geometrical arrangement of atoms within the three different crystal structures; secondly, because of these geometrical differences, there are significant differences in the behavior and properties of one type of structure compared with another. As a general rule hexagonal close-packed metals and alloys are more difficult to deform than cubic metals and alloys, and their properties can be highly orientation dependent. Of the two cubic structure types, face-centered cubic is harder to deform than body-centered cubic.

It is important to realize that these structures or unit cells do not exist within the metal as discrete little cubes or hexagons, as depicted here. Even the smallest recognizable grain or crystallite of solidified metal contains millions of atoms. However, these millions of atoms are arranged in an orderly, three-dimensional lattice-like array whose geometry at any point in the entire array, is characterized by one of these unit cells. This regularity and repetitive nature of the lattice is interrupted only at the boundary of the grain, where it meets another grain which started to grow from the liquid at a different point and with a different orientation.

Now, let us look at what the crystal structures are for some of the common metals. As shown in Table 1, aluminum and copper are each face-centered cubic, magnesium is hexagonal close-packed, iron is body-centered cubic at temperatures up to 1650 F. Above this temperature, the iron atoms are not thermodynamically stable in the body-centered cubic arrangement, and a phase transformation occurs wherein the atoms rearrange themselves into a face-centered cubic structure. At still higher temperatures, above 2550 F, the body-centered cubic crystal structure again becomes the most stable phase. The change from one phase to another that takes place within a metal at a certain temperature is known as an allotropic transformation. Titanium also exhibits an allotropic transformation at about 1625 F. Below this temperature, the hexagonal close-packed (alpha) phase is stable, and above 1625 F, the body-centered cubic (beta) phase is stable.

The occurrence of a phase transformation in titanium is very important and, as will be seen later, forms the basis for classification of titanium alloys as alpha, alpha-beta, or beta types.

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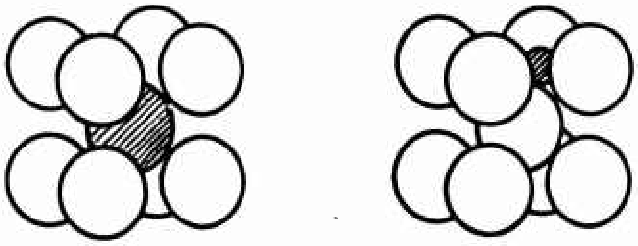
TABLE 1.

METAL	CRYSTAL STRUCTURE
ALUMINUM	FACE-CENTERED CUBIC
COPPER	FACE-CENTERED CUBIC
MAGNESIUM	HEXAGONAL CLOSE-PACKED
IRON	BODY-CENTERED CUBIC (BELOW 1650 F) FACE-CENTERED CUBIC (BETWEEN 1650-2550 F) BODY-CENTERED CUBIC (ABOVE 2550 F)
TITANIUM	HEXAGONAL CLOSE-PACKED (ALPHA PHASE) (BELOW 1625 F) BODY-CENTERED CUBIC (BETA PHASE) (ABOVE 1625 F)

Another very important characteristic of a metal is its ability to dissolve other elements. These other elements may go into "solid solution" in a metal in one of two ways: substitutionally, or interstitially, as shown in Figure 2. Solute elements which have about the same atomic size (within about 15 percent) of the solvent or base metal may form substitutional solid solutions if other factors such as electronegativity and valence are favorable. That is, individual solute atoms replace individual solvent atoms in the original crystal structure, as illustrated in the figure for a body-centered cubic structure (which could be beta titanium, for example). As an example, zirconium is very close to titanium in atomic size and the other factors are favorable. Therefore, titanium is capable of completely dissolving zirconium and vice versa. Other elements, for which the factors promoting substitutional solid solution with titanium are not quite so favorable, will dissolve in titanium only to a limited extent.



SUBSTITUTIONAL AND INTERSTITIAL SOLID SOLUTIONS

FIGURE 2.

Elements which have a very small atomic size, such as carbon, nitrogen, oxygen, hydrogen, and sometimes boron, form interstitial solid solutions with metals. That is, these small elements are dissolved in the interstices, or vacant spaces which exist between the atoms in the crystal structure, as illustrated. The interstices in a body-centered cubic structure, such as beta titanium are not as large as the interstices in a hexagonal close-packed structure, such as alpha titanium. Therefore, one might expect (as is the case) that alpha titanium has a higher tolerance for interstitials such as carbon, oxygen and nitrogen than does beta titanium.

One might ask the question, "How do we get elements into solution in a metal?" The usual way is to melt the metal, together with the alloying elements, and let it cool down and solidify. Another method is to mix fine powders of the metal and alloying elements, press them together into intimate contact and hold the mixture at a high temperature below the melting point. At high temperatures, the atoms will diffuse among one another and effect essentially the same result as melting.

The characteristics of crystal structure, phase transformation and solid solubility lead to consideration of equilibrium phase diagrams. An equilibrium phase diagram is essentially a map describing the quantities and compositions of the various phases present in an alloy at any temperature, under equilibrium conditions. It is an extremely useful tool in understanding and predicting alloy behavior. We will confine our discussion to binary equilibrium phase diagrams, which are the simplest to understand and interpret. Binary denotes that there are two elements involved, e.g., iron and carbon, or aluminum and copper.

Two examples of equilibrium phase diagrams which have been very useful for many practical commercial applications are the iron-carbon and the aluminum-copper diagrams. The iron-carbon equilibrium diagram provides the basis for understanding the strengthening of steel. The aluminum-copper equilibrium diagram explains the familiar phenomenon of age-hardening which occurs in many commercial aluminum alloys. In the same way, equilibrium diagrams of titanium with various alloying elements can be helpful in understanding and predicting behavior and properties of commercial titanium alloys. In a short while, we will present the various common types of equilibrium phase diagrams that are important to titanium alloy technology, but first we will present one particular diagram, of a simple type, for the purpose of illustrating what an equilibrium phase diagram tells us and how it can be used. Let us consider the titanium-vanadium system, Figure 3.

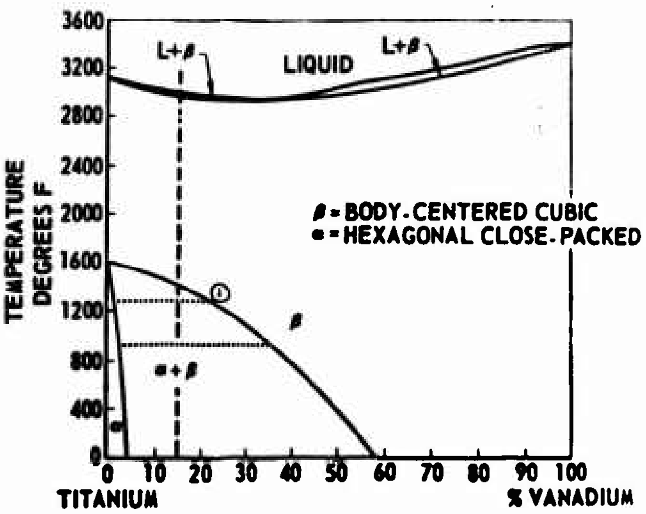


FIGURE 3.

We will start by discussing the behavior of titanium alone, then the behavior of vanadium alone, and then we will get into the significance of the diagram itself. Above 3150 F degrees titanium is liquid. As it cools down below this temperature, titanium solidifies into a body-centered cubic crystal structure called beta titanium. Upon continued cooling this phase remains stable until a temperature of 1625 F is reached. As titanium is cooled below this temperature, the body-centered cubic structure becomes unstable, and the atoms rearrange themselves into an energetically more favorable hexagonal close-packed phase designated alpha titanium, which is stable at temperatures all the way down to absolute zero. Vanadium melts at 3300 F. It solidifies into the body-centered cubic crystal structure, also. However, it does not exhibit a phase transformation as does titanium.

Now, let us mix up powders or chunks of pure titanium and pure vanadium - in the proper proportions - so that we have an average composition of fifteen percent vanadium by weight. Let us heat this mixture up to a very high temperature, and melt it. Next, we will slowly cool this mixture, or alloy, as it is now more properly termed, and examine what happens to it. As we reach a temperature just below the liquid line, solid particles with a body-centered cubic crystal structure will form within the liquid. If we stop cooling, and maintain the alloy at this temperature, it will never completely solidify. It will consist of solid particles of less than 15 percent vanadium content in liquid of higher-than-15 percent vanadium content. Now, if we continue to cool, the solid particles will grow at the expense of the liquid until the liquid is all used up and the composition of the solid is exactly 15 percent vanadium. Thus, we see that in an alloy, solidification takes place over a range of temperatures, as compared with a fixed temperature in a pure metal.

Now that the alloy is completely solidified, continued cooling produces no structural changes until we reach the alpha-beta, beta phase boundary. This temperature is called the beta transus temperature for this alloy.

As we cool below this temperature the body-centered cubic beta phase becomes supersaturated with titanium. It needs to have more vanadium and less titanium in it. In other words, at the temperature designated by the upper dotted line in Figure 3, the beta phase would like to have the composition at Point ①. The way it accomplishes this is to reject titanium-rich hexagonal close-packed alpha phase in the form of small particles or precipitates. This alloy when it reaches equilibrium at this temperature will consist of alpha phase distributed uniformly within a matrix of beta phase. The compositions of the two phases are given by the intersection of the temperature line with the respective phase boundary. The relative quantities of alpha and beta depend upon how close the alloy composition is to the respective phase boundaries along the constant temperature line. If we continue cooling to a lower temperature, such as to the lower dotted line in Figure 3, and wait long enough for equilibrium to be reached, the quantities and compositions of the two phases, alpha and beta, will adjust themselves as prescribed by the equilibrium phase diagram. At this particular lower temperature, for example, there will be considerably more alpha present, and correspondingly less beta phase, but the beta will be very rich in vanadium.

The equilibrium diagram describes the quantities and compositions of the various phases present in an alloy under equilibrium conditions. It does not tell us anything about the time it takes to reach equilibrium. However, in general the higher the temperature the quicker an alloy goes to equilibrium. On the other hand, at low temperatures, it may take an extremely long time. In titanium alloys, for example, below about 1000 to 2000 F, equilibrium is not attained within practical time periods, even after times as long as several days. The mechanism by which an alloy approaches equilibrium is through diffusion, a process by which atoms rearrange themselves within the solid crystalline structure of the alloy. Diffusion is accelerated at high temperatures, where the increased thermal energy of the atoms makes it easier for them to migrate through the crystal structure.

Now, let us look at what happens if, instead of cooling slowly, we were to quench the alloy rapidly from a temperature within the beta region, to room temperature. Provided the quenching were done rapidly enough, diffusion would not have time to take place, and the atoms would be "frozen" in their positions. At room temperature, then, the alloy would consist entirely of highly supersaturated body-centered-cubic beta phase, which would like very much to throw out some of the titanium atoms in the form of alpha phase and adjust its own composition to some higher vanadium content. This tendency for the beta phase to attain a lower energy state is so great that even at room temperature where diffusion is very sluggish, we can notice an increase in the hardness of the alloy after a few days. This increase in hardness (known as age hardening, or just aging) reflects the first step in the quest for equilibrium. It is caused by precipitation of extremely small particles, rich in titanium, which are the precursors of the hexagonal close-packed alpha phase.

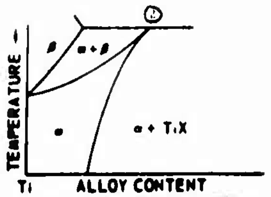
We can increase the magnitude and rate of this precipitation and related hardening by reheating the quenched beta phase to some moderately elevated temperature, e.g., 800 F. In order to attain a desired hardness level, the aging time and temperature must be carefully selected. Aging at too high a temperature or for too long a time causes coalescence of the fine alpha particle which cause the hardening. As a result of this coalescence, the alpha particles become bigger, but there are fewer of them. Since the hardness is more dependent on the number of particles than on their size, coalescence is accompanied by softening or "overaging". This behavior is basically identical with that of aluminum alloys with which most of you are familiar.

In practice, a titanium alloy is usually not quenched from the beta region and aged, but it is held at a high temperature (slightly below the beta transus temperature) to allow some alpha to form in equilibrium with a richer alloy content beta. Quenching from this intermediate temperature permits subsequent aging of the supersaturated higher alloy beta without any appreciable reaction of the "primary" alpha which was formed at the high temperature. This procedure normally results in better mechanical properties.

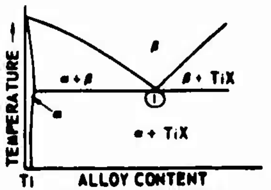
Now, if we had selected a 10 percent vanadium alloy instead of a 15 percent vanadium alloy, and rapidly quenched it, we would have observed different behavior. In this case, also, diffusion would not have time to occur, but in this alloy the beta phase is even more supersaturated with titanium, that is, the vanadium content of the beta is even farther away from equilibrium as compared with 15 percent vanadium. For this reason, during the rapid cooling process, when the alloy reaches about 900 F, the body-centered-cubic beta phase becomes mechanically unstable and transforms by a shearing process to a crystal structure in a lower energy condition, in this case the hexagonal close-packed phase. Since rapid cooling prevented diffusion, this hexagonal close-packed phase will contain 10 percent vanadium. A look at the equilibrium diagram shows that at room temperature, the hexagonal close-packed alpha phase should only contain about 3 percent vanadium. Thus, we now have supersaturated alpha, or what is commonly designated alpha prime. This alpha prime wants to get rid of its excess vanadium by precipitating small particles of vanadium-rich beta and will do so, upon aging, in a manner analogous to supersaturated beta, as described before. This shear transformation, which occurs upon quenching the beta phase in alloys containing less than 15 percent vanadium, is called a martensitic transformation because it resembles the martensitic transformation in iron-carbon alloys, which is the basis for the strengthening of steels.

All right, now we have covered quite a bit of territory in discussing this equilibrium diagram. The purpose was to expose you to some of the concepts and terminology that you will hear later on. The important points to remember are: First, the equilibrium diagram describes the quantities and compositions of the various phases present in an alloy under equilibrium conditions. Secondly, we very rarely have, or want, equilibrium conditions. However, the basis of all heat treatment is the tendency of an alloy to proceed toward its equilibrium condition. If we are clever, we take advantage of this tendency by letting the alloy go as far as will result in a condition that is useful to us.

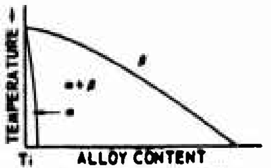
The titanium-vanadium equilibrium diagram is representative of a particular type of titanium diagram called beta isomorphous, which is one of the three most common types. These are shown in Figure 4 and are partial diagrams in that they depict only the solid phases, and the titanium-rich regions. First in Figure 4c it will be noted that alloying elements of the beta-isomorphous type tend to stabilize the beta phase at lower temperatures. Other alloying elements, besides vanadium, which form this type of diagram are molybdenum, columbium, and tantalum. There are other alloying elements, such as manganese, iron and chromium which also stabilize the beta phase to lower temperatures. Equilibrium diagrams of titanium with these alloying elements are called beta eutectoid type diagrams. These diagrams are characterized by the fact that titanium forms a stable intermetallic compound with these elements at compositions intermediate between pure titanium and the pure alloying element. The term eutectoid refers to Point ① on the equilibrium diagram in Figure 4b. An alloy of this composition when slowly cooled from the single phase beta region will decompose at temperatures just below this eutectoid temperature to form two phases, alpha, and the intermetallic compound, here designated TiX. The main difference between beta eutectoid and beta isomorphous type alloys is that during heat treatment, the presence of the hard intermetallic compound must be considered, as well as the presence of alpha and beta. The third common type of titanium equilibrium diagram is called alpha peritectoid. Alloying elements that form this type of diagram with titanium are called alpha stabilizers, that is, they raise the temperature region and broaden the composition range over which alpha is stable. Aluminum, tin, several rare earth elements, and the interstitials - carbon, oxygen, and nitrogen - fall into this category. The term peritectoid refers to Point ② on the equilibrium diagram in Figure 4a. The peritectoid reaction occurs in a manner opposite to that of a eutectoid reaction. That is, as temperature is lowered, two phases which are in equilibrium at temperatures above the peritectoid temperature will react with each other to form a single phase which is stable at lower temperatures.



A. ALPHA PERITECTOID ⟶



B. BETA EUTECTOID ⟶



C. BETA ISOMORPHOUS ⟶

PRINCIPAL TYPES OF TITANIUM ALLOY CONSTITUTION DIAGRAMS

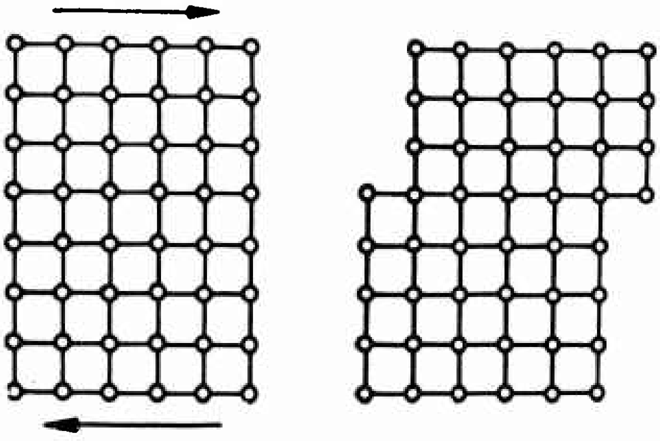
FIGURE 4

The equilibrium diagrams we have discussed have all been for binary alloys. However, most commercial titanium alloys contain at least two different elements besides titanium. Nevertheless, the behavior of complex alloys can be interpreted and explained by simple equilibrium diagrams within certain limits. Any of the important titanium alloys may be classified as either alpha, alpha/beta, or beta alloys depending upon which phase or phases are present in the condition in which it is normally used.

So far, we have discussed crystal structure, solid solution, phase transformations and the equilibrium diagram as the basis for heat treatment of metals and alloys. Now, let us consider the strength and deformation of metals and alloys.

Figure 5 is a cross section through a perfect metal crystal. The circles represent individual atoms in the plane of the cross section.

Suppose, for example that this ideal crystal containing no imperfections were to be sheared with a uniform movement of all the atoms in the top half across all the atoms in the bottom half, each atom being pushed over the atom beneath at the same time. The shear stress necessary to cause this movement of one atomic distance can be calculated from the elastic shear modulus. This calculated stress is about 1000 times the observed shear stress for yield in a real metallic crystal. This tremendous discrepancy can be accounted for by the fact that the crystal structure of metals is not perfect. There are two major types of imperfections found

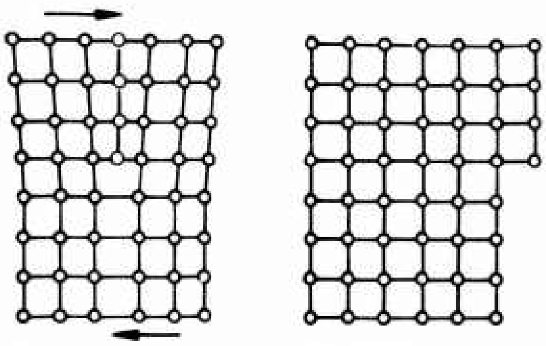


DEFORMATION OF PERFECT CRYSTAL

FIGURE 5

in all metals and alloys, vacancies and dislocations. A vacancy or missing atom, in the crystal lattice is particularly effective in aiding diffusion. Thus, we can visualize an adjacent atom "popping into" the vacancy, and leaving behind it another vacancy, which is then filled by the next atom, which in turn creates a vacancy, and so forth. In this manner, atoms can move around rather easily within the solid, crystalline structure.

The second important type of imperfection is a dislocation. The simplest type of dislocation, and the easiest to visualize is an edge type as shown in Figure 6. Again, this represents a cross section through a metal grain. The circles represent individual atoms in the plane of the cross section. The extra row of atoms causes a dislocation in the lattice. These dislocations are produced by stresses and impurities which are present during solidification of a crystal from the melt. In effect, an extra plane of atoms is jammed part way into the otherwise regular crystal lattice. The strains produced in the vicinity of this dislocation are such that it requires only a small shear stress to "pop" the dislocation over into the next row of atoms, and then into the next row, and so forth, until the entire top half of the crystal has moved one atomic distance over the bottom half, as shown in the right hand side of Figure 6. In this manner, the discrepancy between observed yield strength and the yield strength calculated assuming a perfect crystal can be explained.



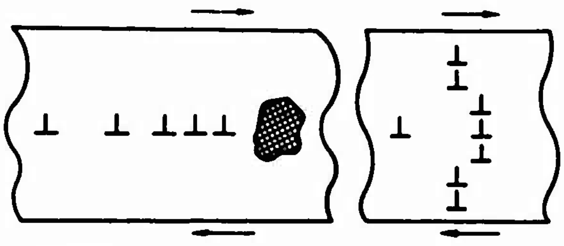
EDGE DISLOCATION IN A CRYSTAL

"SLIPPED" CRYSTAL AFTER APPLICATION OF SHEAR STRESS

FIGURE 6

The following analogy may help you to visualize how dislocations make it easier to deform metals. Assume you have a large heavy rug in your living room, which is not centered properly. It is off to one side by about one foot. If you were to grab it by an edge and try to pull it to center it, you would probably need three people to help you. On the other hand, if you were to create a ripple in the rug on the opposite edge, you could easily push the ripple across the floor, and when the ripple had traversed the rug, the rug would have traversed the floor.

Because metals deform by movement of dislocations, and since we cannot, in a practical way, remove all dislocations, if we want to strengthen metals we must find a way to hinder the movement of dislocations. There are basically two ways to hinder the movement of dislocations: (1) place a foreign object in the path of the dislocation or (2) create an array of other dislocations, whose strain fields interact with the dislocation and prevent it from penetrating. For the first method of strengthening the foreign object might be a precipitated or dispersed second phase, or it might be a dissolved alloying element which doesn't fit too well in the parent lattice and creates a strain field in the vicinity which prevents the dislocations from getting through. The second method of strengthening is what we use when we cold work or strain harden a metal or alloy. Cold working generates large numbers of dislocations which then act as effective barriers to movements of other dislocations, so that a higher stress is then required to produce a given amount of deformation. These methods of strengthening are illustrated in Figure 7.



OBSTRUCTION OF DISLOCATION BY PRECIPITATED PARTICLE OF A SECOND PHASE

OBSTRUCTION OF A DISLOCATION MOVEMENT BY ARRAY OF OTHER DISLOCATIONS

FIGURE 7. SCHEMATIC ILLUSTRATION OF METHODS USED TO STRENGTHEN METALS

FIGURE 7

When a severely cold-worked metal is gradually heated to elevated temperatures, the dislocations within the crystal structure become more mobile and tend to move away from each other. As they do this, small regions which are relatively free of dislocations will be formed. These regions, because they are thermodynamically more stable than the surrounding dislocation-dense areas, will gradually consume their surroundings and grow at their expense. A number of these relatively dislocation-free areas will form and grow simultaneously until they consume all of the original cold-worked areas. The new crystallites or grains will be as soft and as free of dislocations as the original undeformed metal. This process is called recrystallization, and the temperature at which it takes place is called the recrystallization temperature. In titanium this temperature is about 1000 F.

Let us now review briefly what has been covered so far.

First, metals solidify from the molten state in a regular geometric crystal pattern. The three most common types of metallic crystal structure are fcc, bcc, and hcp. Some metals, including titanium, undergo what is known as an allotropic transformation. That is, these metals exist in more than one crystal structure, depending upon temperature. In the case of titanium, at low temperatures, the hcp alpha phase is stable, while at temperatures above 1625 F, the body-centered-cubic beta phase is stable.

Metals possess the ability to dissolve other elements in what is known as solid solution. There are two types of solid solutions: substitutional, in which the dissolved elements are approximately the same size as the dissolving element, and interstitial, in which the dissolved elements are considerably smaller than the dissolving element. An equilibrium phase diagram describes the amount and composition of the various phases present in an alloy system, at any given temperature under equilibrium conditions. Although we seldom use alloys in the equilibrium, or lowest energy, condition, we do take advantage of the tendency of an alloy to approach equilibrium, and we let it go as far as necessary in order to produce the properties which we desire. Usually heat treatment involves a quenching step which produces a supersaturated structure. This supersaturation provides the driving force for subsequent aging reactions which can produce substantial strengthening in many alloys. There are three common types of titanium equilibrium diagrams, beta isomorphous, beta eutectoid, and alpha peritectoid. The first two types are formed by alloying elements which stabilize the beta phase of titanium, while the third type is formed by alloying elements which stabilize the alpha phase. Commercial titanium alloys, depending upon the type and quantity of alloying elements, may consist either of alpha, a mixture of alpha and beta phases, or of beta alone, and they are designated accordingly.

Numerous imperfections exist in what would otherwise be perfect metallic crystals. One type of imperfections, lattice vacancies, contribute significantly to diffusion of metal atoms within the solid crystal structure. Another type of imperfection, dislocations, provide the mechanism by which metals deform, and explain the discrepancy between the actual strength of a metal and the theoretical strength calculated on the basis of perfect crystals. Metals may be strengthened by impeding the movement of dislocations, e.g., by adding appropriate alloying elements, or by precipitating a hard second phase. Another way of impeding the flow of dislocations is to create an array of other dislocations. This may be accomplished by cold working. The effects of cold working can be removed by heating the metal above a certain temperature, called the recrystallization temperature. A metal which is worked at temperatures above the recrystallization temperature, works very easily and the metal remains soft and malleable. This process is called hot working and is used to get metals into desired shapes and sizes.

TITANIUM PROCESS METALLURGY

W. H. Heil*

INTRODUCTION

Some of the combinations of properties that make titanium an attractive structural material, as well as give it its excellent corrosion resistant characteristics, combine to make the refinement of the ore to finished mill product an elaborate, difficult operation that must be carefully controlled and performed on specialized equipment. This is true in the reduction of the titanium oxide to the raw metal and in the mill processing operations. The single most important fact to remember in the processing of titanium and the one characteristic that makes it difficult to produce is the fact that titanium is a reactive metal. This means that at any temperature of 1100 F or over (the higher the temperature the more rapid it occurs), titanium will soak up oxygen from the atmosphere. This oxygen in turn seriously impairs the useful properties of the metal. It is necessary in the reduction and melting of titanium to use temperatures considerably over 1100 F so that other protective means such as working in vacuums or under inert gas blankets are required. Mill processing or hot working of the metal at temperatures up to 2000 F is normally done in air with the oxygen damaged surface being subsequently removed by mechanical or chemical means.

This talk will be broken down into three basic areas of processes as follows:

(1) Reduction of the ore to the metal

(2) Blending, alloying and melting of the raw metal into alloyed ingots

(3) Mill processing and heat treatment.

REDUCTION

There are currently two major titanium metal producers in this country. These are The Titanium Metals Corporation of America and Reactive Metals, Incorporated. Both producers use a reduction process known as the Kroll process. This process is named after Dr. William A. Kroll, who first developed this process in 1928. The process consists of first converting the TiO_2 to a $TiCl_4$ and then reducing the $TiCl_4$ with metallic magnesium or sodium.

Titanium is an abundant metallic element in the earth's crust, but generally it occurs complexed with other metallic elements. Figure 1 is a beach scene in Australia where the mineral rutile (TiO_2) is found as beach sands with purities in excess of 95 percent TiO_2. Figure 2 is a flow chart of the reduction operation.

FIGURE 1

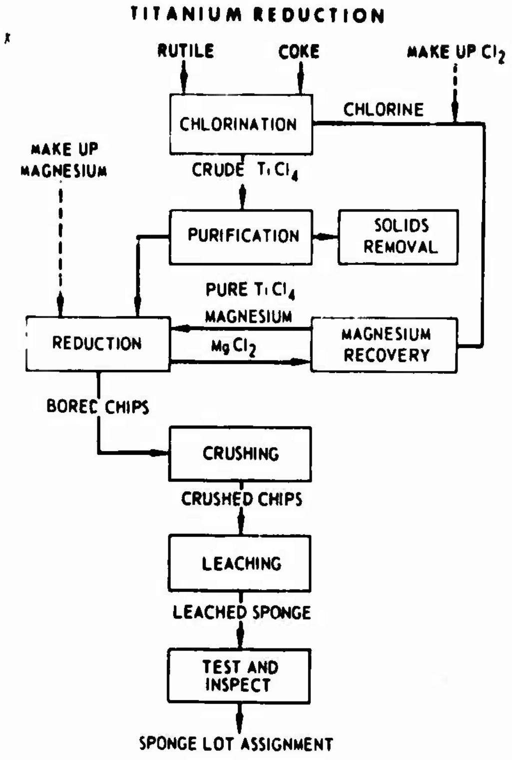


FIGURE 2

The first step in the reduction process consists of introducing the rutile ore into a large chlorinator unit along with a controlled amount of carbon in the form of coke and chlorine gas. An exothermic reaction results in this operation, and bath temperature remains at the red heat level. The titanium in this operation is reduced from the oxide and removed as a gaseous titanium tetrachloride ($TiCl_4$). This titanium tetrachloride vapor, along with the vapors of the other chlorinated impurities such as iron, vanadium, and silicon, are then condensed to a liquid form. In

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the liquid form the titanium tetrachloride can then be separated from the other chlorides by a series of distillations.

From this point the pure liquid titanium tetrachloride is introduced into a solid steel reactor pot that has been charged with magnesium. In this operation, carried on at red heat, the metallic magnesium reduces the titanium tetrachloride to elemental titanium, and in turn the resulting liquid magnesium chloride can be drained off and recycled through electrolytic cells. This recovers magnesium and chlorine, which in turn are then recycled through the operation. This operation is a batch operation; and when all the magnesium has been consumed, the reactor pot is full of a spongy porous titanium mass. The whole reactor vessel is then removed, the welded-on top is removed, and the titanium mass on the inside is removed on a large boring mill. A picture of this reactor vessel is illustrated in Figure 3. The resulting raw titanium, which is called sponge, contains a fairly large quantity of entrapped magnesium and magnesium chloride left over from the reduction operation. This sponge is then crushed to give it a common particle size as well as to open some of the closed areas to make the entrapped magnesium and magnesium chloride available for removal.

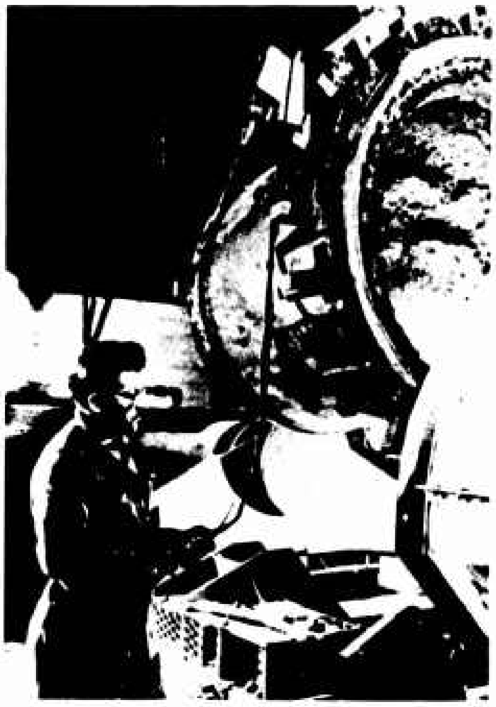

FIGURE 3

At this point the crushed sponge is introduced into a large leaching tank, and the magnesium and magnesium chloride are removed through leaching with an aqua regia acid solution. I would at this time like to point out that containing an acid solution like aqua regia is no easy task. Figure 4 represents TMCA's solution to this containment problem and it is to be noted that the container is made up of commercially pure titanium. It is the largest titanium vessel ever fabricated and is 8 feet in diameter, 66 feet long and weighs 20 tons. The now-pure sponge is then completely washed and dried and assigned to individual sponge lots for production control as well as quality control reasons. At this point chemistry, hardness, particle size, etc., are all examined; and in addition, control samples are X-ray inspected, magnetically inspected, and visually inspected. The sponge is now ready for assignment to the melting operation.

FIGURE 4

Scrap Recycle

I would like to regress a minute and discuss briefly how we prepare our scrap for recycle since I am sure many of you wonder why there is such a limited market for titanium scrap for remelting. In the first place, TMCA does not buy scrap. Enough is generated within our own company to satisfy the limited scrap recycle allowed in melting. In addition, by recycling our own scrap we are allowed complete control over the separation of alloys and contaminated metal.

Figure 5 is a flow chart of the scrap recycle operation. First the scrap must be reduced to a particle size that is common with the sponge and master alloy. To do this the large pieces such as billet and bar ends, plate sections, etc., are first overall pickled to remove heavy oxygen contamination. Next they are introduced into a large reactor, heated, and hydrogenated. With the hydrogen level high enough the metal is sufficiently embrittled to break up in conventional crushing equipment and the correct particle size is achieved. This crushed scrap is then inspected and tested in a manner similar to the sponge and assigned to individual scrap lots for assignment to melting. As mentioned before, TMCA limits the amount of scrap that may be included in the melting operation.

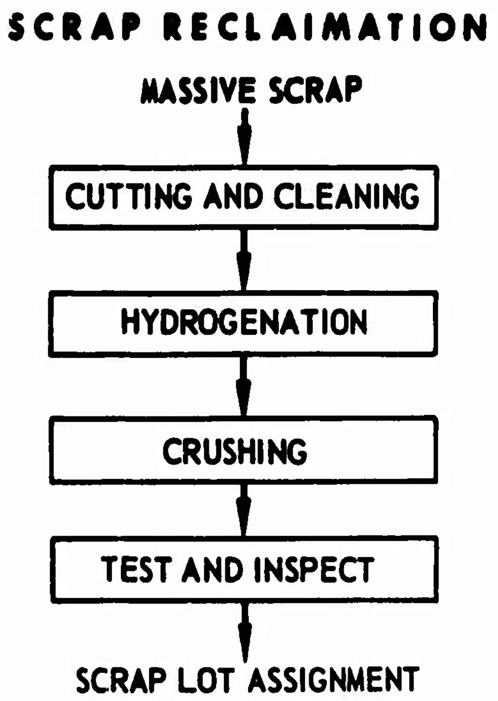

FIGURE 5

BLENDING, ALLOYING AND MELTING OF THE RAW METAL INTO ALLOYED INGOTS

The individual makeup for titanium ingot is composed of three basic elements as noted in Figure 6.

(1) The major element is the sponge for which we have just described the reduction process.

(2) Master alloy additions to obtain the desired chemistry of the alloyed grades, such as Ti-6Al-4V. For this particular alloy we use a master alloy addition that is composed of 60 percent aluminum and 40 percent vanadium.

(3) Recycled scrap additions.

Titanium melting process is known as the consumable electrode melting process. This operation is carried on under vacuum and consists of melting a sponge or a metal electrode by passing an electric arc between the electrode end and a water-cooled copper crucible. The titanium electrode is thus slowly consumed by the arc with the molten metal falling into the molten pool lying in a skull of solidified titanium in the copper crucible. The surrounding vacuum prevents the molten titanium from recombining with the normal components of an air atmosphere and in addition outgasses any hydrogen, residual magnesium, and chlorine from the sponge product. To convert the sponge product, master alloy, and scrap addition to this electrode, known as a sponge electrode, individual lots of carefully weighed and blended sponge, master alloy, and scrap are introduced into an electrode shaped cavity and compacted on a large press. The pressing pressures are such that the whole mass is mechanically bonded together. Several of these compacts are then welded together into what is known as the sponge electrode. This sponge electrode is then introduced into the melting furnace, a vacuum is drawn, and the initial melt commenced.

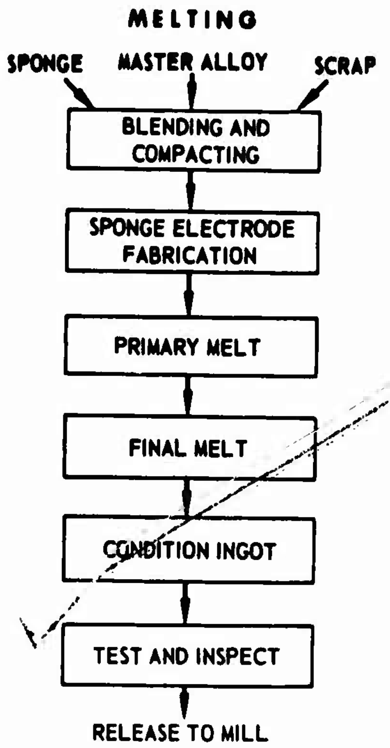

FIGURE 6

After the initial melt the primary metal ingot is removed from the crucible and the outside surface is conditioned free of its skull, or impurities, that migrate to the outside. When the skull has been removed, this primary melt, now known as a metal electrode, is recharged into a slightly larger consumable-electrode vacuum-arc-melting furnace and is remelted into the final ingot configuration. After removal from the crucible the ingot is conditioned by lathe turning the outside diameter; it is sampled top, middle, and bottom, from drillings in the surface, for complete chemical analysis; and lastly, it is ultrasonically inspected for any evidence of pipe or voids. At this point if the chemical analysis is within prescribed limits and the ingot is of sound characteristics, it is transmitted to the mill for mill processing into the final mill product. Figure 7 shows a field of typical titanium ingots ready for mill processing. These particular ingots are 28 inches in diameter by about 5 feet long and weight a nominal 7000 pounds.

MILL PROCESSING

Mill production of titanium is still based upon equipment inherited from the steel industry. The basic equipment, such as rough rolling mills and forging presses, are the same as that which can be found in a steel plant. However, this is where the similarity stops and the requirements for the associated equipment, such as heating equipment, finishing equipment, and the tools for the necessary quality control, are all more specialized.

It is because of these areas that the economics of production, as well as the quality of the product, are compromised whenever titanium is processed in a basically steel working plant. Look at the record. Initially all titanium mill products were produced on steel working equipment with a quality level that would be completely unacceptable

FIGURE 7

FIGURE 8

at today's standards. As the titanium industry grew and specialized titanium processing equipment was introduced, improvements in both quality and economics of production were evident. In fact, currently the bulk of titanium mill products are produced by two mills, both of which have titanium as the only or the major product. That is TMCA and RMI.

The need and importance of this specialized equipment is dramatically illustrated in Figures 8 and 9. The old furnace (Figure 8) has a length limitation of 156 inches and could only accommodate charges of up to 3000 pounds. Also, the batch annealing cycle required about 18 hours and yielded an oxidized surface on the titanium which necessitated conditioning of the annealed product. The new furnace (Figure 9) has unlimited length capability (handles coils), has no weight or time limitations since it handles coils continuously, and maintains a bright surface requiring no further surface descaling and conditioning. One more illustration of old and new is afforded by comparisons of Figures 10 and 11. Figure 10 shows the hot cross rolling mill which was previously used for finish rolling of all alloy sheet and plate. This mill has width and length limitations of approximately 48 x 144 inches and minimum as-rolled thickness of approximately 0.030 inch. It also has limited gauge and flatness control and rolls a product that is hot (1400 to 1900 F) and as a result requires expensive removal of contaminated metal. In addition again this is an individual (batch) type operation which you will recognize as an inherently expensive operation.

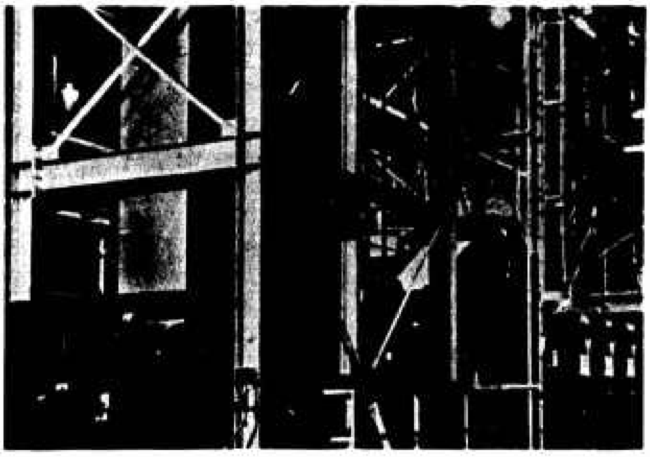

FIGURE 9

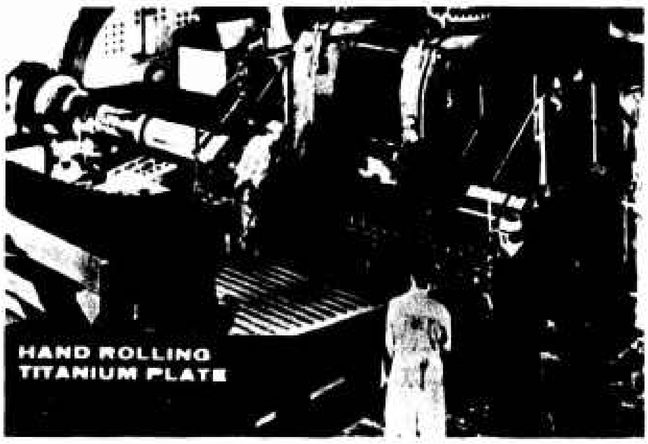

FIGURE 10

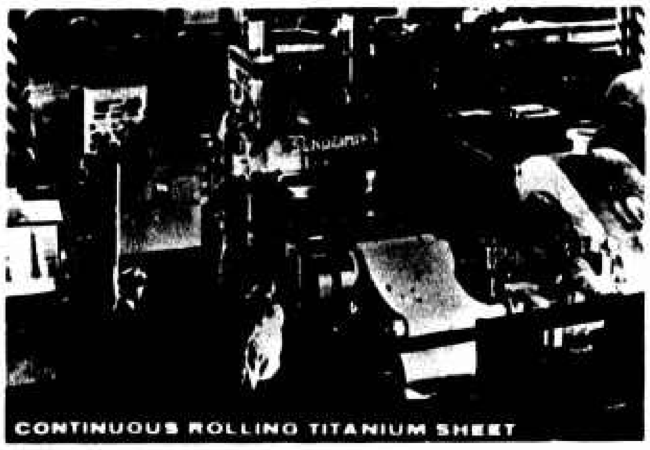

FIGURE 11

Compare this with the mill shown in Figure 11. This is a Sendzimir (Z) mill which continuously cold rolls sheet product up to 48 inches wide with 1/2 AISI gauge tolerance, excellent flatness, and thicknesses down to 0.010 inch. This type of rolling coupled with the continuous vacuum anneal line is the ultimate in rolling a flat roll product for there is precise thickness control and no open air operations from thicknesses of 0.070 inch and less that result in scale and contaminated metal which subsequently has to be removed by grinding or pickling. This equipment, the Z mill, and the continuous vacuum anneal furnace are currently in production on commercially pure titanium as well as the Ti-13V-11Cr-3Al and Ti-5Al-2.5Sn alloys. By year end this process should include the Ti-6Al-4V and Ti-8Al-1Mo-1V alloys and all these grades may be rolled down to 0.010 inch thickness.

With this background I will get into the actual mill processing outline that converts the raw ingot to the finished mill product. Figure 12 is a flow sheet of the conversion of ingot to the various mill products. You will note that this same flow sheet could be representative of a steel product.

Bar, billet, and wire may all be classed in the same category since they all consist of drawing a symmetrical cross section (ingot) down to billet, bar, or wire.

Look first at the forging billet processing that will account for well over 50 percent by weight of the total titanium mill shipments. This operation consists of the necessary number of heating and press forging operations to reduce the ingot diameter to that of the finished billet size. Initial heating is from temperatures in excess of the beta transus (1900 to 2000 F) to facilitate breakup of the large as-cast grains while keeping surface cracking at these grain boundaries at a minimum. Once the as-cast grains are refined, then temperatures below the beta transus may be employed to further the macro and microstructural grain refinement. Finish forging is to a size 1/4 to 1/2 inch oversize to allow surface contamination and forging defects to be subsequently removed by lathe turning on rounds or overall surface grinding on squares, octagons, rectangles, etc. The finished conditioned billet may then be ultrasonically tested for internal defects, checked for hydrogen or oxygen pickup, and acceptance tested. The acceptance test consists of forging a representation sample of the billet stock and annealing or heat treating and testing it in a manner mutually acceptable to both the mill and the forging customer.

When smaller sizes are required (common mill terminology defines a bar product as having a cross section of 16 square inches or less and a width to thickness ratio of 5 or less), rolling is the commonly accepted method of production. That is, a forged billet 4 to 8 inches square is then hot rolled out to the finish bar size and, in a manner similar to billet, the outside contaminated skin is ground or acid pickled off. Small round bar stock is also the starting point for the wire product which consists of drawing, either cold or hot depending on grade, from 5/16 inch down to 0.010 inch diameter or any intermediate size.

MILL PRODUCTS are the wrought shapes of material supplied to the end user. Like steel, titanium is supplied as sheet, strip, plate, bar, forging billet, wire, extruded shapes, pipe, and tubing in a variety of unalloyed and alloyed grades.

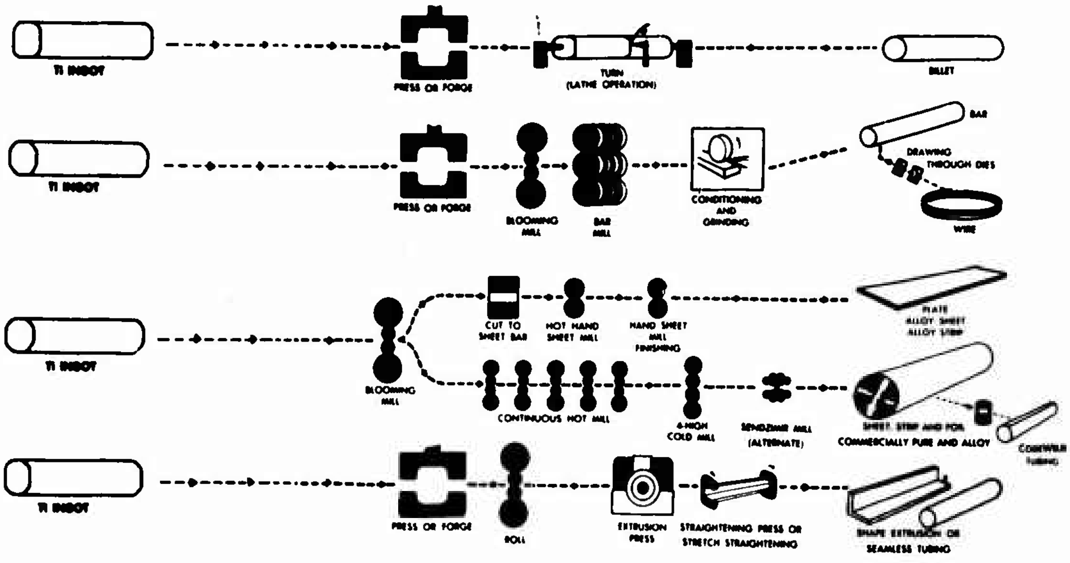

FIGURE 12

Sheet, strip, plate, and foil is the next general category of mill products, which are commonly referred to as flat roll products. By mill terminology, sheet refers to a flat roll product from 0.005 to 0.1875 inch thick and 24 inches or over in width. Strip is the same as sheet except widths are less than 24 inches. Plate includes thicknesses 0.1875 inch and over, and over 10 inches in width, with width to thickness ratios over 5 to 1. Any product 0.005-inch-thick and under is classed as foil.

The general processing of sheet and plate products includes the hot rolling or pressing of ingot to sheet bar slabs. From these slabs individual bars are cut and subsequently hot cross rolled to sheet and plate products on the type of hand mills shown in Figure 10. It is this type of processing that is responsible for the production of all titanium alloy sheet and plate for the past 15 years. Limitations of this type of rolling are obvious and have been previously commented on. As product thickness decreases in the sheet ranges, process difficulties increase proportionally in a hot-rolled product. All hot-rolled sheet products at TMCA less than 0.100 inch thick are finish rolled inside welded steel packs. This thicker total pack allows rolling individual sheets to lighter gauges while maintaining better control over gauge and flatness. However, in spite of these methods, the lower thickness as hot rolled is approximately 0.030 inch. To produce lighter thickness sheet product by this method the excess metal must be ground or acid pickled off. These excessive metal losses, compounded with increased handling, heat treating, and hydrogen pickup problems dictate the higher prices and the more limited availability of these light gauges.

Following the hot-rolling operation the individual sheets are annealed and/or heat treated depending on the requirement. They are then overall belt ground to remove the hot-rolling and heat-treating defects, and finally they are pickled in HF-HNO_3 type baths to remove grind lines, complete the removal of all oxygen contamination and to insure that they meet the required thickness. From 5 to 10 mils of thickness is removed in these conditioning operations. Normal testing of the finished sheet includes tensile, bend, and hydrogen analysis.

My general discussion of sheet products has been restricted to the annealed condition. When we talk of a solution-treated (ST) or solution-treated-and-aged (STA) product, we are compounding the processing problems. The problems are related to the high temperatures used in the solution treating operation and the thermal shock that occurs in water quenching these products from the 1600 to 1750 F temperature range. The latter of these two problems is the more severe since besides making the solution treated product commercially unattractive because of the poor flatness it also compounds the mill processing problems in removing the scale and contamination that occurred in solution treating. Again the lighter the sheet thickness the more serious become both the flatness and contamination problems. Aging eases the above problems somewhat in that the normal aging temperatures of 1100 F will partially reflatten the sheet and tend to simplify the finish conditioning operations.

Also of current concern to TMCA is the compatibility of the water quenching operation with a continuously rolled strip product. At this time I see no way to perform this water quenching operation and retain the advantages of the strip product.

Recently there has been interest in large size plate products. These products are possible in many sizes by conversion on several large steel plate mills. Widths of 80 to 100 inches and lengths of 400 to 500 inches have been produced and one of the limiting factors here is ingot size availability. Normal ingot size is 7000 pounds, although capability exists to produce larger heats. Figure 13 is an example of a large titanium plate product.

FIGURE 13

Foil products in titanium are available in the CP grades, but this product remains in its infancy. The production of a high-quality strip product down to 0.010 inch thickness, as indicated before, will open one door to a quality foil product. The proper specialized mill processing equipment is the other key for this product. In this respect it is similar to titanium wire products and again the processing problems are compounded because of the large surface to volume ratio of both products.

CONCLUSION

The titanium industry is only 16 years old and we are currently going through some radical processing changes that have been dictated by increased product requirements. Complicating these changes in processing is the fact that specialized processing equipment is necessary and often has to be designed from scratch for the particular operation. In reviewing the processing operation itself the single most important factor to remember is that titanium is a reactive metal and must be treated accordingly.

THE MICROSCOPY OF TITANIUM

Dr. F. A. Crossley* and R. E. Herfert**

INTRODUCTION

In the previous papers, a working knowledge of metallurgy in general, and also certain facets of titanium metallurgy were presented. In this paper, we will attempt to show you the fundamental physical characteristics of titanium. We are concerned with the means available to the metallurgist for discovering or determining the constitution and the structure of titanium-base alloys.

In the phase diagrams presented in previous papers, no characterization as to microstructure was presented. Our paper will give a phase relationship as to microstructure and then directly relate it back to the phase diagram. It is the overall purpose of this discussion to show some of the inherent changes in titanium during alloying and processing and its affect on microstructure.

Thus presented, with a limited knowledge of some of the ramifications of physical structures of titanium and some of its alloys, the following papers on particular problems of joining, working, machining, and designing should present more merit.

First, we should probably define what microstructure is. In order to do this, we must first show a relation to crystal structure. Dr. Harmon's paper showed the basic crystal structures present in titanium. Let us, for a moment, review these. Here we see (Figure 1) the face-centered cubic structure typical of aluminum, body-centered cubic structure typical of beta-titanium, and the hexagonal close-packed structure of alpha-titanium. The small structures are called the unit cells. These unit cells define the most basic characteristics of a metal.

Titanium is similar to steel in that it can occur in two allotropic forms. It occurs either as a body-centered cubic or a hexagonal unit cell. These are called, respectively, beta-titanium and alpha-titanium. In the alpha alloys, pure titanium for example, beta is never found except at high temperatures. In alpha-beta alloys, a mixture occurs and, in beta alloys, only the body-centered cubic form appears. In the cubic form, the cell edges are isotropic; that is, equal in all directions. In the case of alpha-titanium, since it is a hexagonal structure, this is not true. Two different dimensions are required. The base dimension is different from the height; in other words, the cell dimensions are anisotropic. It is apparent that the orientation of these unit cells within a forging or sheet material would greatly affect its strength properties.

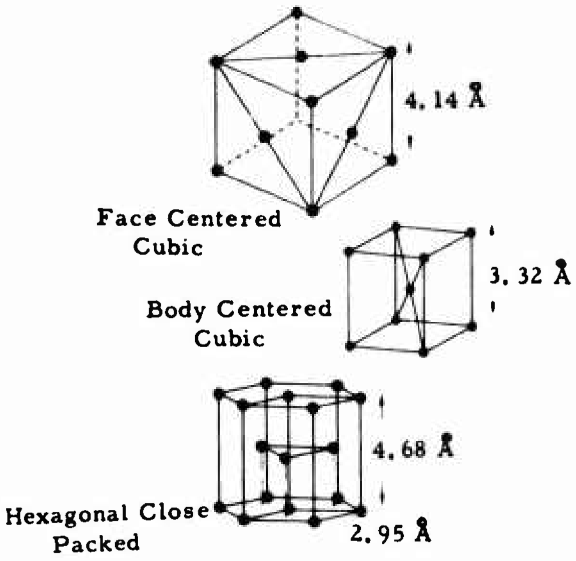

FIGURE 1

When we take a combination of these unit cells, as during the solidification from a melt, we assimilate what we call a single crystal or a single grain. It only has orientation in two dimensions, mainly width and height. Structural materials are not single crystals. They are what we call multi-grained systems, each grain being of one orientation and consisting of a series of these small unit cells. Numerous small grains are present in different orientation. A series of these small unit cells go together to make up a single grain. A series of these grains then make up a structural component, as seen in Figure 2. We are going to focus our attention on the intermediate stage between the unit cell and the structural member; the microstructure of the polygrained component. This science of studying microstructure is called metallography. In order to perform a metallographic examination on a metal, the following steps are followed:

(1) The specimen is carefully sectioned by sawing or cutting from the structure.

(2) It is then mounted in a thermo-melting plastic for ease of handling.

(3) Then, the sample surface is polished until a mirror finish is obtained, using SiC and/or abrasive diamond polish.

(4) The sample is ready for etching, which brings out grain detail.

In order to study these aspects, certain special instrumentation is necessary. These are X-ray diffraction, optical microscopy, electron microscopy, and electron microprobe analysis.

X-ray diffraction is used to tell the precise nature of the cell; i.e., its dimensions or the relative amounts of different structures in one matrix. For example, the amount of alpha and beta-titanium in an alpha-beta alloy or the stress states, or distortion in the unit cell.

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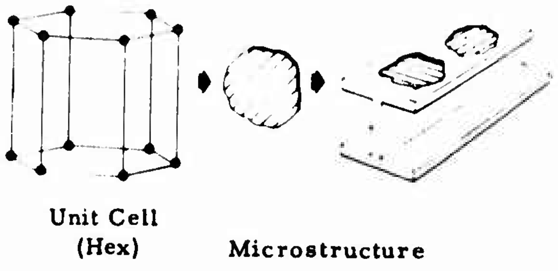
FIGURE 2



In order to examine microstructure, we will use the optical microscope with magnification up to 2000 times and the electron microscope with magnification up to five million times. Grains smaller than the wavelength of visible radiation cannot be resolved by light microscopy. They can, however, be examined with the aid of an electron microscope. If we think in terms of wavelength, visible radiation could be considered this wide, infrared wavelength would be slightly greater, but the wavelengths concerned with electron radiations are only small fractions of these lengths. This enables the high magnification. Since images are formed from interference of wavelength, the shorter the wavelength the higher the resolution and thus magnification.

The greater part of this discussion will be devoted to optical microscopy because it is our most used and most convenient of metallographic techniques.

Dr. Crossley will discuss the factors influencing microstructure and optical-microscopy studies. Then I will discuss electron-microscopy studies of titanium microstructure.

FACTORS INFLUENCING MICROSTRUCTURES*

Alloying

Microstructural characteristics arise from the following: (1) alloying, (2) casting, (3) working, and (4) heat treating. Let us first consider alloying. The lecture on phase diagrams brought out that alloying elements may be classified into four basic groups determined by the type of phase diagrams they form with titanium. These are complete miscibility, alpha stabilizers, isomorphous beta stabilizers, and eutectoid beta stabilizers. The eutectoid beta stabilizers may be divided into two subgroups depending upon the rate of eutectoid decomposition. Binary alloys of silicon and copper have such rapid eutectoid decompositions that compound formation is not suppressed by air cooling. Silicon and copper are therefore called fast eutectoid or compound formers. At the other end of the scale manganese produces such a sluggish beta that decomposition does not occur in hundreds of hours at temperatures below the eutectoid decomposition temperature. Other elements which form eutectoid-type systems with titanium (such as chromium, iron, and nickel) lie between these extremes.

Equilibrium phases occurring in commercial titanium alloys due to intentional alloying are: alpha, the hcp low-temperature allomorph, beta, the bcc high-temperature allomorph, and compounds. With a single exception, the compounds are associated with eutectoid beta additions. The exception is the first intermediate phase in the Ti-Al system. (The weight of evidence indicates this to be Ti_3Al.) Figures 3, 4, and 5 show micrographs of an all alpha, an all beta, and an alpha plus beta plus compound alloy, respectively. The compound in Figure 5 is TiFe precipitated from the hypereutectoid beta phase during the furnace cool from 1700 F. The microstructures shown in Figures 3 and 4 are equiaxed as a result of recrystallization of the cast structures. Alloys containing alpha can only be made equiaxed by recrystallizing below the beta transus temperature. Cooling of such alloys through the beta transus temperature results in transformation products that are usually acicular in character. Such a structure is illustrated by Figure 6. The acicular microstructure is variously called: basket weave, Widmanstätten, transformed beta, transformed alpha, and simply acicular.

A less commonly encountered transformation structure is so-called "serrated" alpha. To the writers' knowledge this occurs only in unalloyed titanium and alpha alloys. A microstructure typical of serrated alpha is shown in Figure 7. The name derives from the irregular or serrated character of the grain boundaries. The serrated structures are formed by "massive" transformation. This is a process of very rapid, diffusionless growth, in contrast to Widmanstätten transformation which involves diffusion. (The massive transformation differs from martensitic transformation in that there is no shape change or surface relief.)

The discussion of nonequilibrium phases resulting from intentional alloying is better deferred to the section dealing with the influence of thermal treatments on microstructure.

Unintentional alloying or impurities also produce phases, or microconstituents, in titanium alloys. The common impurities are carbon, hydrogen, iron, nitrogen, and oxygen. While carbon in excess of 0.15 percent* can result in the presence of titanium carbide, the carbon content in commercial alloys is usually below this level. However, carbides may be expected in titanium castings made in graphite molds. Titanium hydride can be found in some commercially pure or unalloyed grades of titanium since hydrogen solubility at room temperature is less than 100 ppm and may be less than 10 ppm. However, alloying additions commonly employed in commercial practice increase the solubility of hydrogen. As a consequence of this and of the tolerance limits imposed, titanium hydride is not usually observed in commercial alloys except under special conditions of alloy composition, hydrogen content, high stress, and the presence of a notch. In such cases hydrogen contamination at some stage in the further fabrication of the mill product is usually a factor.

Iron as an impurity causes the occurrence of small particles of beta phase in commercially pure titanium or alpha alloys (such as A-110AT, Ti-5Al-2.5Sn). In alpha-beta alloys iron dissolves in the beta phase and loses its identity as a factor affecting the microstructure.

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* Lecture presented by Dr. F. A. Crossley.

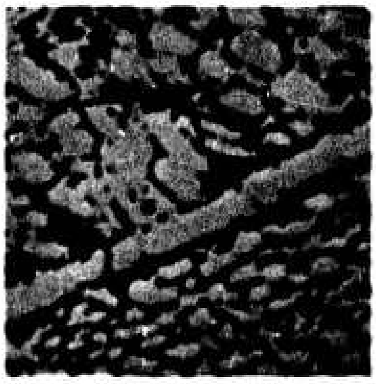
* All compositions are on the basis of weight percent.

N 22769 X250

FIGURE 3. UNALLOYED TITANIUM; 1300 F - 1 HOUR* EQUIAXED α. POLARIZED LIGHT.

N 22777 X100

FIGURE 4. METASTABLE β ALLOY; 1300 F - 1 HOUR* EQUIAXED β. (B120VCA, Ti-13V-11Cr-3Al).



N 6518 X1000

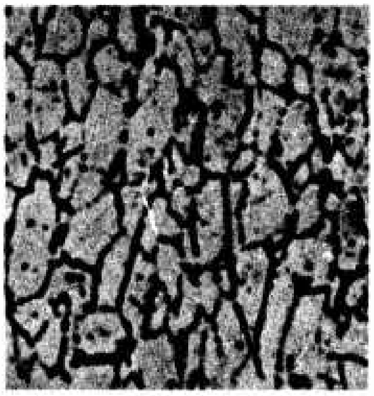
FIGURE 5. α + β + COMPOUND STRUCTURE. Ti-6Al-6Fe: 1700 F - 1 HOUR, FURNACE COOLED TO 1100 F AND HELD 24 HOURS* [α + β (between α grains) + TiFe (particles in boundaries).]

N 25813 X100

FIGURE 6.* ACICULAR α (LIGHT PLATES) + β (Ti-821, Ti-8Al-2Cb-1Ta; MILL ANNEALED).

N 30106 X250

FIGURE 7.* SERRATED α. (Ti-8.4Al; 2000 F - 4 HOUR-IBQ).



N 13811 X500

FIGURE 8.* UNALLOYED TITANIUM: 1470 F - 1 HOUR - WATER QUENCHED. α + β (RESOLVABLE GRAIN BOUNDARY PHASE) + TiH (ACICULAR PHASE). β AND TiH DUE TO IMPURITIES OF IRON AND HYDROGEN, RESPECTIVELY.

Figure 8 shows a micrograph of commercially pure titanium (Ti-55A). The resolvable second-phase particles occurring at grain corners and grain boundaries are beta due primarily to the impurity iron, and the acicular microconstituent, appearing to emanate from grain boundaries, is titanium hydride.

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* Etchant: 20 percent HF, 20 percent HNO_3, 60 percent glycerin. (The designations HF and HNO_3 refer to standard concentrated solutions of these acids of 49 percent and 70 percent, respectively.)

* Etchant: 20 percent HF, 20 percent HFO_3, 60 percent glycerin.

Because of their high solubility in titanium in relationship to their tolerance limits in commercial alloys, nitrogen and oxygen are not associated with the occurrence of microconstituents except as they influence kinetics of precipitation reactions. Oxygen and nitrogen speed up the precipitation of alpha from alpha-beta alloys heated above their beta transus and cooled through their transformation ranges. This effect is illustrated by Figure 9, which shows initiation of beta to alpha transformation for a series of Ti-11Mo alloys of oxygen contents from <0.02 to 0.55 percent. Also, an acicular phase has frequently been observed in metastable beta alloys cooled rapidly from temperatures high above the beta transus. This phase tends to come out in subgrain boundaries as shown in Figures 10 and 11. This acicular product is associated with high oxygen and nitrogen content. This phase is apparently alpha.(1)

Casting

Microstructural features that may result from melting and casting operations derive primarily from segregation. Occasionally, or perhaps rarely, insoluble inclusions of molybdenum may be encountered.

Working

Ingot breakdown may be by forging, rolling, or extrusion. Microstructural features that may result from primary fabrication are the distribution of segregation, or of impurity phases, and preferred orientation such as may occur in rolled strip.

Secondary fabrication, such as hot and cold forming operations, is applied to parts varying in size or thickness from heavy forgings to thin sheet.

Let us consider the microstructural changes wrought by hot-working alpha-beta alloys. Such alloys in the as-cast state have the acicular structure shown in Figure 6. When this structure is worked at temperatures below, but close to, the beta transus it is progressively converted to an equiaxed microstructure in the manner suggested by the series of micrographs in Figure 12. It appears that nuclei of alpha form and grow into equiaxed grains at the expense of the beta matrix (see Figure 12a). At some point as working continues, beta grains as well as alpha grains are nucleated and eventually an equiaxed alpha-beta structure results, as shown by Figure 12c. Since these specimens were air cooled from the forging temperature, the grains which were all beta at temperature transformed to acicular alpha in a beta matrix.

Alpha-beta alloys containing high aluminum content do not readily recrystallize. Hot working substantially below the beta transus temperature produces a sequence of microstructures as suggested by the micrographs in Figure 13. Under these conditions transformation from acicular to equiaxed proceeds differently than as described above. Upon working, the alpha plates grow, and colonies rotate in the direction of working. When sufficient work is introduced, recrystallization begins with the nucleation of alpha and beta grains, the microstructures exhibiting a progressive spheroidization of the beta phase. Low-temperature hot working produces very small grain size as

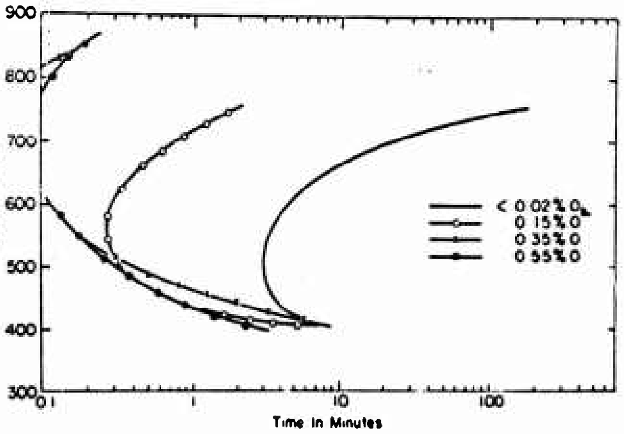
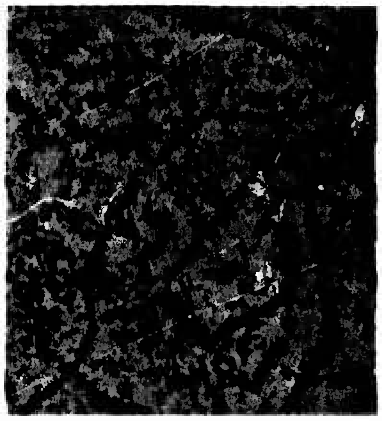


FIGURE 9. COMPARISON OF CURVES FOR INITIATION OF VISIBLE TRANSFORMATION IN Ti-11Mo ALLOYS WITH VARIOUS OXYGEN CONTENTS*

N 8365 X750

FIGURE 10. β WITH MICROCONSTITUENT WHICH APPARENTLY IS α. (Ti-10Mo-10V; 2010 F - 24 HOURS - AC.)*



N 22028 X250

FIGURE 11. β WITH MICROCONSTITUENT WHICH APPARENTLY IS α. (B120VCA, Ti-13V-11Cr-3Al.)*

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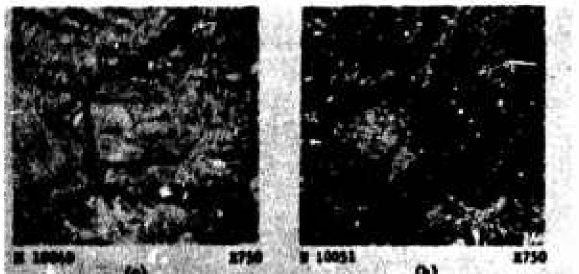
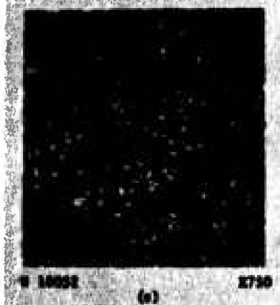
* Etchant: 20 percent HF, 20 percent HNO_3, 60 percent glycerin.



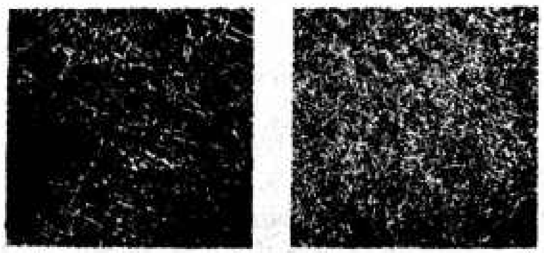
N 10048 X750 (a)
As-forged. Reduced 36%. Development of equiaxed α grains.

N 10051 X750 (b)
As-forged. Reduced 56%. Increased development of equiaxed α grains.



N 10052 X750 (c)
As-forged. Reduced 75%. α + β at temperature, β transformed to acicular α + β during cooling.

FIGURE 12.* α-β ALLOY (Ti-7Al-3Mo). CHANGE IN MICROSTRUCTURE FROM WIDMANSTÄTTEN, OR ACICULAR, TO EQUIAXED WITH PROGRESSIVE FORGING REDUCTION AT 1800 F.



N 10053 X750 (a)
As-forged. Reduced 36%. Coarsening of α plates of acicular structure.

N 10049 X750 (b)
As-forged. Reduced 56%. Spheroidization of β in α matrix.

N 10050 X750 (c)
As-forged. Reduced 75%. Development of equiaxed structure virtually completed.

FIGURE 13.* α-β ALLOY (Ti-7Al-3Mo). CHANGE IN MICROSTRUCTURE FROM WIDMANSTÄTTEN, OR ACICULAR, TO EQUIAXED WITH PROGRESSIVE FORGING REDUCTION AT 1650 F.

indicated by Figure 13c. Comparison of Figures 12 and 13 indicates that considerably more reduction must be accomplished at the lower temperature in order to achieve primary recrystallization during hot working. However, unrecrystallized structures containing sufficient work readily recrystallize upon solution heat treating at temperatures and for times usual in commercial practice. Figures 12 and 13 suggest the wide variation in microstructures that may obtain in a forging when there is wide variation in reduction from one point of it to another. It should be borne in mind that the microstructure developed by working depends not only upon the temperature out of the furnace and the amount of reduction, but also the size of the workpiece in relation to the work tools; that is, the amount of heat extracted from the workpiece during fabrication.

Heat Treatment

Stress-relief anneal, generally in the temperature range from 1000 to 1400 F, does not usually cause a change in the microstructure of titanium alloys. Annealing of worked alloys at higher temperatures causes recrystallization and grain growth and, in the case of alloys consisting of more than one phase, causes redistribution of the phases present. A final heat treatment above the beta transus will reproduce the acicular microstructure. As may be inferred from the above discussion of the conversion from acicular to equiaxed microstructure by hot working, high-temperature anneals below the beta transus produce little change in coldwork-free acicular structures beyond coarsening of the plates.

Grain growth above the beta transus is very rapid; and heating above the beta transus invariably produces a very coarse prior beta grain size. A fine beta grain size can be produced only by subjecting material to high deformation rates just above the beta transus, for example, by extrusion. The fineness of the acicular product is determined by the rate of cooling, the width of the alpha plates increasing with decreasing cooling rate as shown by Figure 14.

Employment of temperatures between those used for stress relief and the beta transus is usually for the purpose of solution heat treatment preparatory to age hardening. Age hardening of commercial alloys is based upon precipitation of alpha from beta. Alloys containing small additions of beta stabilizers or weak beta stabilizers (such as Ti-8Al-1Mo-1V or Ti-6Al-4V, respectively) must be rapidly quenched from high in the alpha-beta field in order to retain beta. More heavily beta stabilized alloys (such as Ti-7Al-4Mo) have good hardening response upon air cooling. Solution heat treatment of alpha-beta alloys for hardening purposes is never done above the beta transus because of the unfavorable effects this has on mechanical properties. Figure 15 shows micrographs of an alpha-beta alloy (Ti-7Al-3Mo) in the solution heat treated and in two aged conditions.

An all "beta" (actually metastable beta) alloy would be aged from a solution heat treatment in the beta field. Micrographs of a metastable beta alloy in two aged conditions are shown in Figure 16. These may be compared with the solution annealed condition of the metastable beta alloy shown in Figure 4.

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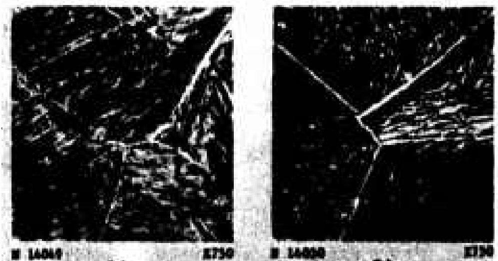
* Etchant: 20 percent HF, 20 percent HNO_3, 60 percent glycerin.



N 14049 X750

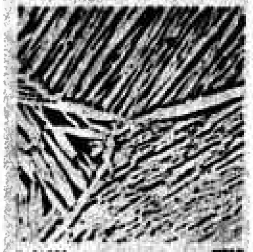
(a)

Fine acicular structure produced by air cooling from above the β transus. (1950°F-1/2 hr-AC).

N 14050 X750

(b)

Structure at left coarsened by the anneal; 1560°F-4 hr-AC.

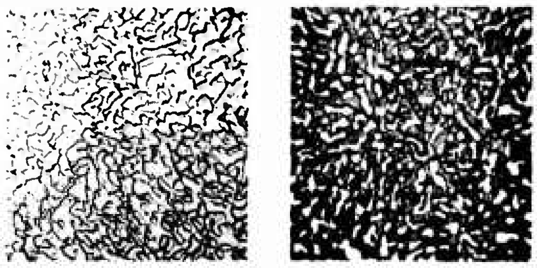


N 14051 X750

(c)

Coarse acicular structure produced by furnace cooling from above the β transus. (1950°F-1/2 hr-AC to 1560°F, hold 4 hr-AC, aged 1000°F-24 hr-AC).

FIGURE 14. INFLUENCE OF HEAT TREATMENT ON THE WIDTH OF α PLATES IN ACICULAR α-β ALLOY (Ti-7Al-3Mo)*



N 14052 X750

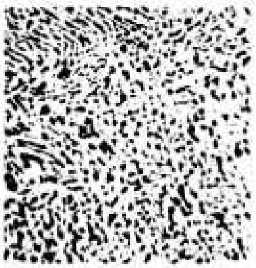
(a)

Solution heat treated 1800°F-1 hr-WQ. α + retained β (majority phase).

N 14053 X750

(b)

Structure at left aged 1000°F-24 hr-AC. α + underaged β.

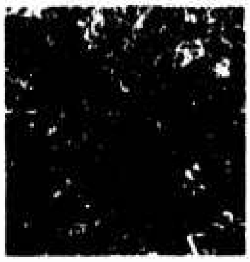


N 14927 X750

(c)

Solution heat treated and aged 1500°F-1 hr-WQ, 1000°F-24 hr-AC. α + overaged β.

FIGURE 15. INFLUENCE OF HEAT TREATMENT ON EQUIAXED α-β ALLOY (Ti-7Al-3Mo)*



N 20166 X1000

*(a)

Aged 900°F-20hr. β + ω + α.

N 20172 X1000

(b)

Aged 1000°F-20 hr. β + α.

FIGURE 16. AGED CONDITIONS OF METASTABLE β ALLOY (B120-VCA, Ti-13V-11Cr-3Al)*

The wide range of microstructures that can be achieved in a single alloy by the combined effects of hot working and heat treatment is indicated by Figures 17 and 18. These figures show the same microstructures at magnifications of 100X and 500X, respectively. Actually, these micrographs represent minor compositional variations on the basic composition Ti-7Al-2Cb-1Ta, but these slight compositional variations are of no significance in terms of the point illustrated. The Ti-7Al-2Cb-1Ta alloy is a predominantly alpha alloy. In such alloys the amount of beta-stabilizing additions is limited either to improve high-temperature creep resistance or to permit weldability. A combination of two sub-beta transus rolling temperatures and several solution annealing temperatures above and below the beta transus produced microstructures ranging from coarse-grained acicular alpha-beta to incompletely recrystallized, essentially all alpha. Figures 17 and 18 show, from left to right and from top to bottom, a progression of microstructures as follows: (A) coarse-grained acicular alpha-beta, (B) fine-grained acicular alpha beta, (C) fine-grained acicular alpha beta plus blocky alpha, (D) acicular alpha beta plus equiaxed alpha, (E) acicular and unrecrystallized alpha beta plus equiaxed alpha, (F) equiaxed alpha plus unrecrystallized acicular alpha plus beta, (G) equiaxed alpha beta, (H) equiaxed alpha, (I) equiaxed plus unrecrystallized alpha, and (J) equiaxed plus unrecrystallized alpha.

In order to round out this review of microstructural varieties in titanium alloys, let us consider the products resulting from quenching from above the beta transus a series of binary alloys involving a beta-stabilizing addition. The variation in hardness of the quench products of such a series of alloys is shown schematically in Figure 19. The diagram indicates the structures that are associated with the various hardness levels. The sequence with increasing beta stabilizer content is as follows: alpha plus alpha prime/alpha prime/alpha prime plus beta plus beta prime/beta plus beta prime/beta.

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* Etchant: 20 percent HF, 20 percent HNO_3, 60 percent glycerin.

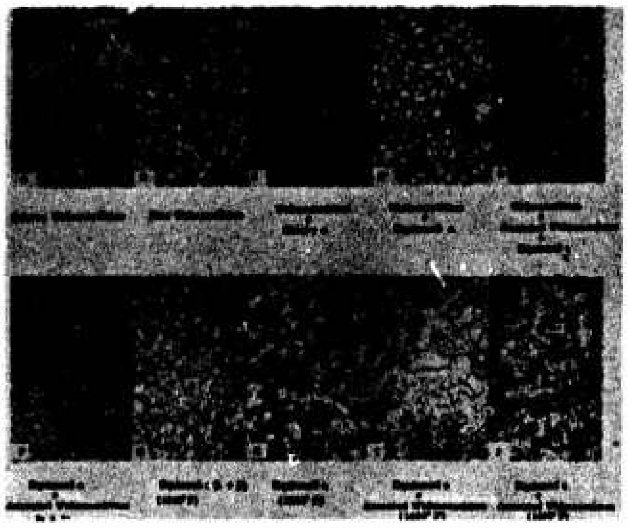


FIGURE 17. REPRESENTATIVE MICROSTRUCTURES

(Original magnification X100).

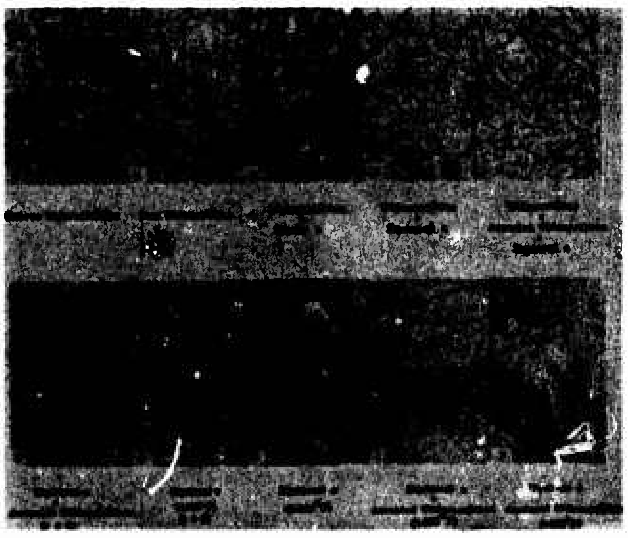


FIGURE 18. SAME MICROSTRUCTURES AS FIGURE 17 AT HIGHER MAGNIFICATION

(Original magnification X500).

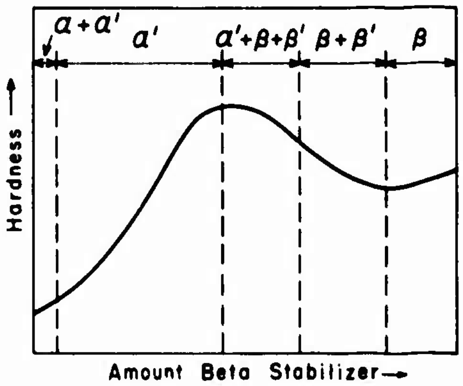


FIGURE 19. SCHEMATIC REPRESENTATION OF RELATIVE HARDNESS AND MICROSTRUCTURAL CONSTITUENTS RESULTING FROM QUENCHING FROM THE BETA TITANIUM BINARY ALLOYS OF PROGRESSIVELY HIGHER BETA STABILIZER CONTENT.

Alpha prime and beta prime are nonequilibrium phases. The former is the result of diffusionless, or shear, transformation, and is, therefore, a martensitic product. It is hexagonal, with a lattice parameter differing from that of equilibrium alpha due to supersaturation. A typical alpha prime microstructure is shown in Figure 20.

FIGURE 20. MARTENSITIC, OR α', MICROSTRUCTURE PRODUCED BY WATER QUENCHING Ti-7Mo ALLOY FROM 1800 F*

Beta prime, also called omega phase, does not always occur among the quench products of binary beta-stabilized systems. That is, it can be suppressed in the quench products, but can form upon low-temperature aging of the beta retained by quenching. In such cases the sequence after alpha prime is: alpha prime plus beta/beta. Although beta prime cannot be suppressed by rapid quenching of some alloys it is, apparently, a nucleation and growth product. It is a transition phase between metastable beta and equilibrium alpha. It is submicroscopic and, therefore, is not discernible by optical microscopy. Its presence is indicated by an abnormally high hardness associated with a structure that appears to be retained beta, and confirmation may readily be obtained by X-ray diffraction. Its structure may be indexed as cubic with the lattice parameter being about three times larger than that of bcc beta. It is coherent with the matrix and is associated with brittleness . Metastable beta in which beta prime is suppressed by quenching may form martensite when subjected to cold deformation.

Alpha-beta alloys cooled from above the beta transus transform to alpha by nucleation and growth unless cooling is sufficiently rapid to suppress such transformation to temperatures below the martensite start temperature, in which case shear transformation occurs. Therefore, the kinetics of transformation can be characterized by conventional time-temperature-transformation, i.e., TTT charts. Such charts are usually determined for conditions of isothermal quenching from above the beta transus. The products of such transformation are acicular and are unlike the microstructures usually encountered in commercial alloys. Micrographs of a Ti-7Mo alloy at various stages of isothermal transformation are shown in Figure 21.

X750

FIGURE 21. MICROGRAPHS OF Ti-7Mo ALLOY ISOTHERMALLY TRANSFORMED AT 1290 F (700 C)

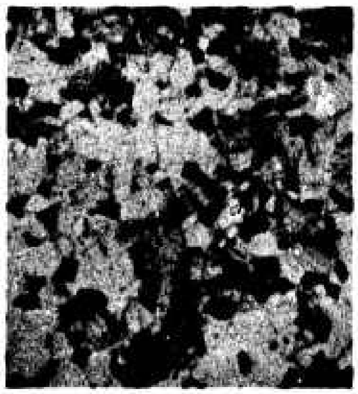
Fast beta eutectoid additions are not made to titanium alloys in sufficient amounts for a compound phase to be produced under the conditions of their recommended usage. However, for the sake of completeness, micrographs of alpha-plus-compound structures are shown in Figures 22 and 23. Figure 22 shows Ti_5Si_3 in the boundaries between coarse acicular alpha plates. Figure 23 shows an equiaxed structure of Ti_2Cu in an alpha matrix. The distributions of Ti_5Si_3 and Ti_2Cu resulted from the eutectoidal decomposition of the beta phase of prior Widmanstätten and equiaxed alpha-beta structures, respectively.

Unless precautions are taken, oxygen or hydrogen contamination, or both, may occur during heat treatment. Hydrogen pickup may occur in descaling or pickling operations if recommended procedures are not followed. Heating titanium alloys in air at temperatures above 1200 F produces enrichment of the surface layers in oxygen. Since oxygen is an alpha stabilizer, this causes an increase in the relative amount of alpha just below the surface in alpha-beta alloys. This condition is called "alpha case", and may be observed by optical microscopy as shown by Figure 24. To avoid detriment to mechanical properties surface layers should be removed to a depth in excess of the alpha case. As pointed out in earlier discussion (refer to Figure 9), oxygen accelerates transformation altering times and temperatures of the nose of TTT curves. Consequently, oxygen contaminated material may give unexpected results when given a conventional heat treatment.

It is possible to pick up hydrogen in certain (taboo) operations - for example, pickling in reducing acids such as HF or H_2SO_4 - in amounts sufficient to be readily detected by optical microscopy. Because of the high diffusion rate of hydrogen in titanium even at room temperature, removal of surface layers in such cases will probably not be enough. The hydrogen may be removed by annealing at temperatures above 1200 F under dynamic vacuum.

N 7508 X750

FIGURE 22. α + COMPOUND Ti_5Si_3. CONDITION PRIOR TO EUTECTOID DECOMPOSITION WAS ACICULAR $\alpha + \beta$. (Ti-6Al-1Si; 1560 F - 3 HOURS - AC.)*



N 11582 X750

FIGURE 23. α + COMPOUND Ti_2Cu. CONDITION PRIOR TO EUTECTOID DECOMPOSITION WAS EQUIAXED $\alpha + \beta$. (Ti-6Al-3Cu; 1560 F - 4 HOURS - AC, 1020 F - 24 HOURS - AC.)*

N 22776 X100

FIGURE 24. OXYGEN CONTAMINATION DURING HEAT TREATMENT PRODUCED AN α CASE, i.e., α PRECIPITATE IN β AT SURFACE OF A METASTABLE β ALLOY (B120-VCA, Ti-13V-11Cr-3Al)*

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* Etchant: 20 percent HF, 20 percent HNO_3, 60 percent glycerin.

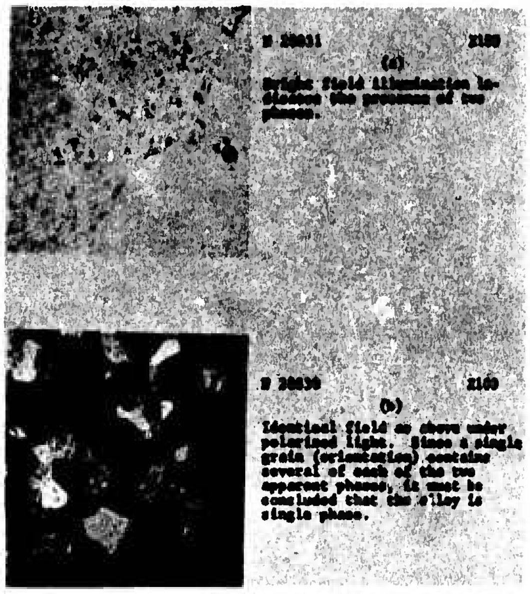
METALLOGRAPHIC MEANS

Optical Microscopy

Optical microscopy because of its ease and convenience is the general-purpose metallographic tool. It is no less useful in titanium metallurgy than for other metal systems. In fact, because the crystal lattice of the low-temperature allomorph, alpha, is anisotropic, more information can be obtained from optical microscopy than in the case of bcc or fcc metal-base alloys if one includes examination under plane polarized light as well as the more generally used bright field illumination. Once the relationship between microstructure and mechanical properties is established for a given alloy, optical microscopy is the first-line tool of investigation for seeking the reason(s) for abnormal mechanical properties. Optical microscopy can give information on the following: fineness and distribution of alloy phases, chemical homogeneity, presence and distribution of impurity phases, surface contamination, and quality control in fabrication and heat treatment.

Examination under plane polarized light is useful for differentiating between optically active alpha and non-optically active beta. It may be noted that alpha grains oriented with the basal plane (which is isotropic) in the plane of polishing will behave like uniaxial crystals; that is, they will not show optical activity when rotated under plane polarized light. Also, it should be noted that not all metallurgical microscopes equipped with polarized light provide essentially plane polarized amounts of elliptically or circularly polarized light. Metals with uniaxial crystal structures such as fcc or bcc give complete extinction at all rotational positions under plane polarized light provided the surface is properly prepared so that it is free of films, flowed metal, or submicroscopic etch pits. When the polarized light contains significant components of circularly or elliptically polarized light, isotropic crystals will not give complete extinction. However, they may be distinguished from anisotropic crystals by the fact that they do not "flash" under rotation. Examination under polarized light is best done with specimens in the unetched condition, as free from surface effects and features as it is possible to produce. For this purpose final surfacing by electropolishing is preferable to mechanical polishing.

In many cases grain size of alpha or predominantly alpha alloys is more readily determined from the polarized light image than from the bright field image. Also, the prior beta grain size of acicular structures of such alloys may be more readily discerned by viewing under polarized light. A qualitative estimate of the degree of preferred orientation in alpha or predominantly alpha alloys may be made by observing the number of grains that simultaneously flash when the specimen is rotated. An example of how polarized light may be used to assist in the interpretation of microstructures is given by the two micrographs in Figure 25. Figure 25a shows the bright field image of a specimen of Ti-7.1Al alloy cold worked and annealed at 1470 F for 200 hours. The specimen was electropolished but not etched. The bright field image indicates that two phases are present. However, it may be noted from the polarized light image of the same field that several grains of each of the apparent phases of the bright field image are encompassed in a region of the same orientation - that is to say, within a single grain as seen by polarized light. This can only mean that the specimen is single phase and that the bright field image is the result of chemical heterogeneity established somewhere in the working or thermal history of the specimen. This heterogeneity was not completely eliminated by the final heat treatment. In this case, the material was vacuum annealed in the alpha-plus-beta phase field in order to remove hydrogen prior to cold working. During the vacuum annealing treatment two phases were present, alpha and beta; however, the beta transformed to alpha upon cooling. Since no significant diffusion of aluminum occurred during cooling, the transformation product alpha and the equilibrium alpha differed in aluminum content by an amount equal to the separation between the boundaries of the alpha-beta field, i.e., about 2.5 percent. After cold working this compositional difference did not prevent the migration of grain boundaries during the annealing treatments. Therefore, a microstructure results which gives bright field and polarized light images that apparently do not agree. It is the polarized light image that presents the true state.



(a)
Bright field illumination indicates the presence of two phases.

(b)
Identical field as above under polarized light. Since a single grain (orientation) contains several of each of the two apparent phases, it must be concluded that the alloy is single phase.

FIGURE 25. MICROSTRUCTURE OF α ALLOY (Ti-7.1Al; 1470 F - 200 HOURS - IBQ) IN THE UNETCHED CONDITION AS SEEN UNDER BRIGHT FIELD AND POLARIZED LIGHT ILLUMINATION.

Segregation may be evaluated by solution annealing just below the beta transus. The ratio of alpha to beta or the absence of alpha gives a qualitative evaluation of the degree and distribution of chemical heterogeneity.

One must be very cautious in preparing titanium specimens for microscopic examination, beginning with cutting of a specimen from the bulk material. Cutting may be done by sawing or abrasive cut off. Titanium, particularly alpha, is susceptible to working effects (twinning). Since working effects may extend significantly below sawed surfaces, care must be taken to remove sufficient material in rough grinding to expose unaffected material. The abrasive cutting of titanium generates considerable heat. Therefore, liberal cooling fluid should be provided so that the risk of altering the microstructure through thermal effects is minimized.

Consideration must be given to the method of mounting specimens in relation to the structures to be viewed. Heating effects in the use of thermosetting mounting materials may cause alterations in the microstructure. For example, if hydride distribution is of interest, heating may cause solutioning and precipitation in a different configuration; or metastable retained beta may start to age. If there is any suspicion that heating effects may alter the structure of interest, then the specimens should be left unmounted or mounted in a room-temperature setting material.

Because of the difficulty in preparing surfaces free of flowed metal, electropolishing is frequently employed as the final polishing step. Although it is possible to prepare surfaces free of flowed metal by alternating mechanical polishing with etching or by mechanically polishing and etching simultaneously by wetting the cloth with a suitable agent, structures should be judged with a very critical eye. If there is any suspicion that the image is erroneous or misleading, then repolish forthwith. Figures 26 and 27 give examples of unsatisfactory micrographs together with satisfactory micrographs of the same specimen. Figures 26a and 27a show micrographs which appear "true" and, therefore, acceptable. However, they lacked clarity. Therefore, the specimens were repolished and etched to produce the micrographs shown in Figures 26b and 27b, which are very clear indeed. This lesson can bear repeating; be wary of microstructures which lack clarity. The less authentic micrograph resulted from a combination of flowed metal on the surface of the polished specimens and overetching in the attempt to remove the flowed metal. Although Figure 26a appears to be underetched, attack of some of the TiBe (or Ti_4Be_3) particles indicates that etching was sufficient.

There should be a constant awareness that in general what we accept as the microstructural features of a specimen are merely reflections of the manner in which the polished specimen has been chemically attacked by the etchant employed. In cases of certain titanium-base compositions, composition of the etchant can have a profound influence on the image produced, as illustrated by Figure 28. The same specimen is represented in both micrographs. The micrograph in Figure 28a resulted from etching with freshly prepared 20 percent concentrated HF, 20 percent concentrated HNO_3, and 60 percent glycerine, and gives convincing evidence that a fine uniformly distributed precipitate is present. On the other hand, the micrograph in Figure 28b resulted from etching with a solution of 2 cc concentrated HF, 6 cc concentrated HNO_3, and water to make 100 cc, and gives not the least suggestion of the presence of a precipitate. On the basis of Crossley's recent investigation of the titanium-rich end of the Ti-Al equilibrium diagram, the single-phase structure is the "true" one.(2) Because of the high concentration of acids, the glycerine-base etchant is faster acting than the aqueous-base etchant.

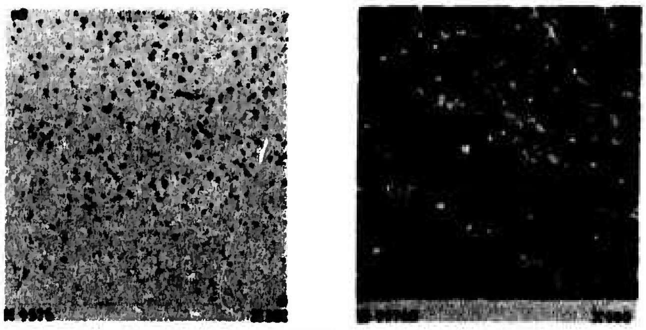


FIGURE 26. Ti-4V-0.75Be; 1650 F - 1 HOUR - WQ, 570 F - 24 HOURS - AC. LEFT: POOR SPECIMEN PREPARATION, FLOWED SURFACE AND OVERETCHED. RIGHT: REPOLISHED TO REMOVE FLOWED SURFACE AND PROPERLY ETCHED*

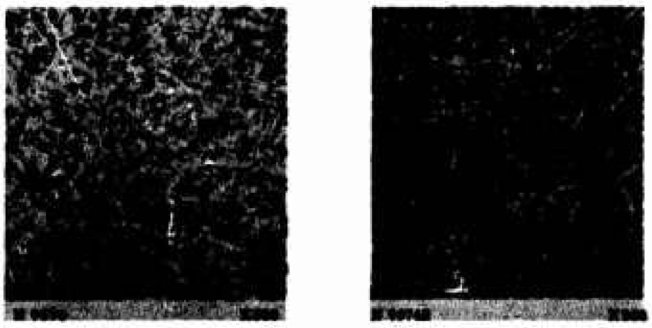
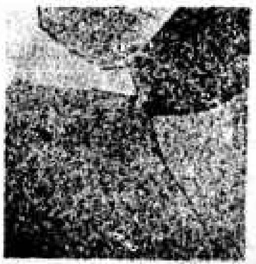


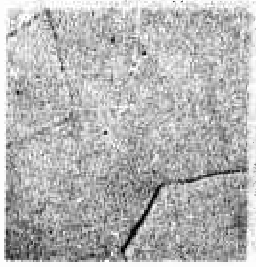
FIGURE 27. Ti-4V-0.75Be; 1380 F - 24 HOURS - WQ, 1100 F - 24 HOURS - AC. LEFT: POOR SPECIMEN PREPARATION, FLOWED SURFACE AND OVERETCHED. RIGHT: REPOLISHED TO REMOVE FLOWED SURFACE AND PROPERLY ETCHED*



N 28690 X500

(a)

Structure produced by etching with 20% HF, 20% HNO_3, 60% glycerin suggests the presence of a fine, uniformly distributed precipitate.



N 28829 X500

(b)

Structure produced by etching with Kroll etchant (2% HF, 6% HNO_3, 92% water) indicates a single phase material, and more nearly reflects the true state of the specimen.

FIGURE 28. EFFECT OF ETCHANT COMPOSITION ON STRUCTURE PRODUCED IN AN α ALLOY (Ti-7.8Al; 1650 F - 48 Hours - IBQ.)

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* Etchant: 20 percent HF, 20 percent HNO_3, 60 percent glycerin.

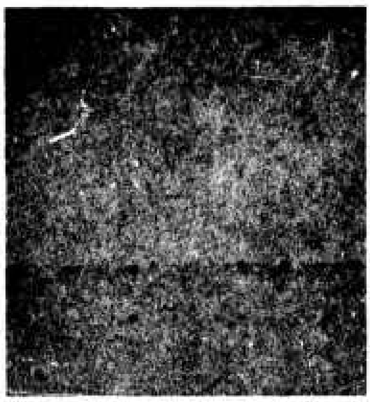
Apparently the precipitation effect is caused by the development of a profusion of etch pits. That this etchant does not usually have this effect is indicated by the number of micrographs presented herein which involved its use. Perhaps the etch pits are sites of clustering or some type of pre-precipitation phenomenon. If this be the case, then the clean micrograph is to be preferred as being more representative, for such zones would be submicroscopic.

Overetching is a common tendency in titanium microscopy. It is recommended that initial etching time be not greater than 5 seconds. If examination should indicate that more etching time is desirable, then proceed cautiously. However, deep etching of such severity that would normally be considered overetching can serve a very useful purpose. It has been found that particles of the embrittling phase Ti_3Al (maximum dimension about 1 μ) occurring in experimental alpha alloys containing sufficient aluminum can be revealed by deep etching. Figures 29 and 30 show particles of Ti_3Al in the grain boundaries of Ti-Al alpha alloys. Swabbing with Kroll etch, 2 percent HF, 6 percent HNO_3, aqueous solution, for 30 to 60 seconds brings out the Ti_3Al particles.

Figure 31a shows what appears to be a precipitate phase in an alpha alloy containing tin (Ti-5.2Al-2.5Sn; 1290 F - 500 hour - IBQ*). Actually the fine particles were electrochemically displaced from the Kroll etchant. The particles can be removed by immersing in nitric acid; however, this leaves pits at the particle sites. Figure 31b shows the same specimen re-electropolished and etched by swabbing for 60 seconds with 0.5 percent HF, 1.5 percent HNO_3, balance saturated aqueous solution of citric acid, followed by swabbing for 60 seconds with saturated citric acid solution. The citric acid suppresses electrochemical deposition, but does not entirely eliminate it; consequently, post-etch swabbing with saturated citric acid solution is necessary to remove traces of spurious precipitate. Immersion in the etch solution rather than swabbing results in considerably more than trace amounts of precipitate. The citric acid apparently holds tin - the supposed precipitate - in solution by forming a complex ion. Finally, an alpha alloy containing tin which is believed to have Ti_3Al present is shown in Figure 32.

N 29906 X1000

FIGURE 29. PARTICLES OF Ti_3Al IN GRAIN BOUNDARIES OF α ALLOY Ti-4.7Al STRESS AGED AT 1020 F - 1000 HOURS - 5000 PSI*



N 30032 X1000

FIGURE 30. PARTICLES OF Ti_3Al IN GRAIN BOUNDARIES OF α ALLOY Ti-8.7Al ANNEALED 1290 F - 500 HOURS - IBQ*

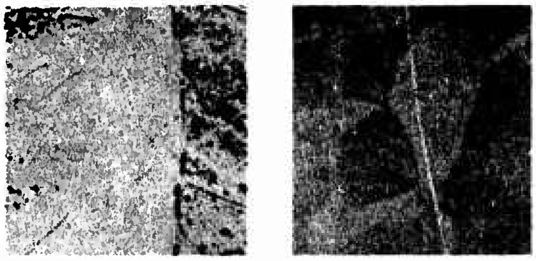


FIGURE 31. Ti-5.2Al-2.5Sn α ALLOY ANNEALED: 1290 F - 500 HOURS - IBQ

(a) Etching by immersion in Kroll solution for 30 seconds resulted in electrochemical deposition of particles believed to be tin. (b) Same specimen after re-electropolishing and etching by swabbing for 60 seconds with 0.5 percent HF, 1.5 percent HNO_3, balance saturated aqueous solution of citric acid, followed by swabbing for 60 seconds with saturated citric acid solution to remove traces of electrochemically deposited precipitate.

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* IBQ = Ice-brine quench.

* Etchant: Kroll etch applied for 30 to 60 seconds.

N 30233 X1000

FIGURE 32. Ti-7.6Al-2.6Sn ALLOY ANNEALED: 1110 F - 1000 HOURS - IBQ. ETCHED BY SWABBING FOR 60 SECONDS WITH 0.5 PERCENT HF, 1.5 PERCENT HNO_3, BALANCE SATURATED CITRIC ACID SOLUTION, FOLLOWED BY SWABBING FOR 60 SECONDS WITH SATURATED CITRIC ACID SOLUTION. Ti_3Al PARTICLES IN BOUNDARIES OF α GRAINS.

ELECTRON MICROSCOPY*

Now that you have examined the microstructure of alpha, alpha-beta, and beta-titanium alloys by optical microscopy, why do we need to use the electron microscope? As you will recall, the optical microscope can only resolve to the limit of visible light. This is still 1000's of atoms in size. If you recall the unit hexagonal cell of alpha titanium described previously, it would take 10 raised to the power of 23 the number of those unit cells to make up just one cubic inch of titanium.

In titanium alloys, the electron microscope is more capable of studying the micro-micro range of unit structure. These would include aging effects, interstitial effects, martensite transformations, deformation studies, and other submicroscopic phenomena, such as the precipitation phenomenon.

The electron microscope has a theoretical resolving power approximately 1000 times greater than the optical microscope. Therefore, its usefulness lies in the realm of microstructural constituents of fineness beyond the resolution capabilities of the optical microscope. As a matter of comparison, let us examine the basic construction of the microscope as compared to the optical microscope. In Figure 33 we see the optical path in both systems. In the optical microscope, magnification is obtained from optical glass lenses; while in the electron microscope, the lenses are electromagnetic coils focusing in and out in concentric circles. The wavelength of the electron source is 0.01's of an Å, whereas the optical microscope is limited to 2000Å - 3000 Å. In Figure 34 we see the actual Hitachi electron microscope.

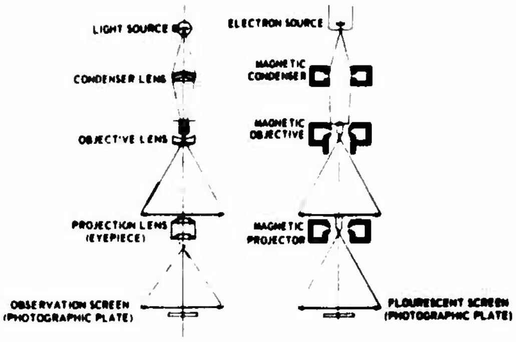

FIGURE 33

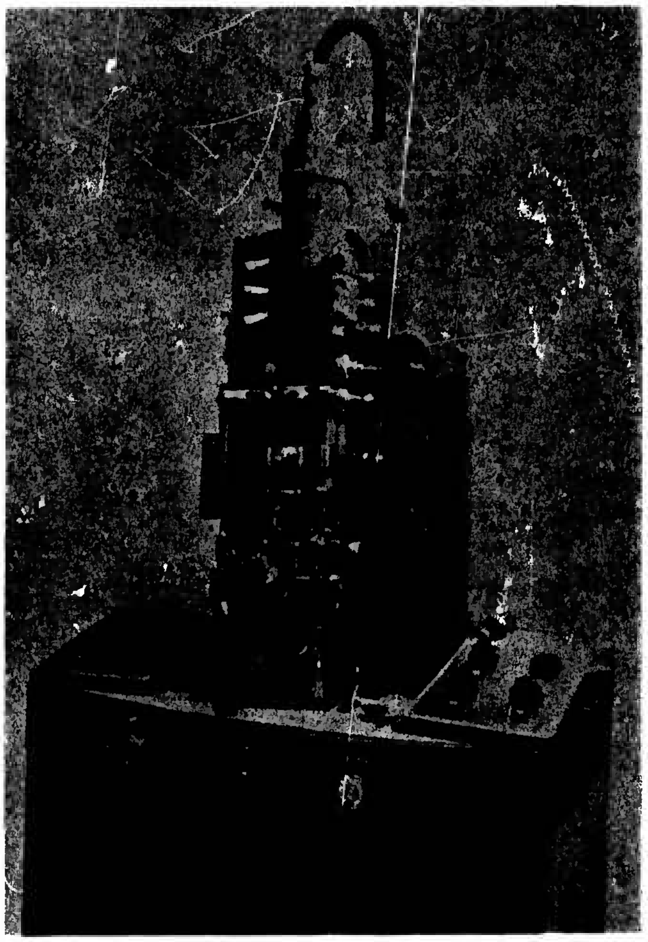

FIGURE 34

Basically, there are two approaches to studying the microstructure of titanium with the electron microscope. Lower magnification studies, <50,000 times on bulk samples, are performed with the use of replicas. A specimen which has been properly polished and etched by conventional metallography may be replicated by methods described in Figure 35. A liquid plastic coating is laid on the specimen in question. After hardening, it is carefully removed. It is then shadowed at an angle with a metal to a thickness of 50 Å to 75 Å and then coated with carbon to 200 Å thickness for support. Actual oxides may be used or even direct carbon as replicas. In both of these cases of carbon and oxide replicas, it is necessary to

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* Lecture presented by R. E. Herfert.

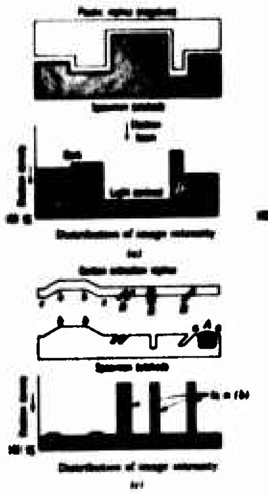


FIGURE 35

dissolve away the matrix by etching, thus destroying the sample. To illustrate this, the following microstructures were obtained from plastic replicas. First let us review the optical microstructure of unalloyed, commercially pure titanium (Figure 36). In the equiaxed grain structure, we observe only grain boundaries and grain configuration. This particular slide shows the effect of thermal treatment in and near the beta transus. The same microstructure under the electron microscopy is shown in Figure 37. The structures and symmetrical patterns which are observed are a result of the etching effect of acids on the grain. This is a result of the particular crystallographic orientation of the grain. The alpha alloys, such as commercially pure titanium shown here, offer very little other than such etching effects microstructurally. The alpha alloys containing beta offer more characteristic changes since phase transformation as well as orientation effects are present. Figures 38 and 39 show low magnification optical photographs of the Ti-8Al-1Mo-1V alloy heated above the beta transus and below. The electron microscope, affords a good view of the two structures of the super-alpha Ti-8Al-1Mo-1V alloy (Figure 40). Note the beta particles on each photomicrograph. The matrix is alpha-titanium. The difference in particle appearance is related to processing variables during rolling. Note the martensitic structures within the grain.

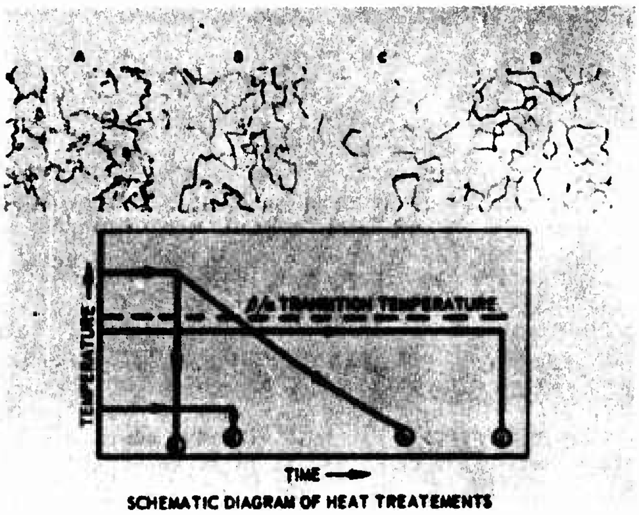


FIGURE 36

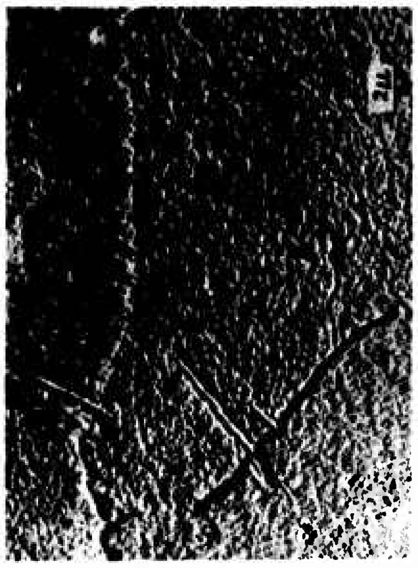
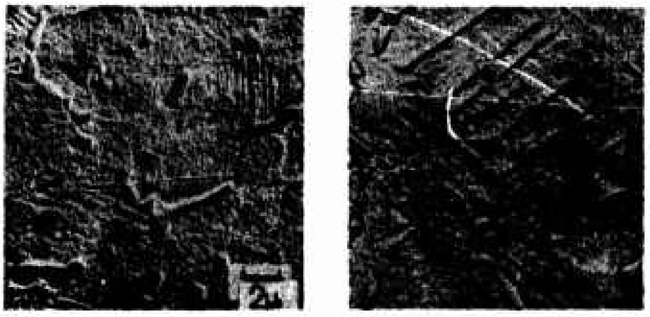


FIGURE 37

FIGURE 33

FIGURE 39



5000X Krolls Etchant Two Stage Replica

FIGURE 40. MICROSTRUCTURE OF DUPLEX-ANNEALED Ti-8Al-1Mo-1V.

We have already seen the super-alpha alloy Ti-8Al-1Mo-1V microstructure and the alpha-titanium microstructure. What happens as we diffusion bond these metals together? In Figure 41 we see the Ti-8Al-1Mo-1V at the top with the characteristic alpha and beta structure. The beta stabilizing elements have now diffused into the alpha titanium creating beta particles as shown. The original "lumpy" structure of alpha titanium is still evident.

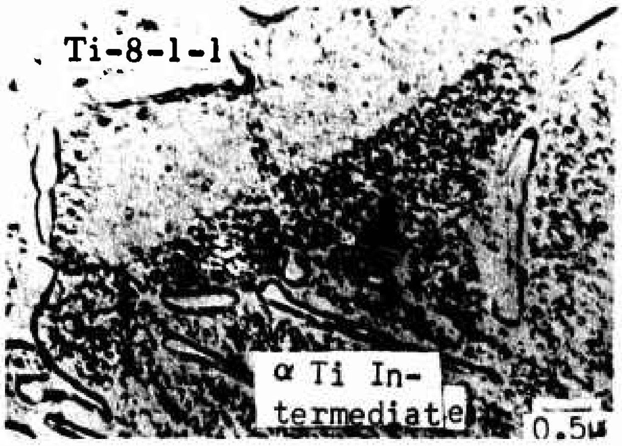
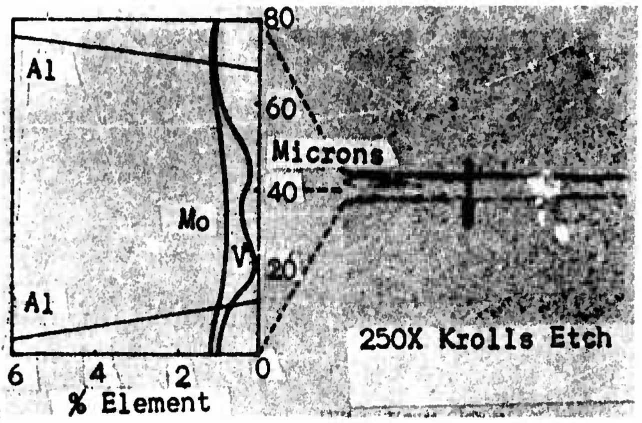


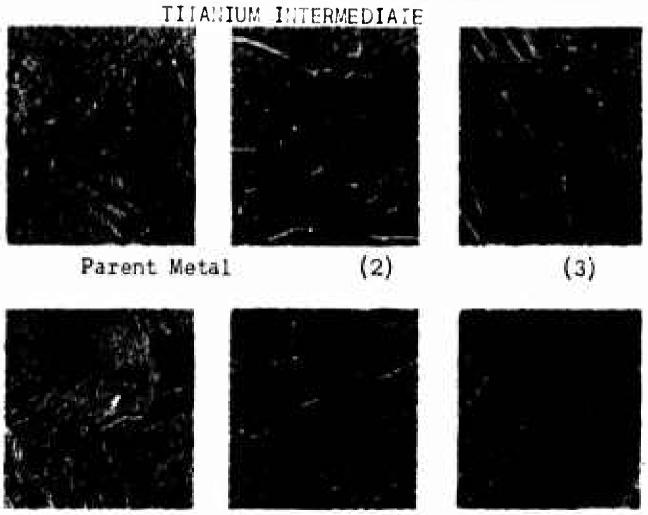
FIGURE 41. MICROSTRUCTURE OF DIFFUSION-BONDED Ti-8Al-1Mo-1V AND ALPHA TITANIUM INTERMEDIATE.

How do we know the beta-stabilizing elements molybdenum and vanadium have moved into the interface? We use a tool which has come into existence in the past 3 to 4 years called an electron microprobe. This instrument is an electron microscope which uses the electron beam to create secondary radiation from the sample characteristic of the elements present. This secondary X-ray radiation is then dispersed into wavelengths typical of each element present. The intensity of this radiation is proportional to the amount of the element present. This beam can be focused down to a 0.5 μ (4/100,000 inch, or 40 microinches) spot and thus be able to chemically analyze microstructural details. As an example of its use (Figure 42), we can now see how the joined area may be analyzed. It is apparent here how the two beta-stabilizing elements have dispersed around the interface.



Diffusion 1775 F - 5 minutes 1000 psi
Bonding Cycle: +1375 F + 15 minutes - 1000 psi

FIGURE 42. ELECTRON MICROPROBE ANALYSIS OF DIFFUSION-BONDED Ti-8Al-1Mo-1V PURE TITANIUM INTERMEDIATE



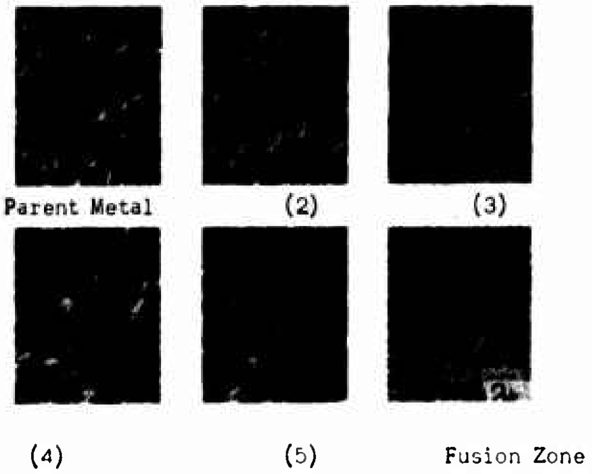
Parent Metal (2) (3)

(4) (5) Fusion Zone

FIGURE 43. MICROSTRUCTURE OF Ti-8Al-1Mo-1V FUSION WELD. PARENT METAL ⟶ FUSION ZONE (85 μ INCREMENTS)

Another very important area where the electron metallography method is very useful is studying the heat-affected zones in weldments. Figure 43 shows a series of photographs taken from the parent metal through the heat-affected zone (HAZ) into the fusion zone of a fusion weld in the Ti-8Al-1Mo-1V alloy. Here can be seen the transformation of alpha plus beta to acicular alpha and transformed beta. You will recall from the previous figure, transformation was initiated in the inside of the particles. In Figure 44 (in a spot weld) we see transformation initiated from the outside of the particle inward. These transformations are not discernable at optical microscopy levels.

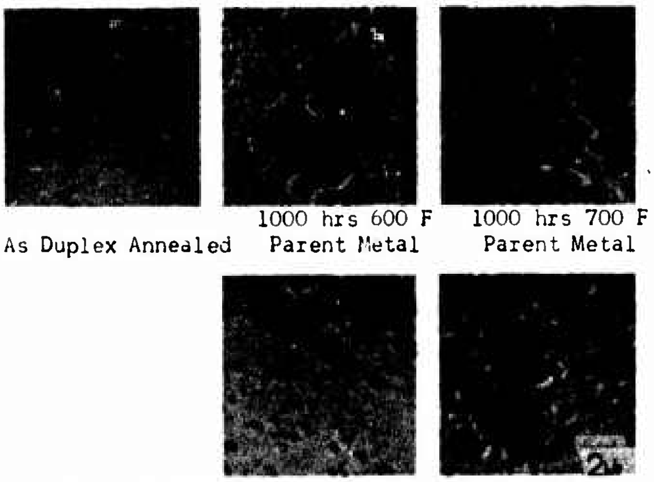
The super-alpha alloy Ti-8Al-1Mo-1V was originally considered to be a major material for applications on the SST. This was mainly due to its high-temperature creep properties. However, as studies proceeded on this material, an embrittling phenomenon was encountered. This was evidenced by a change in microstructure after long-thermal exposure. Figure 45 shows the microstructures resulting from long-time at temperature exposures. Note the transformation of alpha initiating inside the beta particles. This is shown to be much more dramatic in the next Figure, 46. The transformation product actually has a very fine needle-like structure. Simultaneously with this process, a different mechanism is reacting; that is, a precipitation or a nucleation of a super-lattice phase Ti_3Al. This



Parent Metal (2) (3)

(4) (5) Fusion Zone

FIGURE 44. MICROSTRUCTURE OF Ti-8Al-1Mo-1V SPOT-WELDED PARENT METAL → FUSION ZONE (85 μ INCREMENTS)



As Duplex Annealed
1000 hrs 600 F Parent Metal
1000 hrs 700 F Parent Metal
Heat-Affected Zone
Heat-Affected Zone

FIGURE 45. MICROSTRUCTURE OF Ti-8Al-1Mo-1V SPOT WELDED - 1000 HOURS THERMAL TREATMENT PARENT METAL → HEAT-AFFECTED ZONE

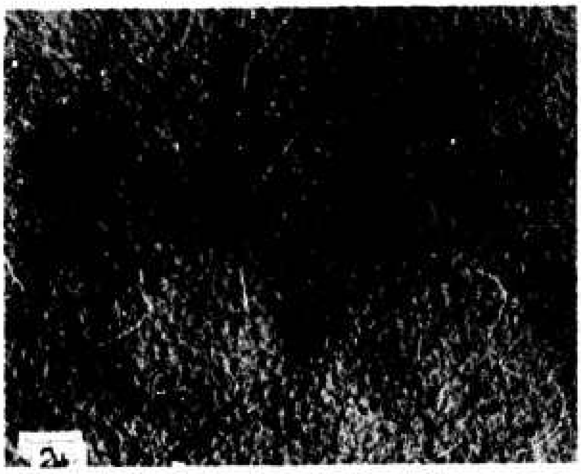


FIGURE 46. MICROSTRUCTURE OF DUPLEX-ANNEALED Ti-8Al-1Mo-1V PLUS 1000 HOURS AT 700 F

will be discussed in more detail a little later. These two reactions found by high magnification microscopy studies are believed to account for the embrittlement.

This brings our discussion to the last application of electron microscopy; that is, transmission electron microscopy. Here an actual specimen of the bulk material is thinned down to a thickness of 1000 Å to 5000 Å, a few micro inches, by chemical etching or electrolytic thinning. The electron beam is actually passed through the structure and resulting patterns are obtained which are a result of the electrons interacting with imperfections in the crystal. Here magnification can extend into several million times. In fact, most recent work has shown a resolution down to two atoms thickness, 2.4 Å.

The resulting microstructure for an aluminum specimen deformed in tension is shown in Figure 47. Notice the dislocation network. It is fairly regular and appears to be forming networks which are called subgrains. In the case of titanium, this is far from the situation present. The complexity of the deformation mechanisms in an HCP metal makes interpretation of the dislocation processes very complex.

FIGURE 47

Figure 48 shows the transmission microstructure of pure alpha titanium. Note the obscurity of any substructure; a few loop dislocations are evident, only. Note here the speckling appearance. This was identified as TiH, picked up during electrolytic thinning, and identified by diffraction. This is not a desired situation. This particular sample had also been deformed in tension.

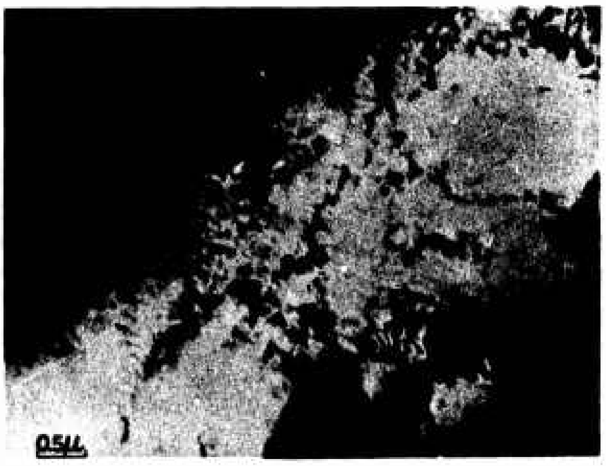


FIGURE 48. TRANSMISSION MICROSTRUCTURE OF PURE α-TITANIUM

Transmission studies of the super-alpha alloy Ti-8Al-1Mo-1V show a wealth of microstructural detail, all of which are not necessarily relatable to dislocation processes. Figure 49 shows the structure of a super-alpha Ti-8Al-1Mo-1V alloy duplex annealed. A beta particle is shown in a matrix of alpha. Note the unresolvable dislocation structure. The striations in the beta particle are felt to be the result of the alpha → beta transformation.

FIGURE 49. Ti-8Al-1Mo-1V DUPLEX-ANNEALED THINNED-PERCHLORIC ETHANOL, ETHYLENE GLYCOL - 200 F, 20-25 VOLTS DIRECT CURRENT

Along with the capability of viewing the microstructure at high magnification, the electron microscope offers a diffraction capability similar to the X-ray diffraction techniques. It is possible by selected area electron-diffraction techniques to single out microconstituents and identify them. This means was used to identify the embrittling Ti_3Al phase occurring in the Ti-8Al-1Mo-1V alloy.

Figure 50 shows the martensitic structure found in selected grains of the same alloy. It appears that in areas like this along the platelets, Ti_3Al forms. This is better seen in Figure 51. These data, I believe, corroborate Dr. Crossley's findings during metallographic examination.

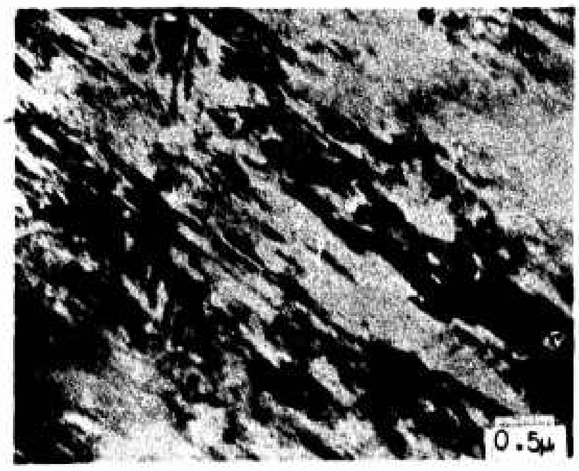


FIGURE 50. Ti-8Al-1Mo-1V DUPLEX ANNEALED

FIGURE 51

Transmission microscopy of a beta-titanium alloy (Ti-13V-11Cr-3Al) shows dislocation arrangements of fine-clustered disorder unlike any seen in the simpler aluminum systems. This is shown on Figure 52.

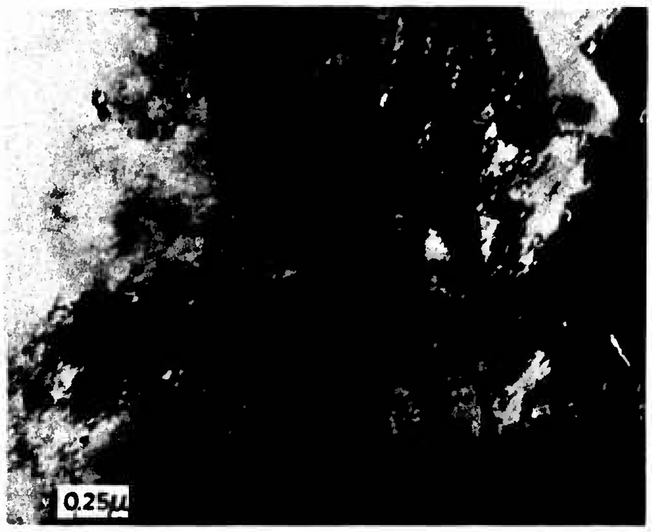


FIGURE 52

SUMMARY

To summarize, it should be apparent that microstructurally, there is a vast difference between the reactions found in titanium as compared to aluminum.

(1) The microstructure of alpha alloys, alpha-beta alloys, and beta alloys present individual characteristics.

(2) Alloying, fabrication, and thermal treatment greatly affect the microstructure of titanium alloys.

(3) Preparation of titanium specimens for metallographic examination is critical as to sectioning and polishing.

(4) The use of specialized lighting techniques, such as polarized light, is essential in the microscopy of titanium.

(5) Titanium is highly susceptible to hydrogen and oxygen contamination.

(6) Electron microscopy is necessary to obtain micro-micro ranges of differences in titanium microstructure.

(7) Dislocation arrangements in titanium are not as easily explained as those in aluminum.

It is evident that the control of microstructure during forming, machining, welding, corrosion, etc., is extremely important. New technologies must be obtained which will furnish the wealth of information now available for aluminum to titanium technology.

REFERENCES

(1) D. W. Levinson, "Investigation of Factors Related to an Unknown Phase in B120-VCA Alloy", ASD-TRD-62-534, Contract No. AF 33(616)-8149, IIT Research Institute, June, 1962.

(2) F. A. Crossley, "Titanium-Aluminum Equilibrium Diagram", IITRI-B6034-13 Final Report, Contract No. N161-25952, U. S. Navy Marine Engineering Laboratory, October 6, 1965; "The Titanium-Rich End of the Titanium-Aluminum System", Oral Presentation AIME 1966 Annual Meeting.

THE CORROSION RESISTANCE OF TITANIUM

H. B. Bomberger*

Titanium is best known for its high strength-to-weight ratio and other attractive mechanical properties. The resistance of the metal to corrosion is also outstanding but less widely known. Titanium and its alloys have been tested and used extensively for about the past 15 years in a great variety of aerospace, marine, and chemical applications and, unlike experience with the other materials of construction, failure by corrosion is essentially unknown except in the harshest environments.(1,2)

The purpose of this memorandum is to discuss titanium's corrosion properties and limitations with special reference to aerospace and marine applications.

GENERAL CORROSION RESISTANCE

The corrosion resistance of titanium, unlike that of most metals, can be defined within rather simple limits. The unalloyed metal appears to be completely resistant to all natural environments including seawater, body fluids, fruit, and vegetable juices. Metal exposed continuously to seawater for about 18 years has undergone only superficial discoloration. Wet chlorine, molten sulfur, most organic compounds (including acids and chlorinated compounds), and most oxidizing acids have essentially no effect on the metal. The metal is used extensively in hot-salt solutions including chlorides, hypochlorides, sulfates, and sulfides, and for handling wet chlorine gas, and nitric acid solutions.

On the other hand, hot concentrated low-pH chloride salts (such as boiling solutions of 30 percent $AlCl_3$ and 70 percent $CaCl_2$) are corrosive. Also, warm or concentrated solutions of HCl, H_2SO_4, H_3PO_4, and oxalic acid are damaging.(3) In general, all acidic solutions which are reducing in nature tend to be corrosive to the metal unless the solutions contain inhibitors. Also, the most powerful oxidizers, including anhydrous RFNA and 90 percent H_2O_2, attack the metal. Exposure to liquid and gaseous oxygen can result in ignition of the metal under impact. Ionizable fluoride compounds, such as NaF and HF, activate the surface and can cause rapid corrosion. Dry chlorine gas is especially harmful. The metal has limited resistance to air at temperatures above about 1200 F and deposits of chlorides and hydroxides can accelerate the rate of oxidation.

Welding does not appear to have a significant effect on the corrosion resistance of unalloyed titanium, as noted in Table 1.

PASSIVATION AND INHIBITION

Interestingly, most solutions, except those containing soluble fluorides, can be inhibited by the presence of even small amounts of oxidizing agents and heavy metal ions. Thus, we find that titanium is used in certain industrial process solutions, including HCl and H_2SO_4, which would otherwise be corrosive. Nitric and chromic acids and dissolved iron, nickel, copper, and chromium salts are especially effective inhibitors, as indicated in Figure 1. Attack by RFNA and chlorine gas can be inhibited by a small amount of water.

Titanium metal is inherently active but forms a thin oxide film which offers the unusual protection observed. This film is not fully protective under reducing conditions, in very powerful oxidizing environments, or in the presence of fluoride ions. However, the stability and integrity of this film is improved substantially by inhibitors. Metallic ions and oxygen from the air apparently absorb on the titanium surface,(4) whereas

TABLE 1. RESISTANCE OF UNALLOYED TITANIUM TO BOILING SOLUTIONS

Solution	Weight Percent	Corrosion Rates in Mils Per Year[a] Non-Welded	As-Welded
$AlCl_3$	20	nil[b]	nil
$CaCl_2$	20	0.6	nil
	40	nil	nil
$FeCl_3$	20	0.7	nil
	40	0.7	nil
NaCl	20	nil	nil
	40	nil	nil
$ZnCl_2$	20	nil	0.5
	40	nil	0.8
	60	nil	0.8
HNO_3	10	0.9	1.7
	20	1.5	2.5
	30	0.4[b]	5.7
	40	2.3[b]	3.3
	50	7.4[b]	4.8
	60	3.3[b]	3.0
	70	0.7	2.1

(a) 48-hour tests in 500 mil of solution.
(b) Significantly higher values have been reported elsewhere.

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* Manager, Product Development, Reactive Metals, Incorporated, Niles, Ohio.

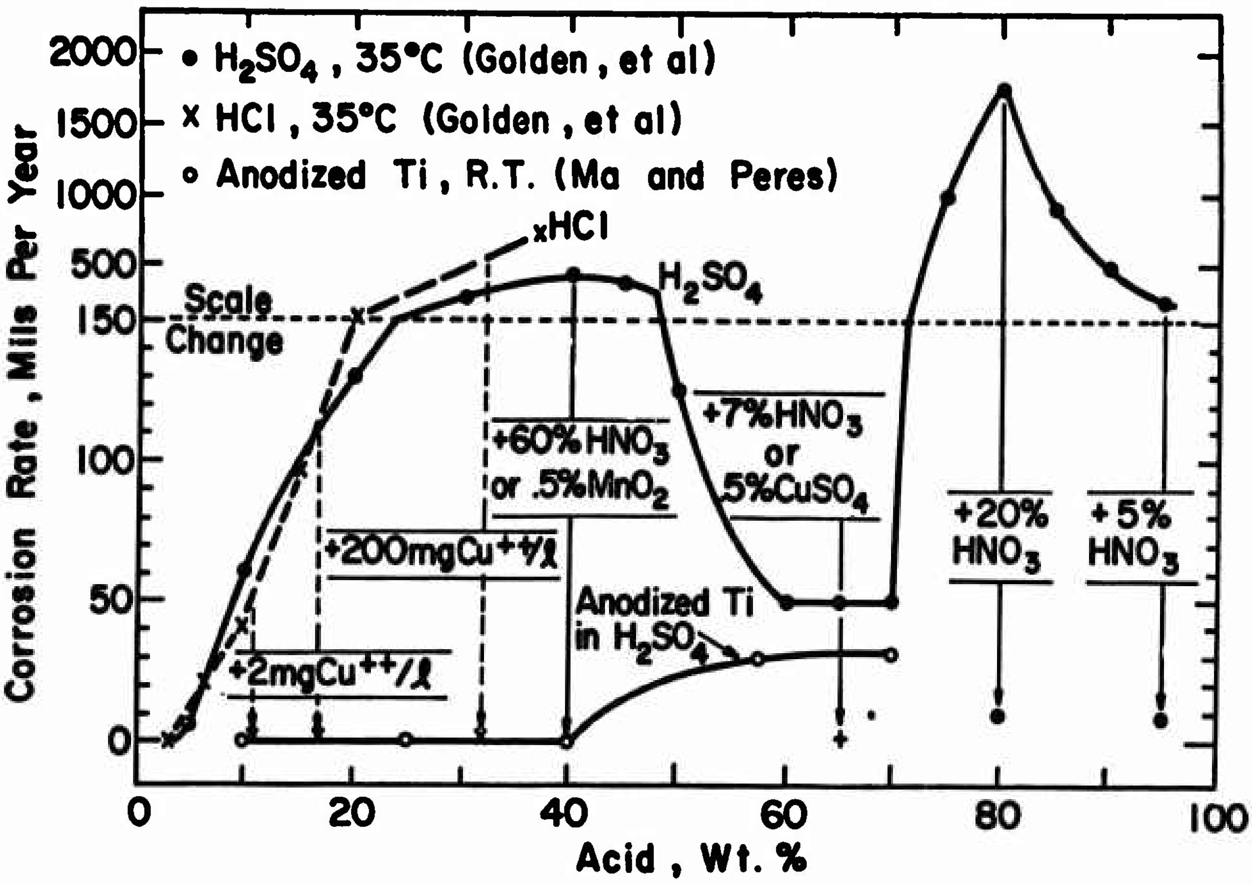


Figure 1 Commercial Ti in Acids With and Without Additions

TABLE 2

GALVANIC COUPLE TESTS WITH UNALLOYED TITANIUM IN SEA WATER AT HALF TIDE AND IN SEA AIR^6

Materials Coupled to Titanium	After 369 Days at Half Tide^a			After 56 Months in Sea Air^a		
	Uncoupled	Area 7xTi	Area 1/7 xTi	Uncoupled	Area 7xTi	Area 1/7xTi
FS-1 Magnesium	65.1^b	920.^{c}	Lost	0.88^e	1.17^e	3.52^e
Alclad 24S-T3	0.23	0.89	Lost	0.055	0.213	0.291
52S-1/2 H	0.46^d	0.75	4.60	0.085	0.036	0.81
Alclad 75S-T6	0.63	0.83	Lost	0.053	0.079	0.393
Copper	0.58	0.94	2.00	0.085	0.135	0.241
Mild Steel	8.60	12.20	12.90	6.13^f	9.82^f	Lost
Monel	0.07	0.06	0.13	0.015	0.020	0.032
Inconel	Nil	Nil	Nil	0.003	0.003	0.003
302 Stainless	0.044	0.008	0.096	0.008	0.009	0.002
316 Stainless	Nil	Nil	Nil	0.004	0.003	0.006

[a] Corrosion rates in mils per year after exposures at Kure Beach.
[b] Exposed 44 days.
[c] Exposed 2 days.
[d] Exposed 193 days.
[e] Exposed 3 years and 160 days.
[f] Exposed 1 year.

exposure to strong oxidizing conditions (such as nitric acid, air at moderately high temperatures and anodic treatments), promote resistance through growth of the oxide film. Dissolved oxygen is an important inhibitor in mildly reducing or hot chloride solutions but if its supply is restricted as in deep crevices, crevice corrosion may occur.

GALVANIC CORROSION RESISTANCE

Titanium does not suffer from galvanic corrosion except in certain powerful chemicals which are highly corrosive to the metal. In fact, contact with more noble metals has, in all practical cases, a very desirable effect. This effect is fundamentally the same as the application of a small positive EMF since it promotes anode polarization and oxide film growth and integrity.

Titanium can, however, affect the corrosion resistance of other materials with which it may be in contact. Salt spray tests conducted for 100 and 200 hours on titanium and titanium alloys joined to 2S and 24S aluminum, HK31 and AZ31B magnesium, mild steel, 410 stainless, 17-7PH stainless, and Monel indicate that titanium has slightly less tendency to promote galvanic corrosion of these materials than 18-8 stainless. This experience with 18-8 grades should be a useful guide for titanium. In most cases the commercial alloys Ti-8Mn, Ti-6Al-4V, Ti-5Al-2.5Sn, and Ti-4Al-4Mn were similar to or had less galvanic effect than unalloyed titanium.(5)

In common salt solutions, seawater, and certain acids titanium does not have an important effect on most inactive metals, but it can accelerate corrosion of the less resistant metals. For example, unalloyed titanium has been used successfully for years in contact with the 18-8 type steels in hot nitric acid. Table 2 gives data observed by the writer and coworkers on galvanic couples after long exposures to marine environments. These data indicate that titanium has very little effect on the performance of Monel, Inconel, 302 stainless, and 316 stainless in seawater and sea air during long exposure times, but more active metals may corrode more rapidly.(6)

EFFECT OF ALLOYING

The development of titanium alloys for corrosion resistance has been limited largely to chemical applications since alloys for structural applications appeared to have adequate resistance to the environments. As noted later, however, some of the higher-strength alloys are affected by the environment.

In general, alloying does not appear to have any adverse effects on the general corrosion resistance of titanium to natural environments and most mild chemicals. Certain elements do, however, reduce resistance to the most aggressive conditions.

Two basically different concepts have been employed to improve the resistance to nonoxidizing acid solutions. The one method involves the addition of a small amount of a noble metal which then forms low over-voltage cathode areas on the surface. These areas promote local cell action and anodic polarization. The other concept involves the addition of substantial amounts of a more corrosion-resistant metal such as molybdenum or tantalum. A few data on these materials are shown in Table 3 and briefly illustrate the wide application ranges possible through alloying.

SEAWATER EMBRITTLEMENT

As noted earlier, titanium has a reputation for being highly resistant to seawater. However, a special test developed recently by Brown at the Naval Research Laboratory shows that certain alloys containing sharp notches or defects causing high stress concentrations, lose resistance to fracture on exposure to seawater.(7) This behavior appears to be similar to the failures of high-strength steels in liquid environments reported by Stiegerwald.(8) Interestingly, this phenomenon does not seem to occur on sheet products lighter than about 0.050 inch.

The significance of this phenomenon on service performance is questionable in view of the excellent performance record of titanium alloys. Alloys, including Ti-8Mn and Ti-5Al-2.5Sn, found recently to exhibit this phenomenon have been employed successfully in aircraft, without known failures, during the past 10 years.(9,10) Apparently, the conditions required to demonstrate the effect have not been encountered in service.

Laboratory tests involve exposing cracked-plate specimens, under three-point loading or as a cantilever beam, in air and in an aqueous environment until failure occurs. Sheet specimens can be prepared in a similar manner but are usually tested under uniaxial loading. First, the specimens are usually notched and then stressed under a cyclic load to initiate a small fatigue crack to about 25 percent of the specimen depth. Machined notches, with a root radius of 0.002 inch or less, have also been used effectively. Predetermined static loads are then applied for long periods of time or until the specimens fail. Figure 2 shows the stress intensities sustained by Ti-6Al-4V after a non-optimum heat treatment. A ratio less than one for the failure stress in the liquid over the failure stress in air indicates an environmental effect. Characteristic fractures also indicate whether or not the fracture mechanism is influenced by the environment. Figure 3 illustrates a typical fracture. In this case Ti-7Al-2Cb-1Ta plate, in a sensitive condition, was tested by three-point loading in ASTM synthetic seawater.(9) The corrosion-enhanced fracture has a characteristically rougher surface than those achieved by fatigue or plane-strain fracturing.

A number of commercial and experimental alloys have been tested to determine their behavior in seawater. A general summary of these data, given in Table 4, shows that some of the alloys are sensitive to seawater and others are unaffected. A more detailed study has shown that behavior of a given alloy depends on (1) the composition and (2) the processing history of the material.

In general, high aluminum contents were found to promote and additions of molybdenum and vanadium to decrease the sensitivity to seawater and other aqueous solutions. For example, the alloy Ti-7Al-2Cb-1Ta is quite sensitive to seawater embrittlement but a modification of the alloy to Ti-6Al-2Cb-1Ta-0.8Mo resulted in a material unaffected by seawater. Furthermore, thermal cycling and lengthy exposures within the temperature range

TABLE 3. NOMINAL CORROSION RESISTANCE OF TITANIUM AND CERTAIN TITANIUM ALLOYS

Solution, Wt.%	Temperature	CORROSION RATES IN MILS PER YEAR[a]		
		Unalloyed Titanium	Ti-.2Pd	Ti-30Mo
25% NaCl	Boiling	Nil	Nil	Nil
25% $AlCl_3$	Boiling	2,000	1	Nil
30% $FeCl_3$	Boiling	1	Nil	5
5% HCl	Boiling	1,100	7	Nil
20% HCl	R.T.	25	4	Nil
20% HCl	Boiling	5,000	770	5-10
20% HCl + 1% $FeCl_3$	Boiling	110	115	1,500
5% H_2SO_4	Boiling	1,900	20	Nil
40% H_2SO_4	R.T.	65	9	Nil
40% H_2SO_4	Boiling	13,000	-----	2-10
40% H_2SO_4+1% $Fe_2(SO_4)_3$	Boiling	110	90	750
65% HNO_3	R.T.	Nil	Nil	Nil
65% HNO_3	Boiling	2-20	25	50
10% Oxalic	212 F	3,500	4,800	1.5

[a] 48-hour tests in 500 mil of solution.

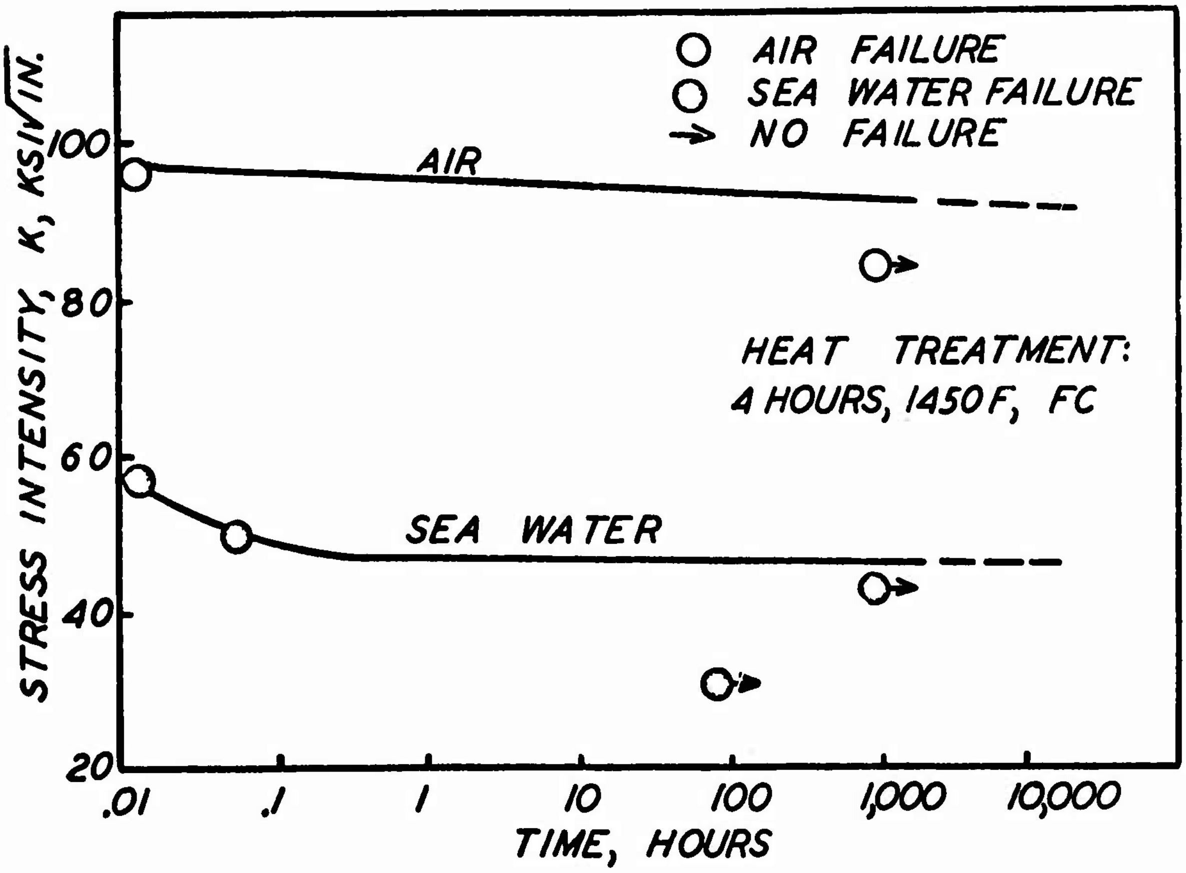
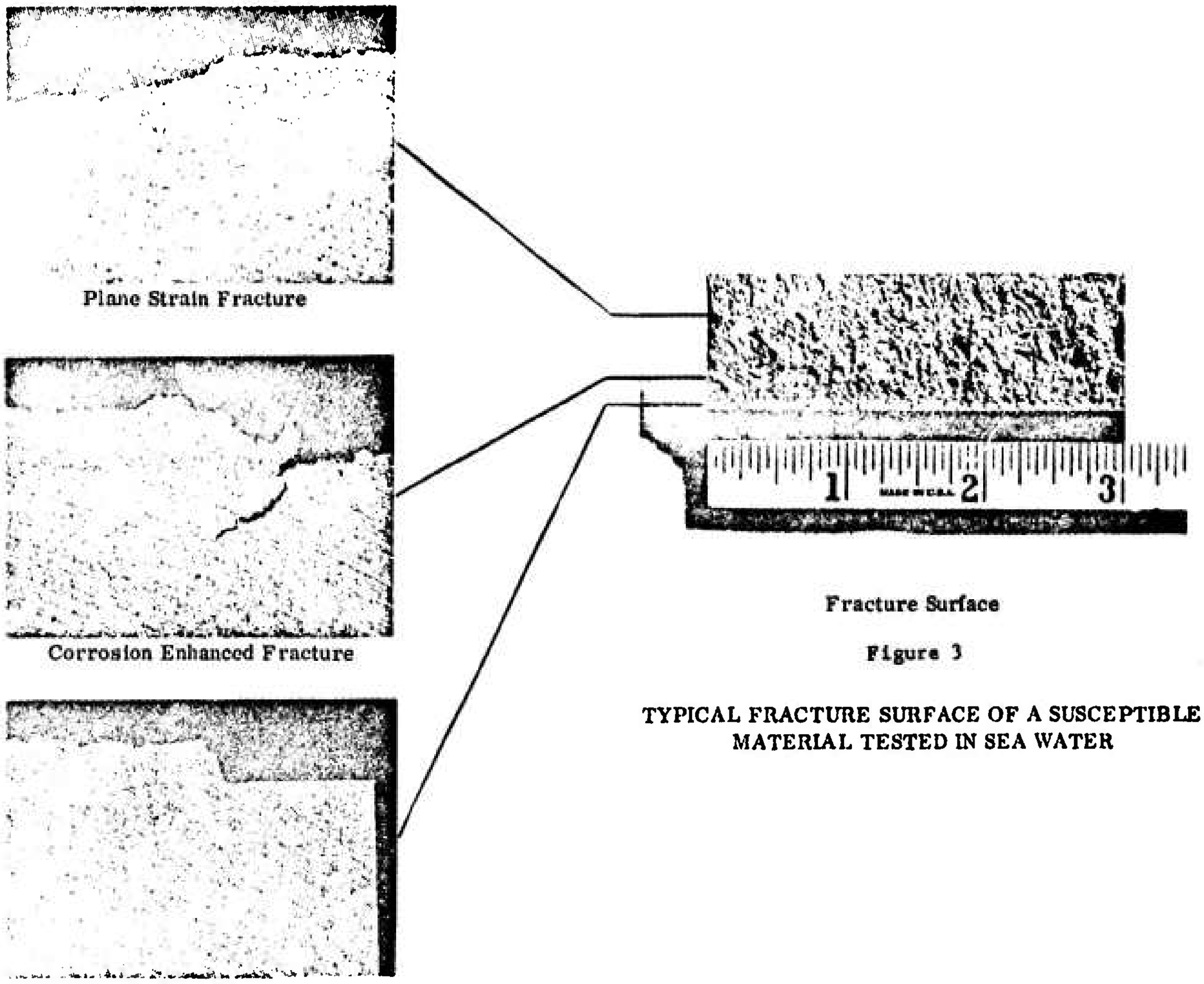


FIGURE 2. EFFECT OF TIME ON FAILURE STRESS INTENSITY OF SENSITIZED Ti-6Al-4V .675-INCH PLATE



Plane Strain Fracture

Corrosion Enhanced Fracture

Fatigue Crack

Fracture Surface

Figure 3

TYPICAL FRACTURE SURFACE OF A SUSCEPTIBLE MATERIAL TESTED IN SEA WATER

TABLE 4

GENERAL EFFECT OF SEA WATER ON ANNEALED TITANIUM ALLOYS[9, 10]

INSENSITIVE	SENSITIVE
Unalloyed Titanium	Ti-.32 Oxygen
Ti-7Al-2.5Mo	Ti-7Al-2Cb-1Ta
Ti-6Al-2Cb-1Ta-.8Mo	Ti-8Al-1Mo-1V
Ti-5Al-2Sn-1Mo-1V	Ti-5Al-2.5Sn
Ti-6Al-4V	Ti-8Mn
Ti-4Al-3Mo-1V	

of about 900 to 1500 F tend to promote sensitivity. Thus, we find that an alloy which is rather insensitive, such as Ti-6Al-4V, can be made sensitive by abnormally long treatments in this temperature range. Also, some of the sensitive alloys such as Ti-7Al-2Cb-1Ta can be rendered insensitive by solution annealing at high temperatures (1700 to 1850 F) and cooling rapidly through the sensitizing region. This general concept is illustrated in Figure 4. Work is underway to explain the mechanism and establish detailed time-temperature-transition diagrams for the important alloys so seawater sensitivity can be avoided.(9,10) Specific data, illustrating the important influence of thermal history, are given in Table 5.

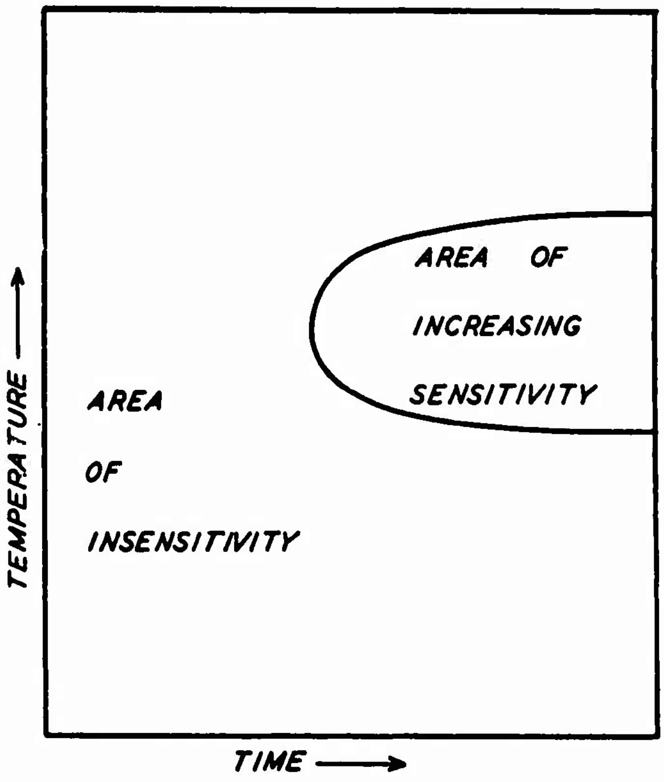


FIGURE 4. GENERAL EFFECT OF PROCESSING TIME AND TEMPERATURE ON THE SEA-WATER SENSITIVITY OF TITANIUM ALLOYS

TABLE 5

INFLUENCE OF THERMAL HISTORY ON SEA WATER SENSITIVITY[9]

Alloy Plate[a]	Treatment[b]	Failure Stress at Crack Root, Ksi In Air	Failure Stress at Crack Root, Ksi In Sea Water	Stress Ratio S_{sw}/S_{air}
Ti-8Al-1Mo-1V (.800" Thick)	1450 F	267	235	.88
	1550 F	248	223	.90
	1800 F	250	257	1.00
	1850 F	258	258	1.00
Ti-6Al-4V (.750" Thick)	1300 F	217	184	.85
	1400 F	242	204	.84
	1750 F	290	290	1.00
	1850 F	235	235	1.00

[a] Plate fatigue cracked and tested as cantilever beam.

[b] One hour at temperature and air cooled.

There are good reasons to believe that the area of sensitivity, shown in Figure 4, corresponds to an embrittling reaction in the titanium-aluminum system, as suggested by Crossley and Carew.(11) This embrittlement is believed to result from the development of an ordered structure or the formation of a Ti_3Al compound. The tendency for the reaction to occur clearly increases with the aluminum content, whereas molybdenum and vanadium decrease this tendency, presumably, by decreasing the diffusion rate of the aluminum. This mechanism does not, of course, explain the sensitivity noted in the Ti-8Mn and Ti-0.32 oxygen alloys. Apparently their behavior also results from an inherent instability but may occur by a different mechanism than that promoted by aluminum.

HOT-SALT CORROSION

Several years ago a discovery was made in the laboratory that titanium and titanium alloys can be damaged by halogenated compounds at temperatures above 500 F. Chloride salts and especially sodium chloride, were found to be the most troublesome agents. Residual salts on the metal were found to pit the surface or even crack certain alloys under high tensile loads. This phenomenon, like the problem of seawater embrittlement, has been observed only in laboratory tests and not in actual service applications. Cracking of titanium parts has been encountered by fabricators, however, in stress-relieving operations when vapors of chlorinated hydrocarbon cleaning fluids were not completely removed from part enclosures. This latter problem was promptly corrected.

Since the original finding that hot halogenated salts are damaging to titanium, the phenomenon has been studied very extensively. While much has been learned about the reaction, relative susceptibility, and related variables, it is generally agreed that the laboratory tests do not simulate service conditions well nor predict field performance. Cycle tests, used to partly simulate service conditions are, apparently, less damaging than the normal static tests.(13,14)

The extent of damage by salts is directly related to the temperature, exposure time, and tensile stress level. The processing history, alloy composition, salt composition, and other environmental conditions also have important effects.(12) Figure 5 illustrates the general influence of temperature on susceptibility to damage of annealed Ti-6Al-4V sheet coated with sodium chloride. Temperatures and stress levels greater than those indicated by the solid line can result in increasingly noticeable corrosion and stress-corrosion damage. General corrosion becomes prevalent at the highest temperatures when the metal is in contact with chloride salts.

The position of the curve in Figure 5 can vary with the quality of the product but even more with the alloy grade. The relative resistance of Ti-4Al-3Mo-1V, Ti-6Al-4V, and Ti-8Al-1Mo-1V has been reported in this order with the last alloy being the most susceptible to salt damage at elevated temperatures.(13,14)

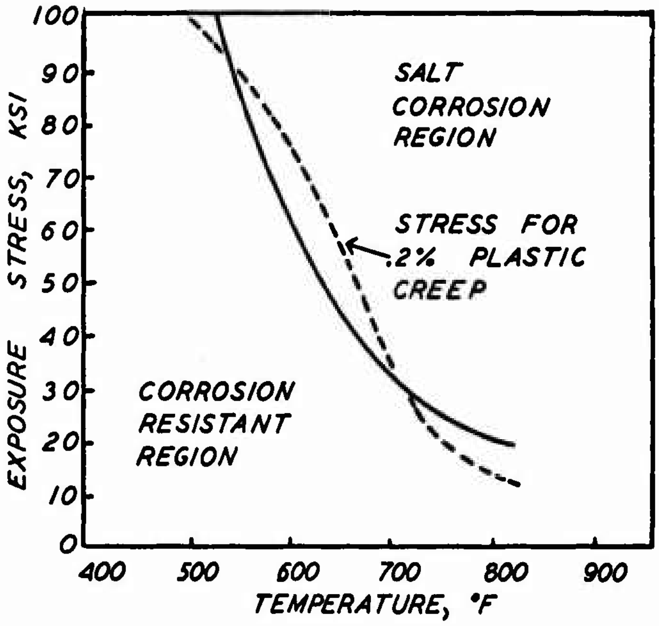


FIGURE 5. SALT CORROSION RESISTANCE OF ANNEALED Ti-6Al-4V SHEET

A few data are given in Table 6 which indicate the importance of the processing history employed. This particular heat of bar product as mill annealed displayed unusually good resistance to salt on testing at temperatures up to and including 800 F. However, a 24-hour treatment at 1050 F, and shorter treatments at 1800 F and 1700 F produced a very sensitive condition. The microstructure of this material was fine grained and was not changed significantly by the 1050 F treatment. Studies with an electron microscope, however, indicated slightly less beta in the aged samples.(12) We also know that some re-distribution of alloying elements occurred by diffusion; and this apparently, resulted in the sensitive condition. The basic cause for the sensitivity to salt may thus be the same as that involved when the alloy becomes sensitive to seawater.

Work on the Ti-13V-11Cr-3Al alloy has shown that this material can be readily sensitized to crack in dilute hydrochloric acid and hydrochloric acid vapor. In this case, a good correlation of sensitivity with the processing time-temperature parameter was demonstrated.(12) Work on Ti-8Al-1Mo-1V and Ti-5Al-2.5Sn has shown that sensitivity to salt corrosion can be decreased by solution annealing these grades at about 1840 and 1800 F, respectively.

TABLE 6

MECHANICAL PROPERTIES OF Ti-6Al-4V ALLOY BAR

		CREEP TEST					TENSILE PROPERTIES AFTER CREEP TEST				
Sample[a]	Condition	NaCl Coat[b]	Temp. (°F)	Time (hr.)	Load (Ksi)	Plastic Strain (%)	Ultimate Tensile Strength (Ksi)	0.2% Yield Strength (Ksi)	Elongation in 1 in. (%)	Reduction in Area (%)	Visual Salt Penetration
1	½ hr. 1450 F, AC	No	---	0	--	----	167.0	155.5	17.0	52.7	----
2	½ hr. 1450 F, AC	No	---	0	--	----	168.2	156.5	17.0	54.2	----
3	½ hr. 1450 F, AC	Yes	550	312	90	0.32	183.6	151.4	13.0	51.9	None
4	½ hr. 1450 F, AC	Yes	650	312	65	0.40	183.6	160.7	14.0	51.4	None
5	½ hr. 1450 F, AC	No	750	50	40	0.40	180.7	162.5	14.5	48.8	----
6	½ hr. 1450 F, AC	Yes	750	50	40	0.24	179.7	165.9	15.5	50.2	None
7	½ hr. 1450 F, AC	Yes	750	200	40	0.72	173.6	162.9	13.0	52.8	None
8[c]	½ hr. 1450 F, AC	Yes	750	300	50	0.70	182.5	168.9	13.0	44.3	None
9	½ hr. 1450 F, AC	No	800	50	30	0.56	180.1	169.1	13.0	52.0	----
10	½ hr. 1450 F, AC	No	800	50	30	0.48	179.8	171.0	14.0	50.3	----
11	½ hr. 1450 F, AC	Yes	800	50	30	0.27	180.2	168.9	16.0	50.4	None
12	½ hr. 1450 F, AC	Yes	800	50	30	0.30	181.7	170.3	14.0	51.0	None
13	24 hr. 1050 F, AC	No	---	0	--	----	167.3	160.6	15.5	47.3	----
14[c]	24 hr. 1050 F, AC	Yes	750	300	50	1.6	169.6	160.9	0.0	1.2	Deep
15	½ hr. 1500 F, AC	Yes	750	300	50	0.38	168.7	150.5	17.0	48.5	None
16	½ hr. 1600 F, AC	Yes	750	300	50	0.69	169.8	149.0	5.0	5.6	Slight
17	½ hr. 1650 F, WQ +8 hr. 950F, AC	Yes	750	300	50	0.37	136.9	-----	0.0	0.8	Deep
18	½ hr. 1700 F, WQ +½ hr. 1400F,AC	Yes	750	300	50	0.58	147.0	146.5	1.0	4.3	Deep

[a] All samples from same 0.5-inch bar, tested as 0.250 inch round tensile coupon after heat treatments.

[b] NaCl applied as thick slurry with brush prior to creep tests.

[c] Samples 8 and 14 were adjacent in original bar.

This work shows that the susceptibility to hot-salt corrosion, as well as to seawater embrittlement, is influenced considerably by processing and, therefore, should be controllable.

Surface coatings, although vulnerable to damage, may also offer a good means for controlling salt corrosion. Ductile metal plates, consisting of aluminum, nickel, and zinc show promise for further development. Flame-sprayed aluminum and nickel and electroless nickel plates, however, were too porous to offer good protection. Hot-dipped aluminum offered protection when it covered the titanium alloys completely. On the other hand, zinc coatings applied by flame spraying or dipping appeared to be completely protective even when porous. The protective mechanism in this case appears to be different from that of a physical barrier and is believed to be electrochemical in nature.(12)

A better understanding of the salt-corrosion mechanism may also offer important information on its control. It is now generally agreed that oxygen is required in the reaction of titanium and chloride salts because the reaction cannot proceed in a good vacuum. Moisture may also have an effect since higher reaction rates were reported in moist air than in dry air. The composition of the reaction product varies with time but consists primarily of titanium dioxide and traces of sodium oxide and titanate, and titanium dichloride.(12,13) Theoretical calculations and experimental evidence also indicate that chlorine gas and hydrochloric acid are also small but important intermediate products of the reaction. The sodium oxides and titanium chlorides are not really detected because of the small amounts involved and their instability. This is especially so in moist air. Titanium chloride readily reacts with oxygen and moisture in the air. In the first case, chlorine gas is liberated and, in the second case, hydrochloric acid. Both of these products when hot and dry are highly corrosive to titanium and very readily crack the sensitive alloys. They react immediately to produce more unstable titanium chloride. Thus, the writer believes, the reaction process becomes cyclic and a small amount of sodium chloride can do considerable damage by this means.

Objections voiced about this proposed mechanism are (1) that the chlorine and hydrogen chloride gases are not readily detected and (2) that they do not cause damage on material removed from the immediate area. However, since the reaction occurs at the salt-metal interface, and since both the dry chlorine and hydrogen chloride gases react rapidly with the metal, the concentration and volume of these active gases available at any given time must always remain very small and localized. An alternate theory was advanced that the products of reaction are titanium dichloride and sodium hydroxide and that the latter material promotes the damage. While the thermodynamics may support such a conclusion, it is not possible for an acidic salt and a strong base to form simultaneously and coexist.

Thermodynamics suggest a large number of possible reactions. A few of the most interesting and least complicated ones, based on known requirements and observed products, are given in Table 7.

TABLE 7

STANDARD FREE ENERGY CHANGES FOR POSSIBLE REACTIONS IN THE SALT CORROSION OF TITANIUM

NO.	REACTION	ΔF (KCal)	
		440 F	1340 F
1	$Ti\ (s) + 2NaCl\ (s) + \frac{1}{2}O_2(g) = TiCl_2(s) + Na_2O(s)$	- 11.0	+ 9.0
2	$TiCl_2(s) + Na_2O(s) = TiO(s) + 2NaCl\ (s)$	-101.4	-110.3
3	$Ti(s) + \frac{1}{2}O_2(g) = TiO(s)$ (Sum of 1 and 2, also 7 and 9)	-112.5	-101.3
4	$Ti(s) + 2NaCl(s) + O_2(g) = TiCl_2(s) + Na_2O_2(s)$	- 47.0	- 32.0
5	$TiCl_2(s) + Na_2O_2\ (s) = TiO_2(s) + 2NaCl(s)$	-156.7	-150.5
6	$Ti(s) + O_2(g) = TiO_2(s)$ (Sum of 4 and 5, also 8 and 9)	-203.7	-182.5
7	$TiCl_2(s) + \frac{1}{2}O_2(g) = TiO(s) + Cl_2(g)$	- 7.5	- 13.9
8	$TiCl_2(s) + O_2(g) = TiO_2(s) + Cl_2(g)$	- 98.7	- 94.2
9	$Ti(s) + Cl_2(g) = TiCl_2(s)$	-105.0	- 88.3
10	$2TiO(s) + Cl_2(g) = TiCl_2(s) + TiO_2(s)$	- 83.8	- 68.3
11	$TiCl_2(s) + H_2O(g) = TiO(s) + 2HCl\ (g)$	0.0	- 6.5
12	$Ti(s) + 2NaCl(s) + O_2(g) + H_2O(g) = TiO_2(s) + 2HCl\ (g) + Na_2O\ (s)$	-102.3	- 79.2
13	$Ti(s) + 2NaCl\ (s) + \frac{1}{2}O_2(g) + H_2O(g) = TiO(s) + 2HCl(g) + Na_2O(s)$	- 11.1	+ 2.0
14	$Ti(s) + 2HCl(g) = TiCl_2(s) + H_2(g)$	- 60.0	- 48.3
15	$2Ti(s) + 2NaCl(s) + 1.5O_2(g) = TiCl_2(s) + Na_2TiO_3(s)$	-460.7	-214.5
16	$2Ti(s) + 2NaCl(s) + 2O_2(g) = TiO(s) + Na_2TiO_3\ (s) + Cl_2\ (g)$	-468.2	-227.4
17	$2Ti(s) + 2NaCl(s) + 2.5\ O_2\ (g) = TiO_2(s) + Na_2TiO_3(s) + Cl_2\ (g)$	-559.4	-308.6
18	$TiO_2\ (s) + 2NaCl\ (s) + \frac{1}{2}O_2\ (g) = Na_2TiO_3\ (s) + Cl_2\ (g)$	-152.0	+ 56.3

Large negative free-energy values indicate a strong tendency for a specific reaction to proceed to the right. These data and experience indicate that the net effect of salt at high temperatures is to accelerate oxidation of the metal to TiO_2, as indicated primarily by reactions 3 and 6. Other important reactions, involving key intermediate reaction products, are numbered 1, 7, 8, 9, 12, and 14.

The proposed formation of intermediate corrosion products, such as chlorine and hydrochloric acid, may be an important consideration in the use of titanium alloys in high-speed aircraft. At high velocities, and especially at the low pressures at high altitudes, such gaseous products would tend to escape very rapidly from the reaction site. Thus, salt damage to a sensitive alloy may possibly be curtailed or not experienced under such service conditions.

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TITANIUM ALLOY STRUCTURAL FORGINGS - STATUS REPORT 1966

James E. Coyne*

INTRODUCTION

This is essentially a progress report of the state-of-the-art of forging titanium and its alloys. Let me first state that titanium alloys are quite forgeable. By this it is meant they are shaped into engine, missile, and airframe hardware in today's production forging equipment, hammers, and presses. The evidence which substantiates this statement is the large number of jet engine and missile components plus the growing lists of structural parts that have been produced in the last 10 years.

There are many shapes classified and sold as forgings. Figure 1 illustrates the various types of forgings. It is evident from the information presented in this illustration that the greater the degree of sophistication the greater the number of tools (die sets) employed. The state of the art in titanium forging has not reached the no-draft design yet but I am confident it will come with increased usage of titanium in airframe structural hardware.

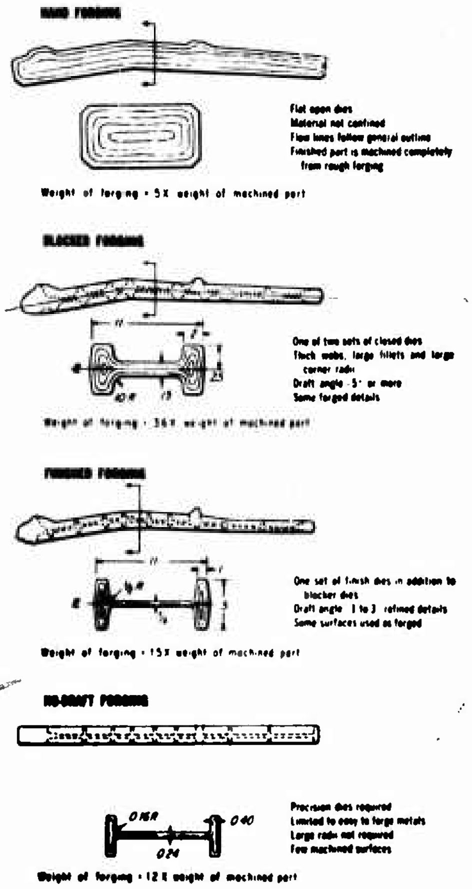

FIGURE 1. TYPES OF FORGINGS

MECHANICAL ASPECTS

Figure 2 is an example of how a large structural component would be made and gives some idea of what it takes to deliver a finished forging in any alloy. Sketched here is the forging sequence for making a 130 pound, 1400 square inch plan-view-area aluminum bulkhead forging.

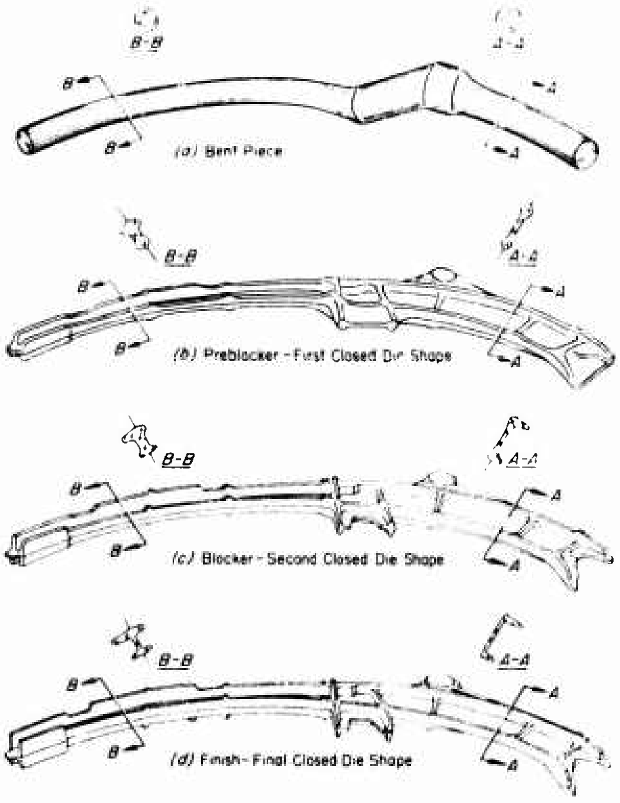

FIGURE 2. FORGING SEQUENCE FOR ALUMINUM BULKHEAD FORGING

This business of defining forgeability can become quite complex and involved. The forging engineer in considering forgeability is concerned with (1) the energy required to plastically deform a piece of forging stock into a shape and (2) the amount of plastic deformation the alloy can withstand without cracking. You, as users of our products, might describe forgeability as what it costs to get a shape which meets some property specification.

A comparison of the forgeability of titanium alloys with the other alloys follows.

Ratings of Alloy Families With Respect To Forgeability

(1) Aluminum

(2) Carbon and low-alloy steels; e.g., 4340

(3) Die steel; e.g., D6ac 5 percent Cr

(4) Stainless and PH stainless steels

(5) Titanium; e.g., Ti-6Al-4V, Ti-6Al-6V-2Sn

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(6) Iron-nickel base; e.g., A-286, Inco 901

(7) Super iron-nickel; e.g., Inco 718, Udimet 630

(8) Nickel base; e.g., Waspaloy, René 41

(9) Super nickel base; e.g., Udimet 700, Astroloy.

In the above list, the degree of forgeability decreases from top to bottom. However, you will note as we discuss this subject of forging titanium that there are no sharp boundaries differentiating one alloy forging from another and in some instances, some titanium alloys are as forgeable as alloy steels.

The increased emphasis on titanium as a major structural alloy has introduced new problem areas. They are:

(1) The size of the hardware desired: Components ranging up to 4,000 $inch^2$ in plane-view area are being considered.

(2) The degree of sophistication desired: Our customers want and ultimately expect titanium forgings delivered with the same sophistication as the aluminum forgings which they are now using in subsonic airframes.

(3) Service life required: New aircraft are requiring service lives of up to 30,000 hours. This means reliability beyond present-day standards.

(4) Alloys involved: Like every other alloy family, some titanium alloys have better forgeability than others: therefore, the alloys selected for use can present a problem.

Until recently, most of the titanium forged has been in rather simple shapes. Compressor wheels, rings, and shaft-type forgings, Figure 3, have been supplied the jet-engine builders. The hemispherical shapes, Figure 4, have been supplied the missile builders. The factors the forging engineer must consider in making a specific shape are listed below:

(1) Forgeability
(2) Geometry
(3) Plan-view area
(4) Die limitations
(5) Metallurgical requirements
(6) Economics

Forgeability as stated previously encompasses the energy needed to deform an alloy plus the tendency of the alloy to crack while being deformed. You have learned from previous papers that titanium alloys have a low temperature phase called alpha and a high temperature phase called beta. You have been told that titanium alloys are structure sensitive and there has to be a proper balance of the α and β phases to achieve satisfactory mechanical properties. To achieve the proper structure, the forger of titanium hardware is limited on just how hot he can heat a piece of stock prior to forging. This limits the top of the temperature range a forger can us in processing a specific alloy. The bottom of the forging range is determined as the approximate temperature at which the alloy will rupture with any appreciable deformation.

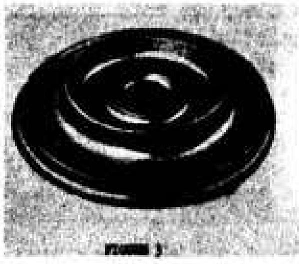


FIGURE 3

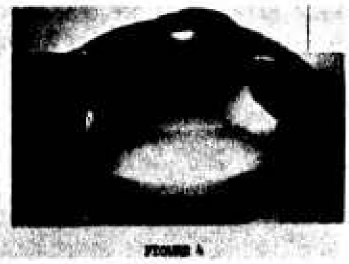


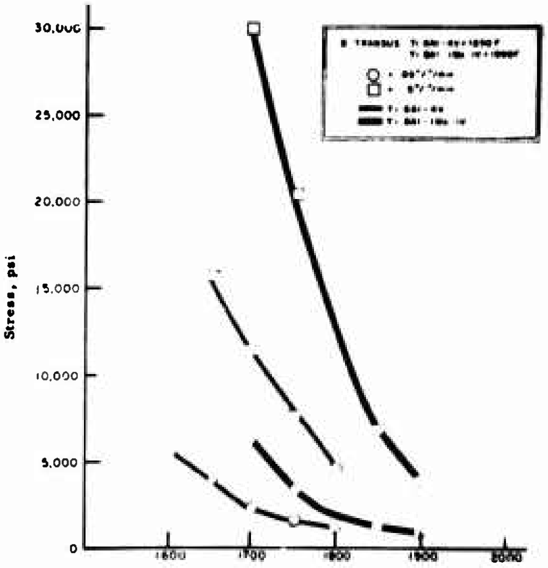
FIGURE 4

Table 1 rates the titanium alloys for forgeability. The pressure requirements here are for press forging. Approximately 50 percent more energy should be added to these figures for hammer forgings as titanium alloys are strain-rate sensitive. This characteristic of titanium alloys is shown in Figure 5.

FORGING CHARACTERISTICS OF TITANIUM ALLOYS

Alloy	Type	Die Forging Range, F	Required Pressure[a], 1000 psi	Resistance to Cracking
Ti-5Al-2.5Sn	Alpha	1775 - 1850	75 - 85	Good
Ti-8Al-1Mo-1V	Alpha-Beta	1775 - 1850	75 - 85	Fair - Good
Ti-5Al-5Sn-5Zr	Alpha	1700 - 1800	75 - 85	Poor - Fair
IMI-679	Alpha-Beta	1650 - 1725	75 - 85	Fair - Good
Ti-6Al-4V	Alpha-Beta	1650 - 1800	75 - 85	Good - Excellent
Ti-6Al-6V-2Sn	Alpha-Beta	1575 - 1675	65 - 75	Excellent
Ti-7Al-4Mo	Alpha-Beta	1680 - 1825	75 - 85	Good
Ti-13V-11Cr-3Al	Beta	1600 - 1800	85 - 100	Excellent

[a] For forging in hydraulic press.

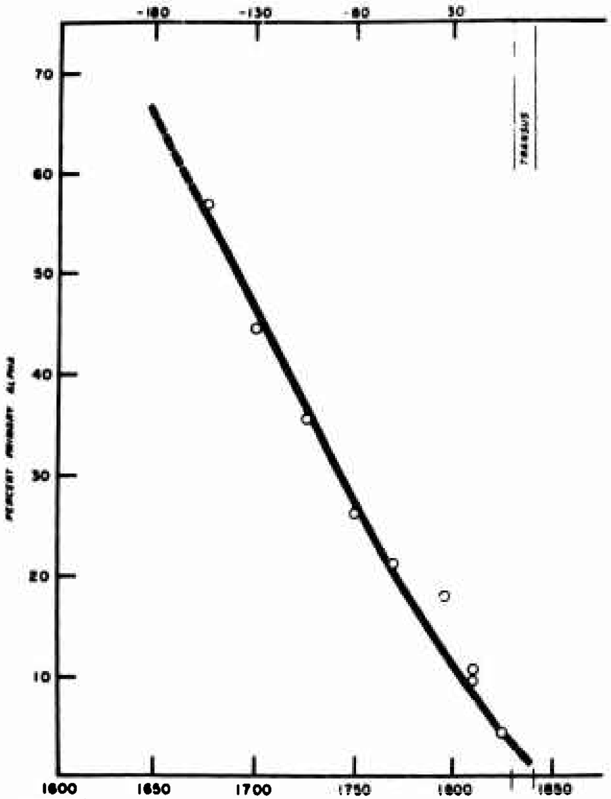


Yield Strengths of Ti-6Al-4V and Ti-8Al-1Mo-1V in Forging at Two Strain Rates

FIGURE 5

Here the yield strength of two commercial alloys, Ti-6Al-4V and Ti-8Al-1Mo-1V are plotted with respect to temperature. If forged at 1775 F, (50 F below the α + β/β transus) Ti-6Al-4V has a yield strength of about 6,000 psi at a strain rate of 5 in./in./min. At 1700 F (70 F lower) the yield strength is doubled. Ti-8Al-1V-1Mo alloy at 1850 F (50 F below the α + β/β transus) has approximately the same yield strength; however, at 1775 F (75 F lower) the yield strength is about three times that at 1850 F. Close to this temperature Ti-8Al-1V-1Mo also becomes quite crack sensitive. Since both alloys are strain-rate sensitive, and we know that strain rates in hammer forging (greater than 2000"/"/min.) are greater than press forging (20-40 in./in./min.), it is easy to understand why the Ti-8Al-1V-Mo alloy is more difficult to forge than Ti-6Al-4V. The forger also knows that in the case of Ti-8Al-1Mo-1V not only does the flow stress of the alloy increase significantly as the temperature decreases, but the tendency to cracking increases markedly. This explains the more restricted forging or working range for one alloy as compared to another.

It is important then in forging titanium alloys to select the proper forging temperature and to make maximum use of this heat by keeping heat loss to a minimum. One might ask why not increase forgeability by going to higher temperatures and expanding the forging range? Today, we are restricted by certain specifications from using higher forging temperatures; for example, there are some specifications controlling our processing which read as follows: "Parts are subject to rejection if forged within 50 F of the α + β/β transus". If just 25 F were added to the forging range it would be quite beneficial. This would increase the range where yield strength is low and the material is not as sensitive to strain rate besides being less sensitive to cracking. There are reasons, certainly, for such restrictions, one being to insure against overheating and producing a coarse grained, fully transformed structure which may be brittle under some conditions. Figure 6 shows the percentage of primary alpha present in Ti-6Al-4V with respect to forging temperature and α + β/β transus. Material forged to have 5 to 10 percent primary alpha in the microstructure had tensile properties equivalent to material forged at lower temperatures with a greater amount of primary alpha present in the microstructure. These data are shown in Table 2. Revision in this type of specification is in order for some alloys. The engine or airframe builder could still demand a structure which was not fully transformed but it would be the responsibility of the forging house to meet this requirement while taking advantage of the relief given. It would certainly require better quality control within the forging houses.



AMOUNT OF PRIMARY ALPHA PRESENT IN Ti 6Al-4V (1830-1840 TRANSUS) WITH RESPECT TO FORGING OR HEAT TREATING TEMPERATURE

FIGURE 6

TABLE 2. TENSILE PROPERTIES (70 F) OF Ti-6Al-4V PANCAKES FORGED AT VARIOUS TEMPERATURES

Forging Temperature	% Primary α	0.2% Y.S. (KSI)	U.T.S. (KSI)	El. %	R.A. %
1675° F	57	142.0	150.2	12.5	33.8
1700° F	44	143.0	154.2	12.5	29.9
1725° F	36	142.4	154.8	13.0	31.9
1750° F	26	140.0	148.0	12.5	40.1
1785° F	18	139.0	149.0	14.0	37.0
1805° F	11	147.0	153.3	13.0	33.2
1825° F	5	141.0	150.3	12.0	30.5
1840° F	0	138.0	148.0	6.0	10.1

Transus - 1830° F

Heat Treat - 1300° F (2) A.C.

So far, it has been established that the titanium alloys exhibit various degrees of forgeability based on:

(1) Forging temperature range
(2) Susceptibility to cracking
(3) Sensitivity to strain rate.

Table 3 lists general information regarding forging design allowances which can be used as a guide. In using this information, one must consider the alloy being forged.

TABLE 3. FORGING DESIGN - TITANIUM ALLOYS

Parameter	Blocker			Conventional			Close Tolerance	
	Large	Medium	Small	Large	Medium	Small	Medium	Small
Minimum Draft Angle, degrees	5 to 7	5	5	5	5	3 to 5	3 to 5	3
Minimum Web Thickness, inch	0.75 to 1.0	0.62 to 0.75	0.62	0.62 to 0.75	0.50 to 0.62	0.25 to 0.38	0.25 to 0.31	0.20
Minimum Rib Width, inch	0.88 to 1.25	0.75 to 1.00	0.62 to 0.75	0.62 to 0.75	0.50 to 0.62	0.31 to 0.50	0.25 to 0.38	0.19 to 0.25
Minimum Corner Radius, inch	0.44	0.35	0.31 to 0.38	0.31	0.25 to 0.31	0.16 to 0.25	0.12 to 0.19	0.12
Minimum Fillet Radius inch	1.00 to 2.00	1.00 to 2.00	0.88 to 1.50	1.00 to 1.50	0.88 to 1.00	0.75 to 0.88	0.38	0.25
Machining Cover, inch	0.38	0.31	0.25	0.25	0.12	0.09	0.03	0.03
Die Wear/Surface, inch	0.25	0.19	0.12	0.12	0.12	0.09		0.03
Thickness Tolerance, inch (±)	0.38 0.03	0.25 0.03	0.25 0.03	0.25 0.03	0.12 0.03	0.09 0.03		0.04 0.01
Length Tolerance, in/ft (±)	0.03	0.03	0.03	0.03	0.03	0.03		0.03
Straightness, inch	0.25	0.25	0.19	0.19	0.09	0.06		0.03

Note: Large: > 400 square inch   Medium: 100 to 400 square inch   Small: < 100 square inch

METALLURGICAL ASPECTS

Let us now review the metallurgical aspects of making titanium forgings. This includes achieving the desired mechanical properties with the greatest degree of reliability. One factor which has already been demonstrated is that titanium alloys are strain-rate sensitive. They are also structure sensitive. It is important to note that the forging procedure has a significant effect on microstructure.

Microstructure is affected by:

(1) Forging temperature selected and the subsequent working operations

(2) Cooling rate after forging

(3) Post-forge heat treatment.

If the forging is not given a solution treatment after the forging operation then a post-forge anneal in the 1300 to 1500 F range for most α + β alloys will have very little effect on the microstructure. It essentially was established in the forging operation. The following microstructures are considered significant:

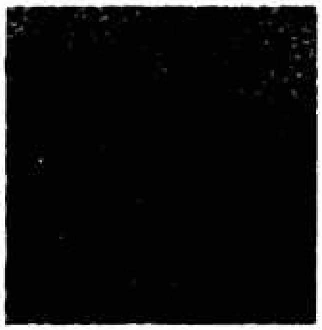


FIGURE 7

The microstructure shown in Figure 7 is considered by many to be an ideal structure for the average α + β, (e.g., Ti-6Al-4V). The primary alpha (the white areas) are quite small, round, and well dispersed.

It is entirely possible to produce the microstructures shown in Figure 8 by processing in the α + β field. These structures would be considered acceptable, but they are less desirable and for certain applications would result in lower service life:

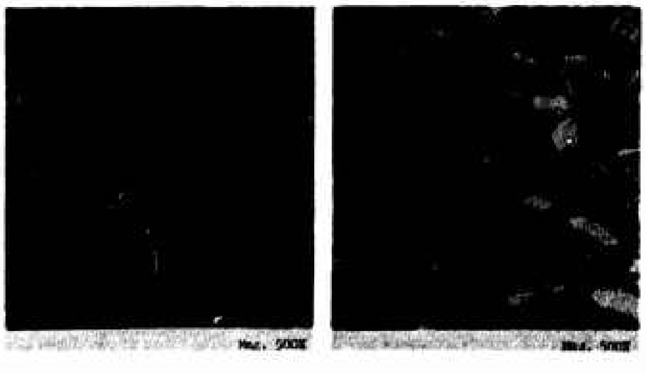


FIGURE 8

The all beta alloy, Ti-13V-11Cr-3Al, is definitely affected by process history. This alloy is extremely structure sensitive. Relatively low forging temperatures are needed in processing this alloy. This is necessary in order to create sufficient lattice distortion to influence the subsequent aging reaction. The microstructures as observed in the electron microscope of a properly and improperly processed Ti-13V-11Cr-3Al forging are shown in Figure 9.

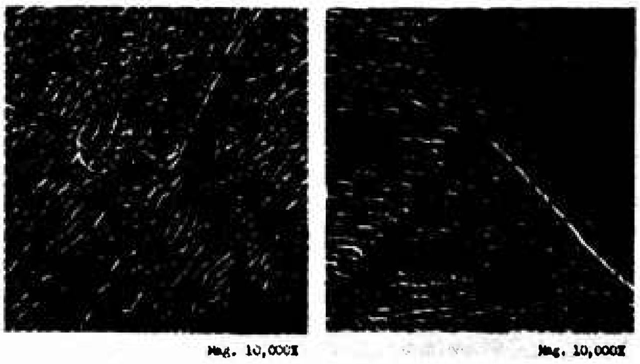


FIGURE 9

The alpha precipitate in the properly processed material is quite dispersed where as the precipitate in the improperly processed material is lined up in the same direction. The effect of these microstructures on mechanical properties is shown in Table 4.

TABLE 4. MECHANICAL PROPERTIES OF THE Ti-13V-11Cr-3Al ALLOY AFTER PROPER AND IMPROPER PROCESSING

Y. S. (KSI)	U.T.S. (KSI)	EL. %	R.A. %	R/T	PRECRACKED CHARPY $\frac{\text{IN. - LBS.}}{\text{IN}^2}$
IMPROPERLY PROCESSED					
---	160.0	2.0	1.0	40	260 - 300
159.8	165.8	2.5	3.9	32	
163.4	171.8	2.5	2.4	36	
PROPERLY PROCESSED					
161.0	170.5	5.7	7.8	24	380 - 410
166.0	175.0	5.7	5.5	28	
162.0	169.5	4.0	7.0	22	

This alloy should be of considerable importance. It is the only production titanium alloy that has the capability of achieving 150-160 ksi yield strength in section sizes exceeding 4 inches in diameter. It is not as tough an alloy as Ti-8Al-1V-1Mo, Ti-6Al-6V-2Sn, and Ti-6Al-4V but it can be made reasonably tough by proper processing.

PRODUCTION HARDWARE

Let us now review what is being supplied in the way of titanium forgings other than jet engine and missile hardware. Titanium rotor hubs weighing approximately 775 pounds are being supplied on a production basis. This is a Ti-6Al-4V forging. Data are given in Figure 10.

FIGURE 10

Titanium landing wheels have been made from the Ti-6Al-4V and Ti-7Al-4Mo alloys. Roll test data from both alloys has been reported to be very good. Data are given in Figure 11.

FIGURE 11

In my opinion the best example of a complex forging is the Ti-6Al-4V engine support mount shown in Figure 12. Little, if any, machining is done by our customer on this part except for the drilling of attaching holes. After forging, this part is etched to remove the oxygen enriched alpha case produced in the heating and forging operations. It is used by our customer in the most part with forged and etched surfaces. This family of forgings have picked up the name "poodle dogs".

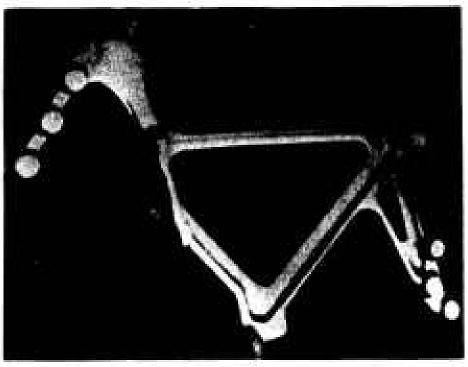


FIGURE 12. Ti-6Al-4V ENGINE SUPPORT MOUNT

Another fine example of a titanium forging is the bulkhead forging shown in Figure 13. This forging is supplied on a production basis in 4340 steel. In the same dies, designed for alloy steel, we have already forged the Ti-6Al-6V-2Sn and Ti-8Al-1Mo-1V alloys. It could be concluded that for many shapes the more forgeable titanium alloys (e.g., Ti-6Al-4V, Ti-6Al-6V-2Sn) can now be supplied to the same refinement now being purchased in the alloy steels.

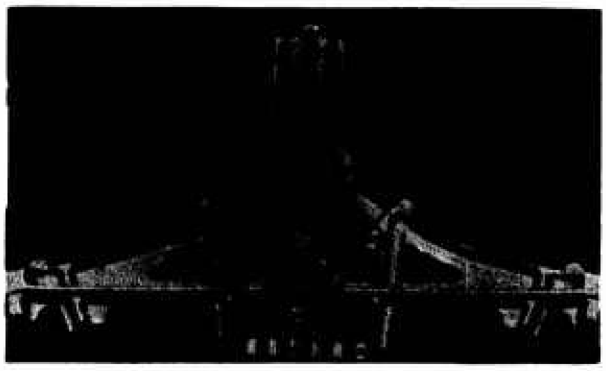


FIGURE 13. BULKHEAD FORGING

This demonstration piece (Figure 14) is an experimental shape which we use to really evaluate the forgeability of a potentially good structural alloy. It has heavy sections, thin ribs and webs, and is a real test for any alloy. The information given in Table 5 lists the tensile properties of eight (8) different titanium alloys in this shape including several new alloys. You will note that in heavy sections there is a reduction in strength particularly in those alloys which are solution treated and quenched, prior to aging, in order to achieve high strengths (150-180 ksi yield strength).

THE FUTURE

With respect to what can be expected in the not too distant future in the way of forged hardware, there are several avenues of approach. The most promising and the most natural to explore is the possible use of higher forging temperatures. This means actually forging in the β field and producing microstructures which are not generally considered acceptable by present-day standards.

Figure 15 is the best illustration that I can present which will show the significant effect of increased temperatures. The forging on the left was forged above the β transus, the forging on the right at normal titanium forging temperatures, that is about 70 F below the β transus.

For the past 2-1/2 years, we have been experimenting with β forging. Some striking data has been generated. Not only do we see better forgeability but mechanical properties are not as adversely affected as was originally estimated.

The following data compares the properties of α + β and β forged Ti-6Al-4V:

Forging Temperature	Yield Strength, ksi	Elongation, percent	Reduction in Area, percent
1775 F	142	14	38
1900 F	140	13	25

Forging Temperature	Notch Tensile Strength, ksi	K_{Ic}
1775 F	200	40 to 50
1900 F	200	60 to 70

Before this type of forging practice can be utilized considerably more experimental work is needed. Most of our work has been associated with the Ti-6Al-4V alloy and results have been most encouraging. Other alloys need to be explored. Though there does not appear to be a significant reduction in most of the mechanical properties by which we rate most metals, little is known about the effect of fatigue. We encourage further investigation in this area and, to be truthful, know

TABLE 5. TENSILE PROPERTIES OF TITANIUM ALLOY STRUCTURAL FORGINGS

Location	0.2 % Yield Strength, ksi	Ultimate Tensile Strength, ksi	Elongation, %	Reduction of Area %	Location	0.2 % Yield Strength, ksi	Ultimate Tensile Strength, ksi	Elongation, %	Reduction of Area, %
	Ti-5Al-2.5Sn - 1350 F (2) AC					Hylite 51* - 1650 F (1) AC + 930 F (24) AC			
1	122.8	131.7	11.0	25.0	1	173.6	187.2	14.5	41.4
2	131.6	144.5	14.0	28.0	2	173.0	189.0	12.5	38.2
3	124.8	133.3	14.0	35.0	3	167.8	185.4	12.5	36.3
4	125.8	135.6	18.0	29.0	9	171.4	184.8	12.0	35.7
5	122.4	133.0	14.0	28.0	10	169.6	183.0	12.0	38.8
6	120.3	130.5	14.0	27.0					
7	117.3	128.5	16.0	27.0					
8	117.0	130.1	15.0	22.0					
	Ti-6Al-4V (0.13% O_2) 1750 F (1) WQ + 1000 F (4) AC					Ti-6Al-6V-2Sn 1675 F (1) WQ + 1050 F (4) AC			
1	147.0	159.0	13.0	37.0	1	188.0	199.5	7.5	29.0
2	146.0	158.2	13.8	35.7	2	189.1	200.9	8.0	24.2
3	147.8	160.0	13.8	48.5	3	185.8	198.0	12.0	31.5
4	136.0	151.0	13.0	37.0	4	159.5	172.3	11.0	27.3
5	130.0	144.8	13.5	40.5	5	153.0	166.2	11.0	22.5
6	127.8	144.0	10.0	25.1	6	146.6	161.2	13.0	28.7
7	129.6	143.8	10.0	24.5	7	148.9	161.3	10.0	38.5
8	124.0	142.0	6.5	18.8	8	153.0	166.8	8.0	23.3
	Ti-8Al-1V-1Mo 1650 F (1) AC + 1100 F (8) AC					Ti-13V-11Cr-3Al - 1335 F (1) AC, + 1450 F (1/2) AC, + 900 F (15) AC			
1	137.5	143.4	18.0	29.4	1	171.8	182.0	3.5	7.8
2	144.1	152.7	17.0	35.4	2	166.8	178.0	6.0	8.6
3	139.9	151.7	21.0	35.4	3	170.0	181.0	5.0	7.8
4	120.9	132.1	12.0	17.1	4	171.8	182.0	3.5	7.8
5	116.2	126.8	8.0	24.9	5	165.0	176.0	5.0	6.2
6	113.6	126.2	14.0	18.5	6	166.0	176.0	4.0	8.6
7	117.9	130.5	12.0	15.2	7	163.2	174.0	4.0	4.7
8	116.8	128.1	8.0	14.2	8	163.0	174.0	6.0	12.2
	IMI-679 1650 F (1) AC + 930 F (24) AC					Ti-6Al-6V-2Sn-3.5Zr-1Cu-1Fe 1550 F (1) WQ + 1050 F (4) AC			
1	135.0	152.0	17.0	48.0	1	196.6	212.6	5.0	10.8
2	133.4	149.0	16.5	48.0	2	205.6	214.4	5.0	14.4
3	137.7	153.8	16.0	45.7	3	202.8	212.4	5.0	9.3
4	132.0	148.4	15.5	41.7	4	197.0	209.4	4.5	11.6
5	128.0	144.0	15.0	40.1	5	175.6	190.4	5.5	12.2
6	125.2	141.0	15.0	41.4	6	170.0	191.8	8.0	23.7
7	126.0	142.6	14.0	38.8	7	172.6	188.2	7.0	16.0
8	126.8	143.0	13.0	37.0	8	174.2	187.2	6.0	20.3

* Ti-4Al-4Mo-4Sn-0.5Si.

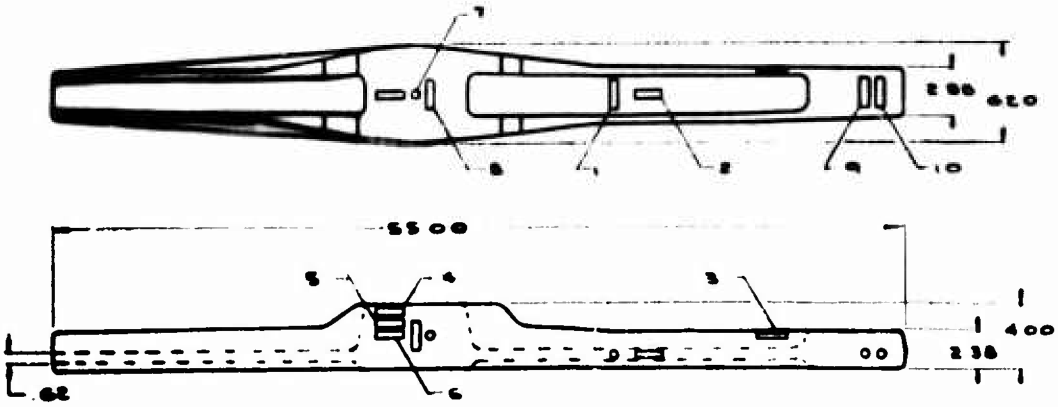


FIGURE 14. TEST LOCATIONS AIRFRAME STRUCTURAL FORGINGS

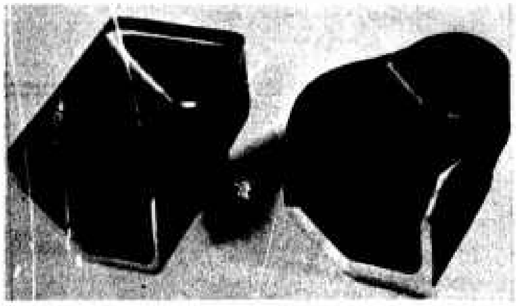


FIGURE 15

that only through your cooperation through mutual test programs can we advance in this area.

NEW ALLOYS

There are many new alloys on the horizon. The recently introduced British alloy, IMI-679, is an example (composition, Ti-2.25Al-11Sn-5Zr-1Mo-0.2Si). This alloy was one evaluated in the Wright Field sponsored Heavy Section Forging Evaluation Program conducted by Lockheed. In full-scale dynamic testing, this alloy failed in 270,000 cycles whereas the Ti-6Al-6V-2Sn and Ti-6Al-4V alloys forged in the same design failed in 150,000 and 160,000 cycles, respectively.

There are modifications of Ti-6Al-6V-2Sn called the Margolin-Farrar alloys which have tensile yield strengths of 190,000 to 200,000 psi with reasonably good ductility (7 percent).

For service temperatures of 800 to 1000 F, Ti-6Al-2Sn-4Zr-2Mo and Hylite 60 (composition, Ti-3Al-6Sn-5Zr-2Mo-0.5Si) are worthy of consideration. These alloys have good fracture toughness and do not show any adverse effect of exposure to temperature and stress in 150 hours tests. These alloys might be of use in critical areas in some of our future aircraft. It is time now to become familiar with them. Both alloys are quite forgeable.

TITANIUM-ALLOY FORGING COSTS

The cost of forgings is affected by many factors and accurate and simple generalizations are not feasible. It is readily apparent from earlier comments that a sophisticated, close tolerance forging with thin sections and minimum draft will cost more on a per pound basis than a bulky, heavy section, blocker type forging with large draft angles.

In order to provide at least some approximations for cost of titanium-alloy forgings, our Sales Department has prepared the following chart for the $\alpha + \beta$ alloys in normal production, Figure 16.

It will be noted that a range of cost is shown for each category and that this range becomes wider as the degree of sophistication increases.

A number of factors are involved here. For example Number 1, if two forgings are produced in the same material to the same design type and requiring the same processing steps, but one weighs 100 pounds and the other 300 pounds, then the 300 pound forging will sell for fewer dollars per pound. For example Number 2, if two forgings are produced in the same material to the same design type and both weigh 200 pounds, but one is a straight wing spar with relatively constant cross-sectional area and the other is a curved bulkhead fitting with varying cross-sectional areas, then the straight wing spar will sell for fewer dollars per pound because it receives less processing.

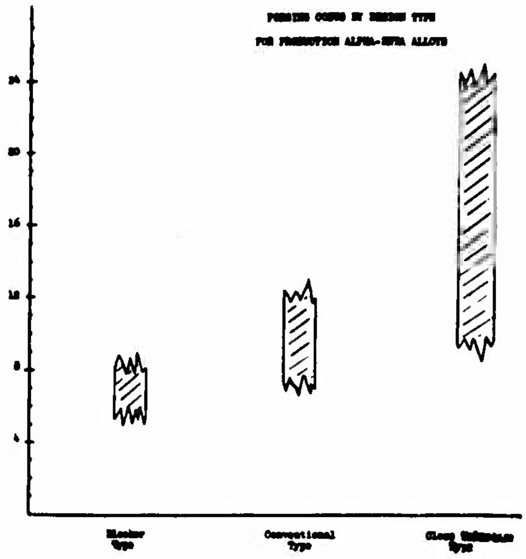


FIGURE 16

As design sophistication is increased more work is added to produce less shipped weight and the effect of these factors becomes more pronounced on the cost per pound. Thus, the range of costs becomes wider as shown.

The figures on this chart include standard operations such as product testing, ultrasonic inspection and heat treatment, but do not include such operations as rough machining, chem-milling, X-ray, or other special processing. The figures also do not include tooling charges which are quoted separately and are even less amenable to simple generalization.

It should be emphasized that caution must be used in applying any rule of thumb or average value for forging costs. What appears to be a minor difference between two forgings may actually require a significant difference in processing, with an attendant difference in cost. Specific parts require specific analysis and estimates.

SUMMARY

We must conclude that most of the titanium alloys are quite forgeable. It is apparent that considerable sophistication can be achieved in design providing adequate tooling is used. There are several avenues which offer considerable promise for further refinement, among these are β forging. However, exploration in this area will be wasted effort unless coordinated with the airframe builders.

TITANIUM EXTRUSION - STATUS REPORT 1966

J. J. Shaw*

The airframe industry and the extrusion industry have been partners for many years. The growth and development of one has led to the growth and development of the other. As recently as 25 years ago, aluminum extrusions were limited to small angles, tees and channels for airframe service, and minor trim moldings for automotive and architectural applications. As the requirements for aluminum aircraft components grew so did the capability of the extrusion industry. The aluminum extrusions available today are supplied in thinner sections of greater circle size and of more complex configurations and offer the designer greater structural efficiency. An example of this change is the integrally stiffened wing skin panels which have replaced spar sections and built-up wings employing sheet and riveting. It is reasonable to say that the present generation of high-performance aircraft are possible only because of these advances in aluminum extrusion capabilities.

The airframe industry today is making a major transition from aluminum to the use of titanium, stainless steels, and other metals. The capabilities that the extrusion industry has offered for aluminum are now desired in these other materials. The efficiency of design offered by the extrusion process will be more important with these materials than with aluminum due to their higher initial cost and the high cost of secondary operations.

The basic extrusion process offers many advantages over other forms of working in aluminum, and in the materials you seek today. These advantages of the extrusion operation are best described by considering the alternate methods of supplying raw material for airframe structural components. Alternate methods considered are machining from rolled bar or rolled shapes, and sheet forming.

The primary advantage of extruded shapes over those produced from rolled bar is the minimizing of machining due to the supply of a section more closely approaching that of the desired aircraft part. This is illustrated in Figure 1.

Here we see an extruded "Tee" section, the rectangular bar from which a similar shape could be produced, and the mountain of machined chips generated in producing this similar configuration. This illustrates the tremendous saving of time, money, and material that extruded shapes offer over this alternative method of shape production. The ability to produce a raw material configuration more closely approximating that of the desired aircraft part has an additional advantage in that the material may be purchased in the solution-treated or solution treated-and-aged condition without serious property sacrifices due to the heat treatment of more massive than necessary sections.

FIGURE 1. BAR, EXTRUSION, AND CHIPS

Another method of producing shaped structural members is sheet forming. Sheet forming will not produce sections of nonuniform cross sections, such as angles with legs of unequal thickness, or filleted "Tees", which may be required for structural efficiency, unless welding or other joining methods are used. The fabrication of shapes by welding increases problems of contamination, and generally requires tedious and expensive inspection operations to insure structural integrity.

Shapes similar to those produced by extrusion could be produced by rolling, but only when significant tonnage - not poundage - is required in order to amortize the high initial tooling cost of a structural mill. Extrusion, with its relatively low tooling cost is unique in its ability to provide limited runs (and all aircraft requirements would be limited runs to a structural mill), in complex designs, with a minimum of cost. It is also doubtful if the surface of a structural mill product, with its problems of rolled in mill scale, would approach that now available in extruded shapes.

Production of titanium-alloy extrusion starts with the [illegible] of a double vacuum melt ingot, as shown in Figure 2. These titanium ingots, are 24 inches in diameter and have a a nominal weight of 4,200 pounds each.

These ingots are heated to forging temperature, soaked through, and forged. Our 1500 ton press, used for this operation, is shown in Figure 3.

The product resulting from the forging operation is shown in Figure 4. These are nominal 9-1/2-inches-round rough-forged extrusion billets.

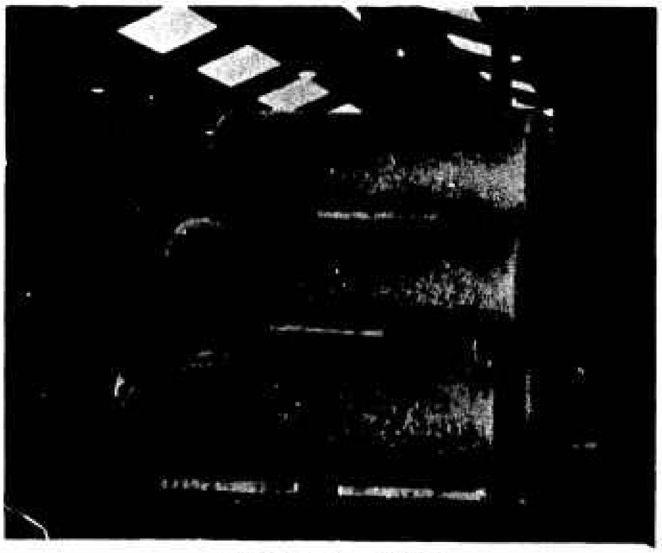


FIGURE 2. INGOTS

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*Chief Metallurgist, Special Metals Division, Harvey Aluminum Company, Torrance, California.

FIGURE 3. FORGE PRESS

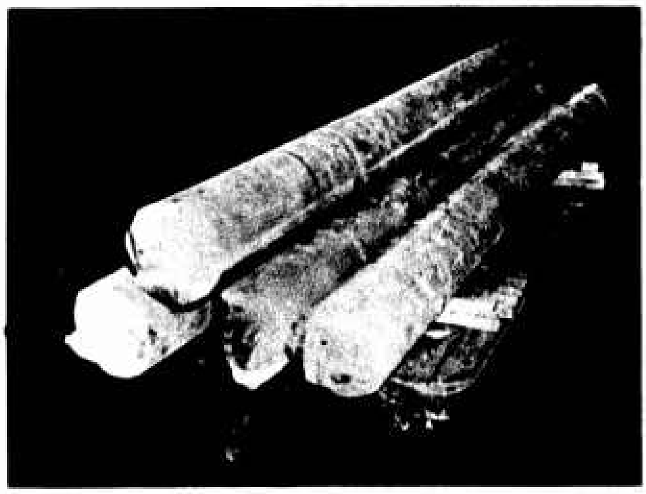

FIGURE 4. FORGED BILLETS

These billets are then cut to a desired length, turned, and faced off. The product of this operation is shown in Figure 5.

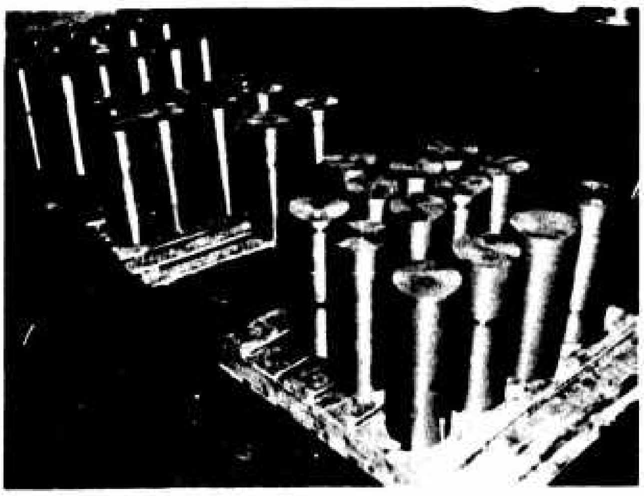

FIGURE 5. EXTRUSION BILLETS

The turned billets are then placed in an induction heater and brought to extrusion temperature. Figure 6 shows a 60-cycle induction unit used for this heating.

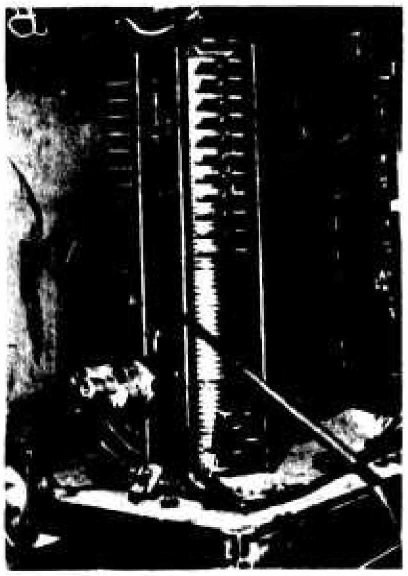

FIGURE 6. INDUCTION HEATER

The hot extrusion billet is then transferred to the press container. Figure 7 is a view of the container end of our 3850 ton extrusion press.

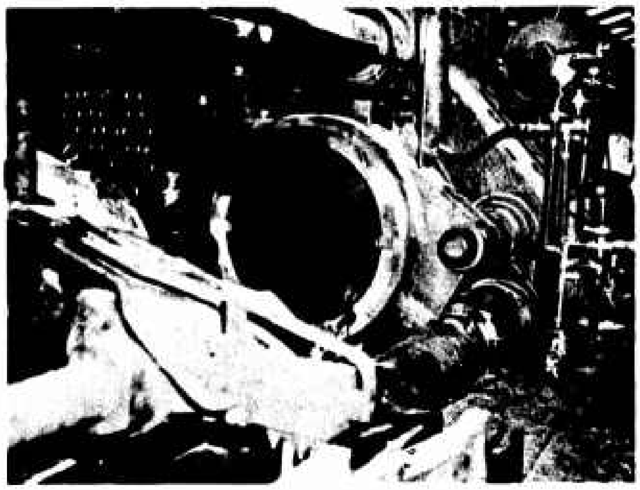

FIGURE 7. PRESS CONTAINER AND RAM

The press ram, shown in the left center of Figure 7, then comes forward, forces the billet into the container, and then, with continuing pressure, forces the titanium through the die.

The die end of the extrusion press, with the die slide forward, and the tooling exposed, is shown in Figure 8.

At this point, depending upon alloy and specification, extrusions follow one of two paths. Extrusions of those alloys and specifications which require hot straightening, are heated to the

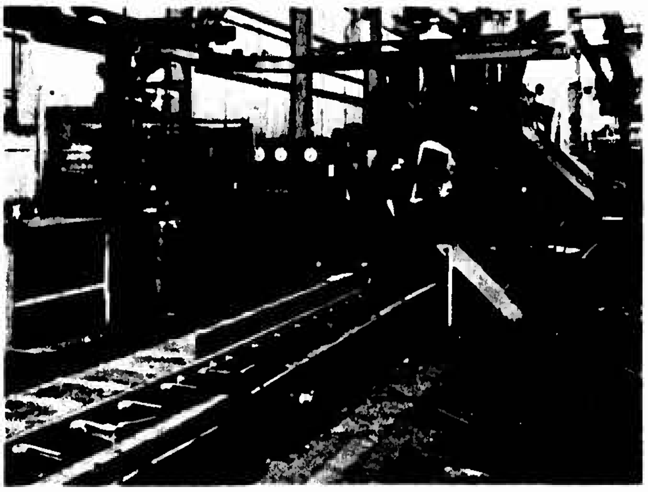

FIGURE 8. EXTRUSION PRESS AND TOOL PACKAGE

required temperature in a walking beam furnace. The entrance end of this furnace is shown in Figure 9. This is a flat-flame roof fired furnace, capable of handling a 28 foot length. The discharge end of this furnace and a 100-ton stretch straightening unit, is shown in Figure 10. The ability to discharge from the furnace directly onto the straightener bed, allows precise control of initial straightening temperature.

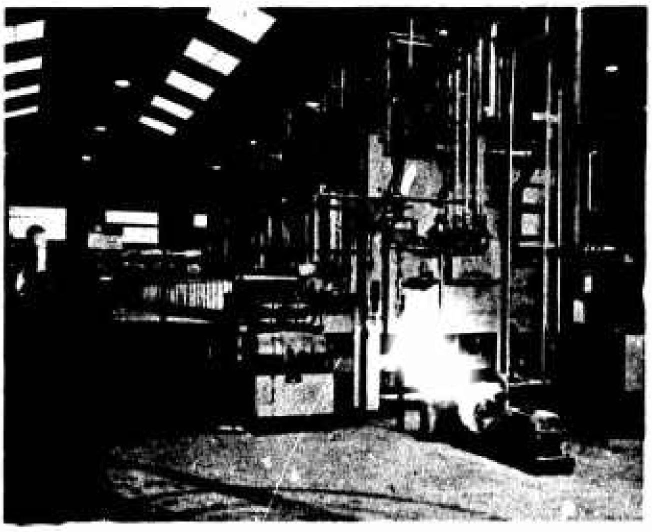

FIGURE 9. WALKING BEAM FURNACE

These extrusions of alloys or specifications which allow or require cold straightening, are straightened as shown in Figure 11. This unit is a 300 ton stretch straightening unit. Other straightening units, with up to 1500 tons capacity, are available.

Some extrusions, again depending upon alloy and specification, are annealed prior to shipment. Our 80-foot-roller hearth annealing furnace is shown in Figure 12.

FIGURE 10. HOT STRETCH STRAIGHTENER

FIGURE 11. COLD STRAIGHTENER

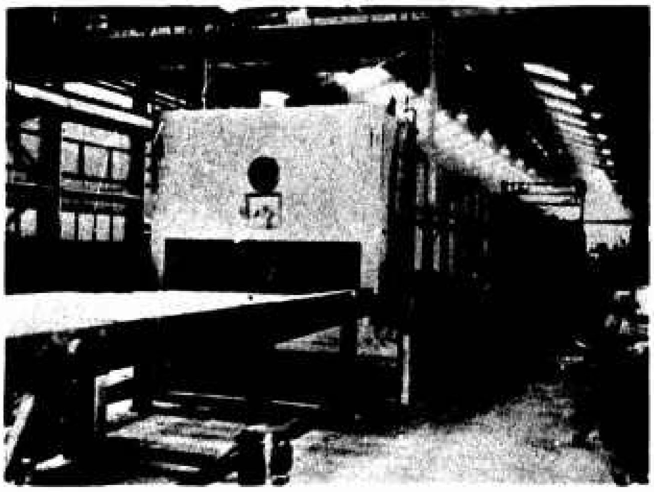

FIGURE 12. ROLLER HEARTH FURNACE

Figure 13 shows a production lot of extrusions which have been processed to this point. These have been straightened and annealed but have not yet been descaled. The descaling operation is performed by immersing the extrusion in molten salt and shocking with a cold water quench or, for those alloys or heat-treat conditions which would be detrimentally affected by this treatment, by mechanical blasting. In any case, the descaled extrusion is now pickled to remove any high oxygen alpha case. Figure 14 is a view of our pickle house, and Figure 15 shows a bundle of extrusions leaving the pickle house on their way to final inspection.

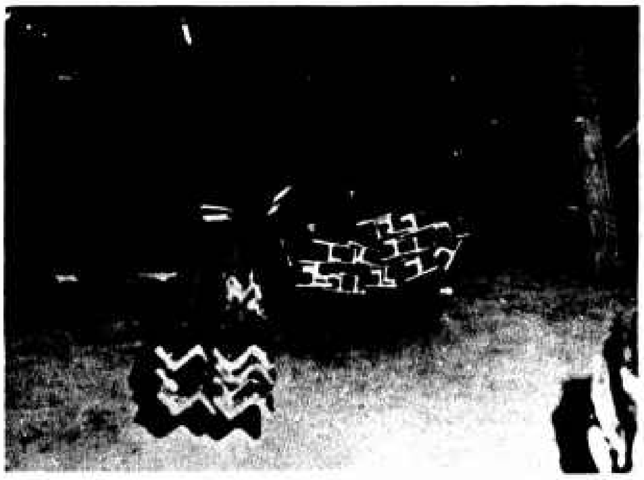

FIGURE 13. EXTRUSIONS NOT YET PICKLED

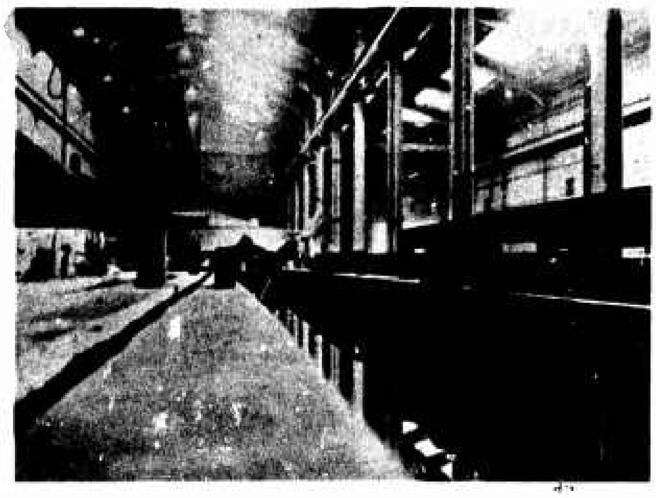

FIGURE 14. PICKLE HOUSE

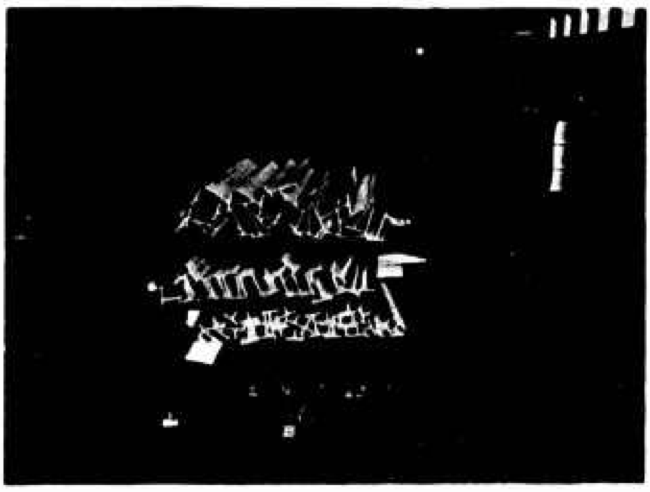

FIGURE 15. PICKLED EXTRUSIONS

This process is substantially the same for titanium as it is for softer metals. Some of the technology developed in the extrusion of these softer metals is transferable to the production of titanium shapes as long as the major difference, temperature and its effects, is remembered. Because of its higher resistance to deformation at a temperature, titanium requires either much higher extrusion pressures or much higher extrusion temperatures than aluminum. Since to extrude at a low temperature would require tool loading in excess of the strength of the tooling materials now available, the titanium extruder is forced to depend upon heating the material to a temperature at which its resistance to deformation is low enough to allow extrusion at pressures within the capability of available tool materials.

The necessity of heating titanium to high temperatures has two effects. The first is that titanium extrusions are worked at temperatures above the beta transus, and therefore, have a beta-worked microstructure. The second effect is on surface condition. The high chemical reactivity of titanium at elevated temperatures requires that it be protected during heating and extrusion from contact with air, the container, and the tooling. The method of protection we use is effective, but is not now and perhaps never will be perfect. This imperfect protection results in reaction between the titanium and air and in the welding of the extruded surface to the tooling. This galling is what gives a titanium extrusion its characteristic surface. Such a surface generally requires further preparation prior to being put in service in an airframe. This surface preparation is generally accomplished by pickling, to remove the high oxygen alpha case, followed by machining. Some work on improving surface finish by drawing has been accomplished. Real improvement of extrusion surfaces will not take place until tool materials are available which allow lower temperatures to be used.

Extrusions are currently produced from the full range of available titanium alloys. Production quantities have been produced in Ti-6Al-4V, Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, and Ti-6Al-6V-2Sn. These can be obtained in the annealed or in the heat-treated conditions. Some of the cross sections which have been commercially produced are illustrated in Figure 16. More recent and larger cross sections are shown in Figure 17. Full-length alloy titanium extrusions are shown in Figures 18 and 19.

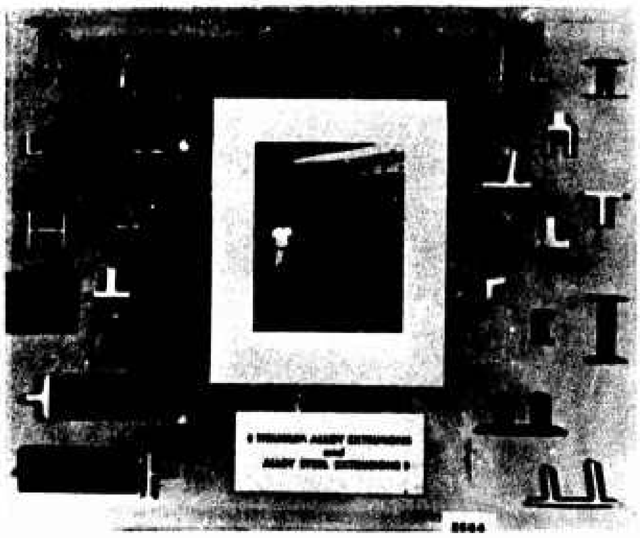

FIGURE 16. DISPLAY BOARD

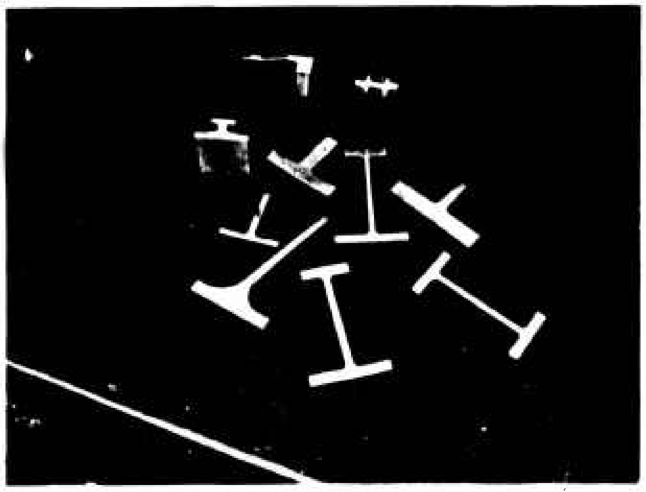

FIGURE 17. NEW SHAPES

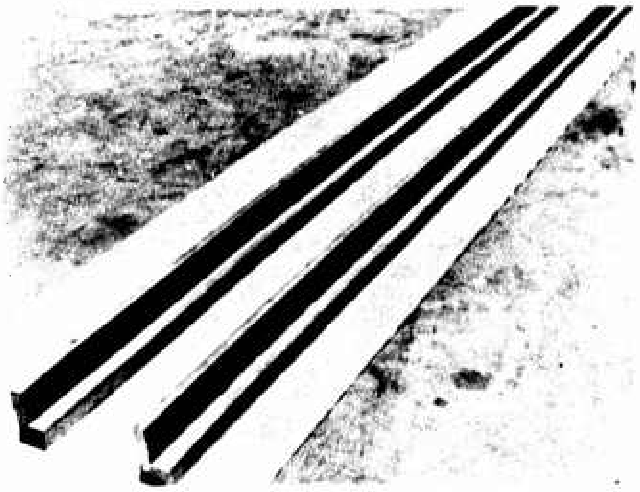

FIGURE 18. FULL-LENGTH ANGLE WITH LEGS OF UNEQUAL THICKNESS

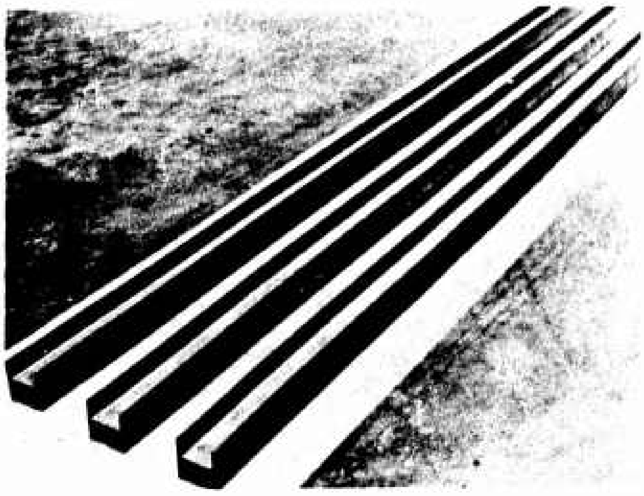

FIGURE 19. FULL LENGTH "H"

While extrusions of these alloys can and are being produced, the sections that are fabricated must be properly designed for balance and appropriate techniques applied in regard to die design and lubrication or else the results shown in Figure 20 will be obtained.

The initial titanium extrusions produced in the United States were fabricated on extrusion presses of approximately 2,000 tons capacity. Work has now progressed to the point where production is routine on 4,000 ton presses and available from presses of 12,000 ton capacity. The use of this larger equipment has advanced extrusions to the point where shapes of circle size through 9 inches are routinely available. The use of this larger equipment also permits the production of longer extrusions. Titanium extrusions of over 60 feet and a total weight of 700 pounds have been produced. Actually the size and length limitation is not that of the extrusion process but the availability

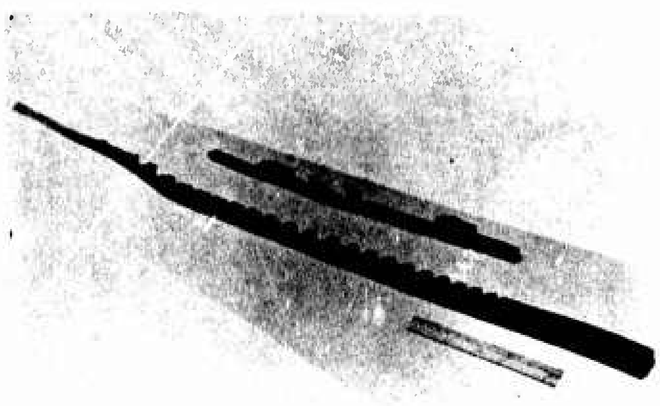

FIGURE 20. TORN-UP EXTRUSION

of finishing equipment to handle, heat treat, and process the lengths that can be produced. The current practice is to cut the extruded length into several lengths of approximately 12 to 20 feet for finishing and delivery to the customer.

Since titanium extrusions are produced at elevated temperatures, their surface and tolerances are similar to those surfaces and tolerances produced by other hot-working operations and should not be compared to those produced by cold-finishing operations. Typical tolerances on extruded sections are on the order of ± 0.020 inch. The actual producible tolerances vary as a function of shape complexity and overall length. The extruded surface may contain tears and seams, typical of a hot-worked surface, to a depth of 0.005 to 0.015 inch.

Titanium extrusion today stands at the position of the aluminum extrusion industry approximately 25 years ago, when it was on the threshold of large-scale production for the airframe industry. The process has proven itself adaptable to the extrusion of all classes of titanium alloys and, therefore, should meet any advancement in alloy development that may come about. The characteristics of the extrusion process are such that it might enable the fabrication of alloys that would not be fabricable by other methods and, therefore, offers greater latitude in alloy development. The techniques developed have shown themselves applicable to the smallest presses and to the largest presses that are available for the fabrication of aluminum. This includes the large 12,000 ton extrusion presses. This large equipment today is fully committed to meet current aircraft needs for aluminum extrusions. The future advancement of titanium into longer, more massive sections of greater circle sizes is dependent upon greater availability of this equipment or on the building of additional presses. We feel that the future will require and justify new equipment in this area. An example of the advancements in aluminum technology that could also be repeated in titanium is shown by Figure 21.

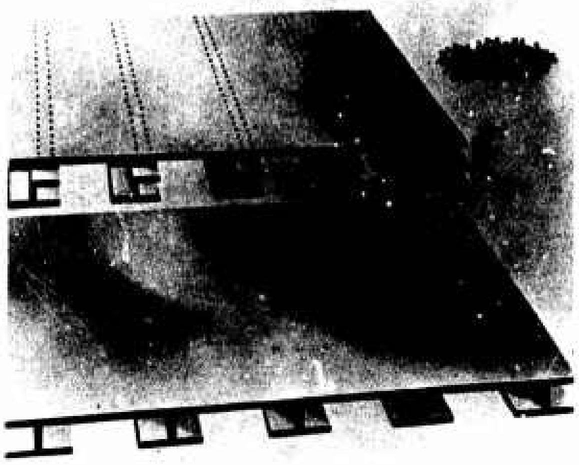

FIGURE 21. PANEL

This figure illustrates the conversion from the smaller piece and bit technology of several years ago requiring assembly, to the extrusion of massive integrally stiffened sections from 2 to 3 feet in width and in lengths up to 75 feet. It is feasible today for us to produce shapes of this same general configuration representing 40 percent of that illustrated. The technology exists and the advancements are dependent upon obtaining necessary equipment.

A trend in the design of titanium extrusions has been a movement towards more complex and larger cross sections, in longer lengths. Advancements in these areas will certainly be forthcoming with greater production of titanium shapes and its attendant improvement in production techniques and control of variables. In the past, most of our production was intended for test programs, in the recent past toward prototypes, and I think we all hope in the near future, production airframe requirements.

CRITICAL ASPECTS OF FORMING TITANIUM ALLOYS

W. W. Wood and R. E. Goforth*

INTRODUCTION

Because of titanium's outstanding strength-to-weight ratio, elevated-temperature properties, and corrosion resistance, it is enjoying a prominence in the metal industry today. This has not always been the case: the titanium industry has had its ups and downs. In the early fifties, it was called our next magic metal. Its early growth was limited, however, by lack of fabricating and processing knowhow and equipment necessary to release it from some of its limitations. In the mid-fifties, titanium was said to be the greatest fiasco in metallurgical history. The big cutback in military aircraft in 1958 plunged titanium's mill-product consumption 50 percent. That same year, its fortunes began to rise because of space-age requirements. Titanium mill-line shipments are expected to top 10,000 tons in 1966. According to Titanium Metals Corporation of America, military airframes consume 39 percent of titanium production, jet engines 24 percent, missiles and space equipment 21 percent, civilian jet aircraft 8 percent, corrosion-resistant equipment 7 percent, and hydrospace equipment 1 percent. As can be seen from these statistics, the titanium industry is highly dependent upon the sophisticated aerospace industry.

The development of new metals is not without its problems. The history of metals technology is mainly one of conflict: needs versus means of fulfillment. In general, metallurgists develop materials that satisfy certain present or anticipated requirements, and then hand the problem of actually making hardware over to manufacturing. The problems of welding, machining, and forming are many times formidable and must be solved by a cooperative effort between metallurgists and manufacturing engineers.

Today, the titanium industry's technological efforts are concentrated on four main areas: (1) perfecting heating and new vacuum and inert-gas shielding techniques used to isolate hot titanium from damaging effects of air, (2) improvement of titanium ductility - strength ratio for the high-strength alloys (up to 260,000 psi), (3) alloy development in search of a superior titanium alloy to extend upper temperature limits to 1200 F, and (4) matching of existing metalworking equipment and methods with the metal's machining and forming capability.

The marriage between titanium and existing fabricating equipment has been very successful. Much of the work to date involving titanium is contracted for on a short-run basis, thus precluding the development of equipment designed specifically for the metal. Forming can be performed successfully by most standard processes, but the equipment must be modified for hot-forming and hot-sizing and provide the necessary atmosphere protection. In the next few years, because of the tremendous increase in requirements, major pieces of equipment will be designed and built primarily for the processing and fabrication of titanium and other high strength-high temperature materials.

It is the purpose of this paper to present some of the effects of external material variables such as temperature, pressure, and forming velocity (strain rate) on the formability of various titanium and other high-strength alloys. Much of the information summarized here is based on data generated by Ling-Temco-Vought under three Air Force contracts,(1,2,3) which had the general objectives of providing a source of formability information for many of the new alloys and serving as a guide in the development of future forming equipment.

THEORETICAL FORMABILITY CONCEPT

Forming technology has developed to such a complex state that scientific analysis rather than trial-and-error and past experience is required to solve many of the present-day problems. One of the problems that has gained prominence in the aerospace industry is that of measuring the forming characteristics of various materials by some simple means short of the production process itself. This was brought about by the increasing demand to produce complex shapes from newly developed high-strength, high-temperature metals and alloys. Also, the long lead times normally required to develop fabrication capabilities are out of the question in modern-day industry. Under an Air Force contract, AF 33(616)-6951, "Theoretical Formability",(1) a concept of predicting formability limits based on geometric parameters, mechanical properties, and forming process was developed. Predictability equations were developed for several conventional forming processes and basic part shapes. The formability index is that property or combination of properties determined from simple uniaxial tensile tests which correlates to the limiting geometric parameters of the material and process. A summary of these indices is given in Table 1. The primary modes of failure in sheet-metal forming are splitting and buckling. Splitting is the result of stretching and/or bending and buckling is due to compressive stresses in excess of the critical. In general, splitting limits are a function of the materials maximum elongation (ϵ) or strain in simple tension and buckling limits are a function of the ratio of the modulus of elasticity (E) to the yield stress (S_{TY}). These general properties affecting formability are given for several materials at room temperature in Table 2. As can be seen from these data, the titanium alloys have relatively low values at room temperature. Although tungsten has a high buckling index, its brittleness precludes deformation at room temperature.

ELEVATED-TEMPERATURE EFFECTS

A limited amount of titanium forming may be performed at room temperature; however, hot forming is usually preferred and much more widely used. Formability is greatly improved when performed at elevated temperature. This is illustrated by the typical temperature effect on titanium properties and the resulting increased formability indices at elevated temperature shown in Figure 1. At room temperature, the buckling and splitting index are low to medium, whereas at elevated temperatures, they are both relatively high.

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TABLE 1. APPLICATION OF FORMABILITY INDICES

Forming Process	Splitting Indices		Buckling Indices		
	$\epsilon_{2.0}$	Others	E_T/S_{TY}	E_C/S_{CY}	Others
1. Brake Forming		$\epsilon_{.25}$(corr.)			
2. Dimpling	for $\alpha \cdot 40^{\circ}$				
3. Drop Hammer Beading		$\epsilon_{.50}$(corr.)			
4. Rubber Press Beading		$\epsilon_{2.0}\ S_u$			
5. Sheet Stretch	Fracture in free area				
6. Andro-form		$\frac{E_T}{S_{TY}}\ \frac{1}{\epsilon_{2.0}}$	Both long. and trans.		
7. Joggling		$\epsilon_{.02}$		Shear Buckling	
8. Linear Stretch	Varies with "t"		From Springback		
9. Rubber Stretch	Independent of "t"		From Springback		
10. Rubber Shrink				From Applied Elastic Stress	$1/S_{CY}$ for Plastic Buckling
11. Roll Forming			Heel-in	Heel-out	
12. Spinning				From Applied Elastic Stress	E/S_u for Plastic Buckling
13. Deep Drawing					$\frac{E}{S_{CY}}\ \frac{S_{TY}}{S_{CY}}$ for Elastic and Plastic Buckling

TABLE 2. PROPERTIES AFFECTING FORMABILITY

	2024-T3	Rene' 41	Tungsten	Ti-8Al-1Mo-1V	Ti-13V-11Cr-3Al	Ti-6Al-4V
E	10.6	31.6	59	16	14.8	15.4
S_{TY}	50	100	220	135	135	120
E/S_{TY}	212	316	268	119	110	128
ϵ	.18	.30		.10	.18	.10

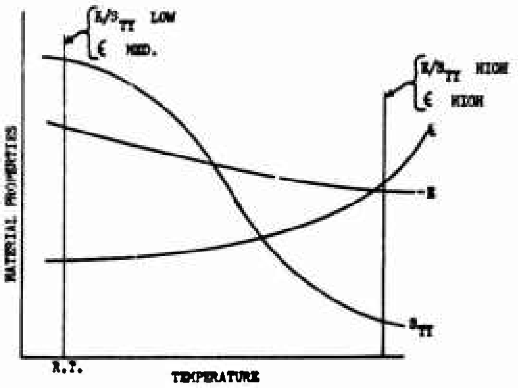


FIGURE 1. FORMABILITY CHARACTERISTICS FOR TYPICAL TITANIUM ALLOY

Hot sizing is also necessary in order to eliminate residual stresses and springback and provide dimensional control. Structurally, residual stresses must be eliminated because of reduced properties due to the Bauschinger effect and also to reduce stress-corrosion problems. Hot forming and sizing are often accomplished in a single operation using one setup of tools. In other cases, preformed parts (formed at room temperature) are final hot sized in a separate die and by another piece of equipment.

The theoretical formability concept was extended to include elevated temperature due to the importance of, and the advantages gained by, "hot forming". This was accomplished under Air Force Contract AF 33(657)-10823, "Advanced Theoretical Formability". Tensile tests were conducted for a variety of materials, including Ti-8Al-1Mo-1V and Ti-13V-11Cr-3Al, at temperatures up to 3000 F for some materials. Formability indices were then plotted versus temperature in order to determine the optimum forming temperature. Forming limit curves established in the first contract(1) were then theoretically determined for ten conventional processes. Brake forming, linear stretch forming, and deep drawing limits were then verified experimentally. Some of these results will be presented.

Brake Forming

The formability index in brake forming is the maximum corrected elongation measured over 0.25-inch gage length ($\epsilon_{0.25\ \text{corrected}}$) on a simple tension test. The correction is based on a measured lateral contraction $(\epsilon_W)_{0.25}$ in order to compensate for the difference in stress condition that occurs in simple (uniaxial) tension as compared to the plane strain state in bending.

$$(\bar{\epsilon}_L)_{0.25\ \text{corr.}} = (\bar{\epsilon}_L)_{0.25} - \frac{(\bar{\epsilon}_W)^2_{0.25}}{(\bar{\epsilon}_L)_{0.25}} \qquad (1)$$

where,

$(\bar{\epsilon}_L)_{0.25\ \text{corr.}}$ = formability index

$(\bar{\epsilon}_L)_{0.25}$ = true strain measured across fracture in longitudinal direction over a 0.25-inch gage length (tension test)

$(\bar{\epsilon}_W)_{0.25}$ = true strain measured across fracture in the transverse or width direction over a 0.25-inch gage length.

This index plotted versus temperature is shown in Figure 2 for the following materials: Ti-13V-11Cr-3Al, Ti-8Al-1Mo-1V, AM-350 (precipitation-hardenable semiaustenitic stainless steel), and A-286 (austenitic stainless steel). A substantial increase occurs in the 1200 F to 2000 F range for all four materials. There is a 64 percent increase in brake formability of Ti-13V-11Cr-3Al between 1200 and 2000 F, and a 160 percent increase for Ti-8Al-1Mo-1V. This clearly indicates the benefits of brake forming in the upper temperature regime.

The forming limit curves for two of the materials are shown in Figure 3. The minimum bend radius-to-thickness ratio (R/t) has been significantly [illegible] with the addition of temperature (2000 F). Th[illegible]tion of the curve (constant R/t) at the higher bend angles correlated with the formability index ($\epsilon_{0.25}$ corrected) and the following equation resulted:

$$R/t = \frac{1}{e^{2\epsilon_{0.25\ \text{corrected}}}-1} \quad . \qquad (2)$$

Stretch Forming

The forming limit curve for linear stretch forming is illustrated schematically in Figure 4. Failure occurs by either splitting or buckling, depending upon the geometric parameters involved. Predictability equations developed analytically and established experimentally$^{(1)}$ are given for each area of the curve. The splitting index was found to be the 2-inch gage length elongation in simple tension. No correction was necessary, since the stress state on the linear stretched part was found by actual measurement to be very close to simple uniaxial tension.

Parts with geometric parameters (h/t, h/R) that plot above curve (ab) in Figure 4 will fail by splitting. The curve is defined by Equation 3 shown on the schematic graph. Elastic buckling occurs when a part plots to the right of curves (bc) and (cd). The buckling index was found to be the ratio of the elastic modulus (E) and the tensile yield strength. Equations 4 and 5 which are also shown in Figure 4 define the buckling limit curves.

The splitting index ($\epsilon_{2.0}$) in linear stretch forming which also happens to be the same in sheet stretch forming is plotted versus temperature for several materials in Figure 5. As was the case for brake forming, a significant increase in formability occurs in the 1200 to 2000 F range for three of the

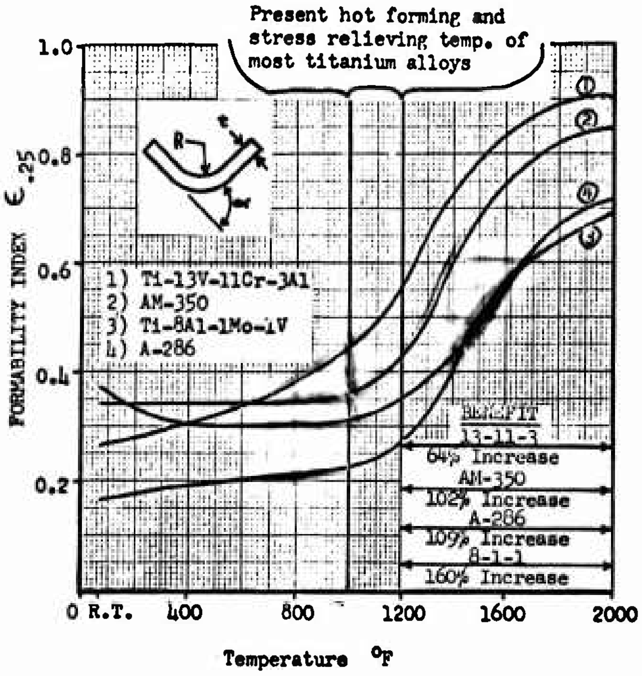
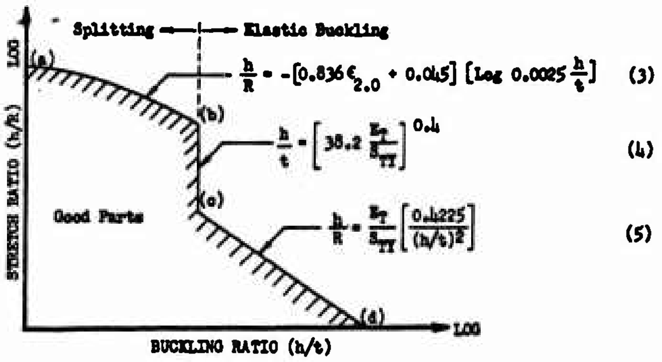


FIGURE 2. BEND FORMABILITY INDEX VERSUS TEMPERATURE



$$\frac{h}{R} = -[0.836\epsilon_{2.0} + 0.045]\left[\text{Log } 0.0025\frac{h}{t}\right] \qquad (3)$$

$$\frac{h}{t} = \left[38.2\frac{E_T}{S_{TY}}\right]^{0.4} \qquad (4)$$

$$\frac{h}{R} = \frac{E_T}{S_{TY}}\left[\frac{0.4225}{(h/t)^2}\right] \qquad (5)$$

FIGURE 4. TYPICAL FORMING LIMIT CURVE IN LINEAR STRETCH FORMING HEAT-OUT ANGLES AND CHANNELS

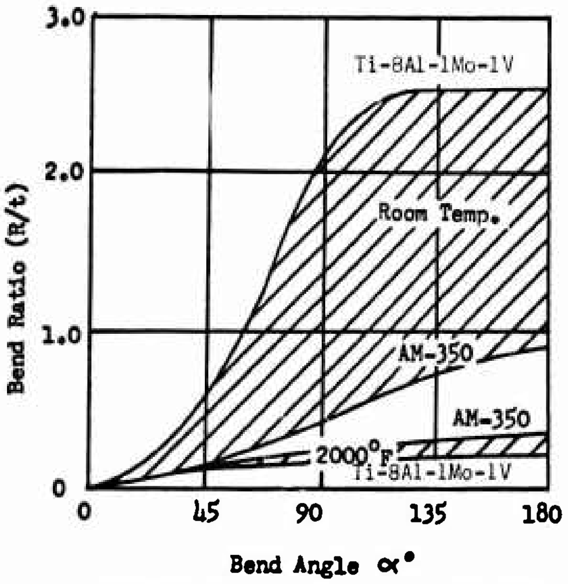


FIGURE 3. MINIMUM BEND RATIO (R/t) VERSUS BEND ANGLE

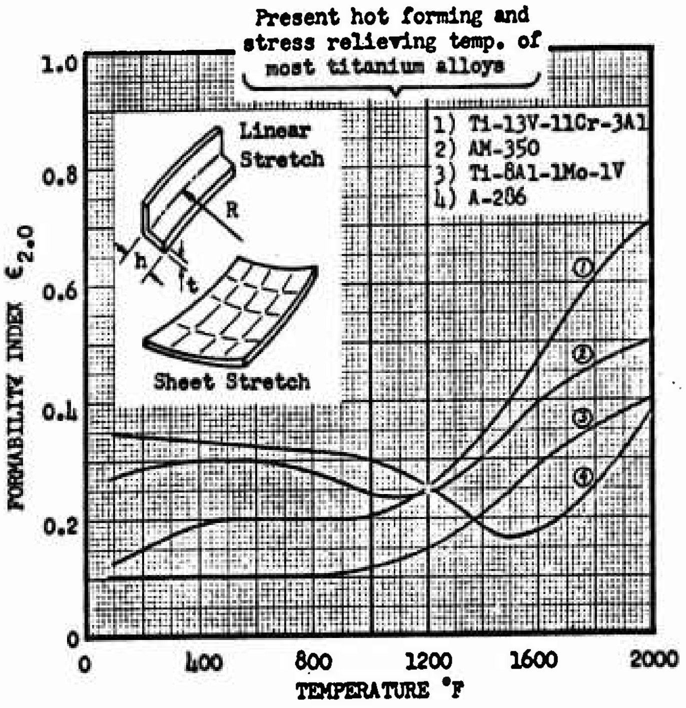


FIGURE 5. SPLITTING FORMABILITY INDEX IN LINEAR STRETCH AND SHEET STRETCH FORMING VERSUS TEMPERATURE

materials: Ti-13V-11Cr-3Al, AM-350, and Ti-8Al-1Mo-1V. A-286 has a gradual decrease in formability from ambient to 1000 F, a somewhat sharper decrease from 1000 to 1500 F, and a rather steep increase from 1500 to 2000 F. The total result is only slight increase in formability of A-286 at 2000 F, as compared to room temperature. In fact, A-286 has excellent forming characteristics at very low temperatures.(2)

The buckling index (E_T/S_{TY}) plotted versus temperature is shown in Figure 6. Here again, there is a significant increase in the 1200 to 2000 F range. Forming limit curves for Ti-13V-11Cr-3Al and Ti-8Al-1Mo-1V at room temperature and 2000 F are shown in Figure 7. The increased formability is significant and again clearly indicates the benefits of forming in the upper temperature regime.

Deep Drawing

The forming limit curve for deep drawing is illustrated in Figure 8. The index for formability in this process was found to be a complex function of the normal compressive buckling ratio (E_C/S_{CY}) times the tensile-yield to compressive-yield ratio (S_{TY}/S_{CY}). The reasoning for this index is seen to be quite simple by first realizing that the stability of the flange during drawing is a function of E_C/S_{CY}; however, the tensile strength in the cylindrical portion of the cup determines the ability of the flange to be drawn and the compressive flow stress in the flange determines the relative ease for the flange to be drawn. The result is that the higher E_C and S_{TY} and the lower S_{CY}, the better the formability, i.e., the higher the index $(E_C/S_{CY})(S_{TY}/S_{CY})$, the greater will be the formability. For elastic buckling, $h/R_b = f(E_C/S_{CY})(S_{TY}/S_{CY})$, and for plastic buckling, $h/t = f(E_C/S_{CY})(S_{TY}/S_{CY})$. The index plotted versus temperature is shown in Figure 9. A tremendous increase in deep-draw forming limits occurs in the 1000 to 1600 F range for the two titanium alloys. Optimum forming occurs at 500 F for AM-350 and at 1000 F for A-286. Forming limit curves for Ti-13V-11Cr-3Al and Ti-8Al-1Mo-1V at ambient and 1600 F are shown in Figure 10.

Summary

The benefit of forming titanium in the upper temperature regime is clearly indicated and the development of equipment and/or tooling to take advantage of this effect is needed. Significant increases in formability occur in the 1200 to 2000 F range for the titanium alloys studied. Critical temperature points for the two titanium alloys are given in Figure 11. Contamination in the form of continuous oxidation and gas absorption is a real problem at elevated temperature, especially above 1200 F. This necessitates strict atmosphere control of the part. Also, forming above the beta transus temperature generally necessitates a reheat treatment subsequent to the forming process for the heat-treatable beta and alpha-beta alloys.

In order to prevent metallurgical damage such as constituent melting in the grain boundary, a limit of 0.75 times the melting point has been generally accepted. For titanium, this is about 2250 F.

Potential hot-forming methods and developments needed are outlined in Table 3.

PRESSURE EFFECTS

The Guerin rubber forming process has been used for several years in the aircraft industry for single-action shallow recessing and flanging operations. Some of the rubber forming presses go to 5000 to 7000 tons' capacity. Pressures obtained can be increased by either using a larger capacity press or a smaller pad container. Normal operating pressures for the Guerin process are in the 2000-psi range. The rubber-bag forming technique is a modification of the Guerin process and is designed to utilize direct hydraulic pressure. The presses are designed for pressure up to 10,000 psi, which is substantially higher than the Guerin process.

For flexible die double-action deep-drawing operations, the hydroforming, marform, and hi-draw techniques are used. These processes utilize male

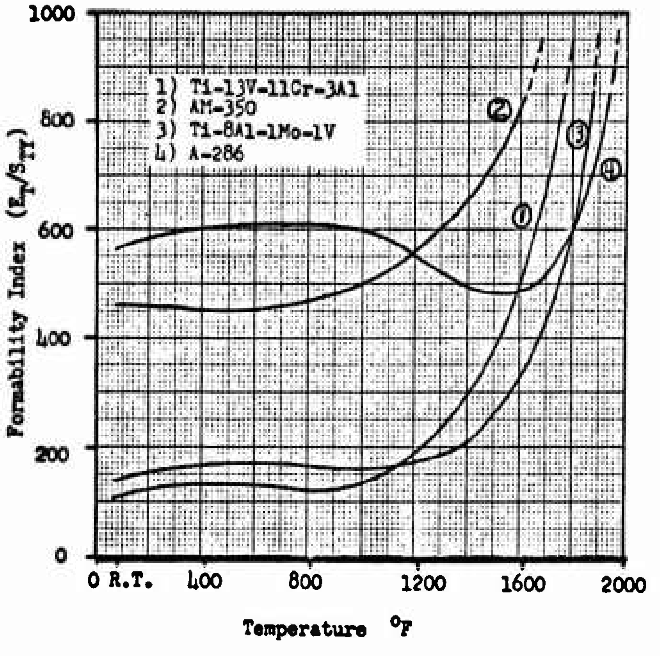


FIGURE 6. BUCKLING FORMABILITY INDEX IN LINEAR STRETCH FORMING VERSUS TEMPERATURE

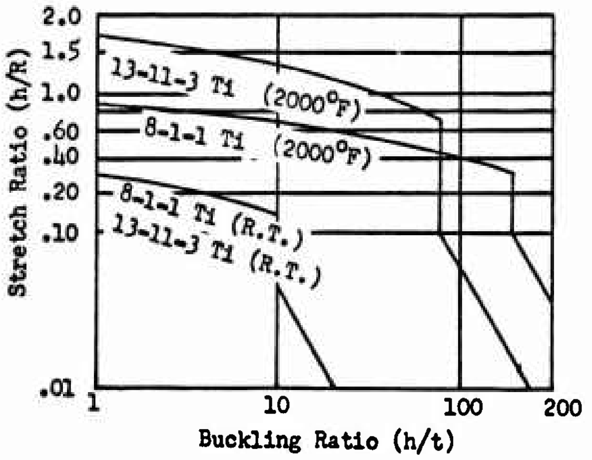
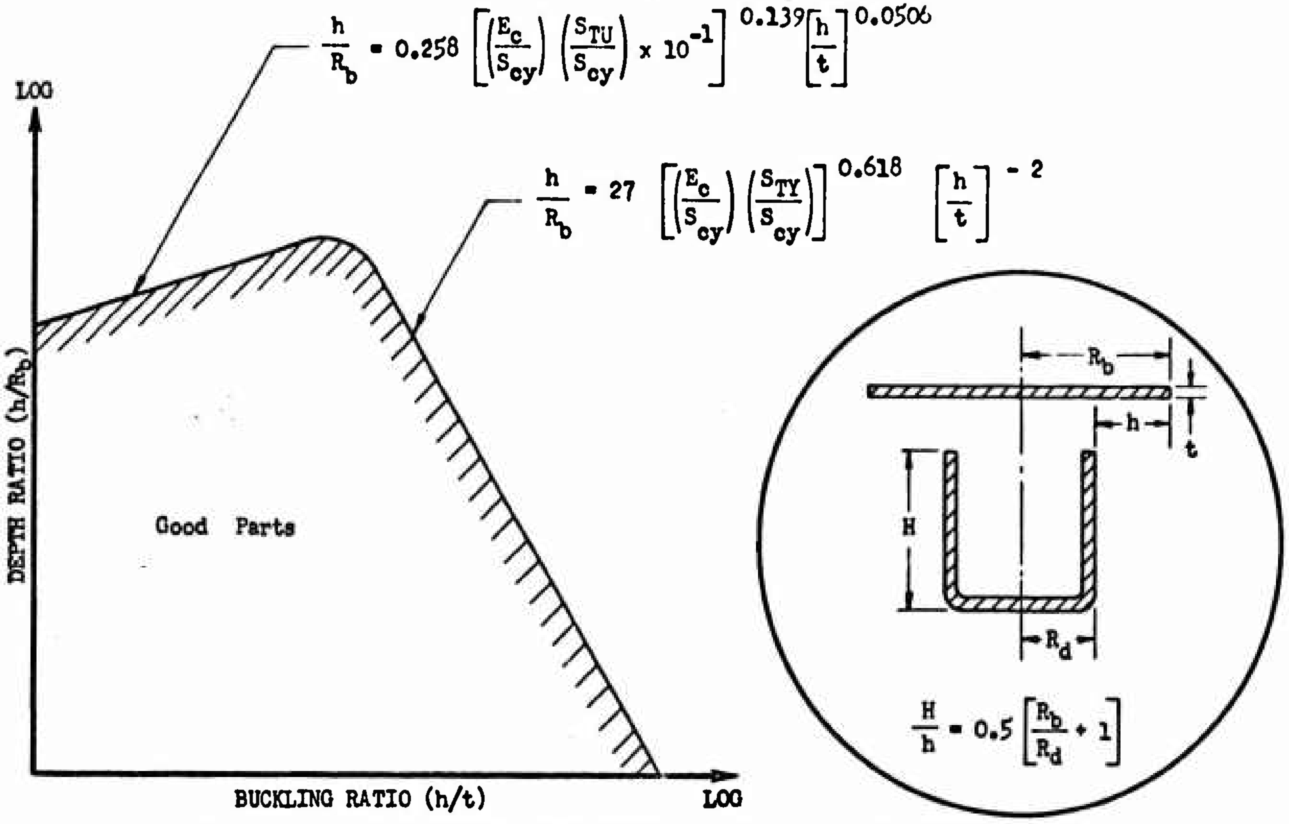


FIGURE 7. FORMING LIMIT CURVES FOR LINEAR STRETCH FORMING HEEL-OUT ANGLES AND CHANNELS



$$\frac{h}{R_b} = 0.258 \left[\left(\frac{E_c}{S_{cy}}\right)\left(\frac{S_{TU}}{S_{cy}}\right) \times 10^{-1}\right]^{0.139}\left[\frac{h}{t}\right]^{0.0506}$$

$$\frac{h}{R_b} = 27 \left[\left(\frac{E_c}{S_{cy}}\right)\left(\frac{S_{TY}}{S_{cy}}\right)\right]^{0.618}\left[\frac{h}{t}\right]^{-2}$$

$$\frac{H}{h} = 0.5\left[\frac{R_b}{R_d} + 1\right]$$

FIGURE 8. TYPICAL FORMING LIMIT CURVE IN DEEP-DRAWING CYLINDRICAL CUPS

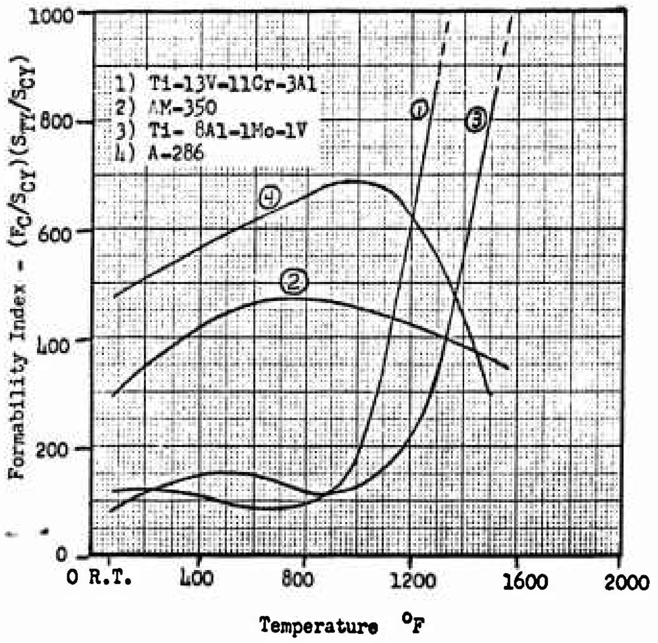


FIGURE 9. FORMABILITY INDEX IN DEEP DRAWING VERSUS TEMPERATURE

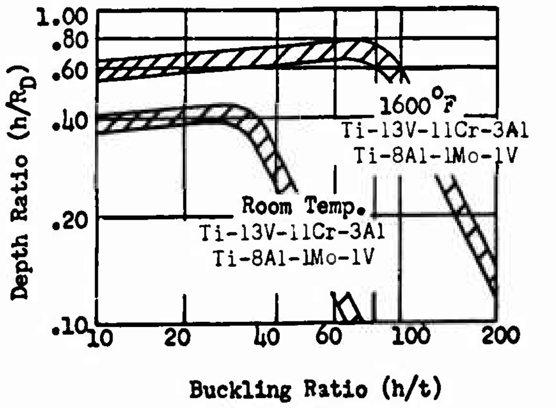
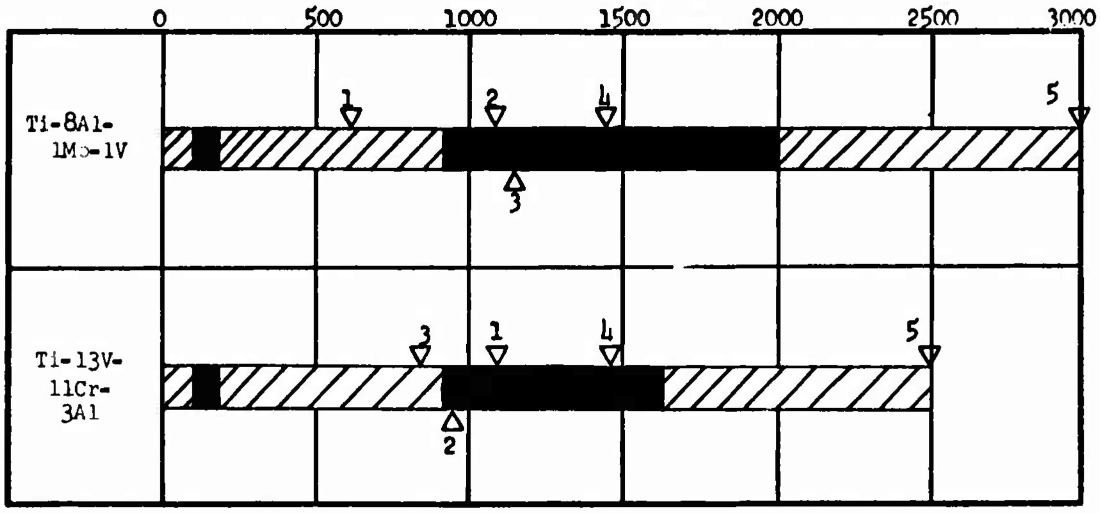


FIGURE 10. FORMING LIMIT CURVES FOR DEEP-DRAWING CYLINDRICAL CUPS FROM Ti-13V-11Cr-3Al AND Ti-8Al-1Mo-1V ALLOYS



(1) STRUCTURAL LIMIT (0.675TY AT RT)
(2) STRESS-RELIEF TEMPERATURE
(3) CONTAMINATION PROBLEMS
(4) RECRYSTALLIZATION
(5) MELTING POINT
█ OPTIMUM FORMING RANGES

FIGURE 11. CRITICAL TEMPERATURE POINTS FOR TWO TITANIUM ALLOYS

TABLE 3. TEMPERATURE CONSIDERATIONS

POTENTIAL HOT FORMING METHODS	DEVELOPMENT NEEDED
Heating of Part	**Tooling Material**
Radiation	**Steel (1000°F)**
Resistance	**High Grade Cast Iron (1400°F)**
Induction	**Nickel Alloys (2100°F)**
Heating of Tool	**Ceramic (3000°F)**
Integrally Heated Dies	**Atmosphere Control of Part**
Resistance Heating	**Heating Methods**
Furnace Heating	**Insulation Methods**
Heating of Equipment	
Hot Platen Presses	
Hot Fluid	
Hot Fluidized Solid	

punches working against either a diaphragm or solid rubber, and with movement of the blank restricted as it is held between the rubber and blank holder. Pressures go up to 15,000 psi over a 26-inch-diameter container.

Because of the increased usage of high-strength alloys in the aerospace industry, forming pressure requirements have necessarily increased. In order to evaluate the effect of pressure in forming, the pressure limitations in rubber forming were analyzed under Air Force Contract AF 33(657)-7314, "Sheet Metal Forming Technology", for several materials for part definition, shrink flanging, and springback.

Part Definition

The effect of rubber forming pressure on part definition is shown in Figure 12 for Ti-13V-11Cr-3Al and 17-7PH stainless steel. For these typical high-strength alloys, it can be seen that current production limits of 10,000 psi are inadequate. In order to obtain a reasonable value of 3t free form radius for the 0.063 gage material, a pressure of 50,000 psi is required. For this reason, the high-strength alloys are virtually ruled out for current production rubber forming, except for the very thin gages.

Shrink Flange Forming

The effect of shrink flange limits for various pressures is given in Figure 13 for 17-7PH and 2024-0. It is shown, for a fairly severe radius of curvature R of 10 inches, the maximum 17-7PH flange that can be formed with 10,000 psi is 0.6 inch; whereas for the larger radius of 30 inches, it is 1.8 inches. For this reason, flanging of the high-strength alloys on the rubber press is generally limited to the larger radii of curvature on the order of 25 to 30 inches. More severely curved parts have to be formed on matched dies. In comparison, it is shown that the same parts requiring 40,000 psi for 17-7PH require only 10,000 psi for aluminum.

Springback

The relationship between pressure and springback for three materials and two gages is shown in Figure 14 for rubber pad forming. It is indicated that pressure has a critical influence on springback. Material properties have an even greater influence on springback, which is directly related to the ratio of the tensile yield to modulus, S_{TY}/E. At 10,000 psi, the springback values for 0.020-gage Ti-6Al-4V, Ti-13V-11Cr-3Al, and 17-7PH are 17, 15, and 6 degrees, respectively. At 50,000 psi, the values are 13, 12, and 4 degrees. Beyond 50,000 psi, little gain can be made on springback. The reduction in springback reduces the effort required in tool development and finish forming.

Summary

The increased need for components of titanium alloys, superalloys, high-strength steels, and refractory alloys results in the need for higher forming pressures. For this reason, conventional rubber forming presses will decrease in usage due to insufficient pressure capabilities. Advanced concepts in rubber forming will be required to provide these high pressures. Other high-pressure processes such as static gas and fluid forming techniques should also be evaluated for potential use. An outline of the potential high-pressure forming methods and the developments needed is given in Table 4.

VELOCITY EFFECTS

The Space Age has ushered in many new forming processes. The most important being the high-velocity processes such as explosive, electromagnetic, electrohydraulic, pneumatic-mechanical, and explosive gas forming. Under Air Force Contract AF 33(657)-7314, "Sheet Metal Forming Technology",(2) the effect of forming velocity on various materials' ductility was studied.

Most materials are very applicable to high-velocity forming as long as it is performed below a critical velocity above which the material behaves in a brittle manner. A number of materials exhibit a significant increase in ductility with forming velocities to 700 ft/sec, well into the high-explosive forming range. Figures 15 and 16 illustrate the effect of velocity in dome forming and tube bulging for three materials. The curves illustrate the significant improvement in uniform elongation for titanium over static forming values. However, titanium has a relatively low critical forming velocity in the lower range of high-explosive forming. Critical impact velocity effects are such that even at elevated temperatures, titanium alloys must be formed in the low-explosive velocity range.

An outline of the potential high-speed forming methods and developments needed is given in Table 5.

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(2) Wood, W. W., et al, "Sheet Metal Forming Technology", Technical Documentary Report, ASD TDR 63-871 (Parts I and II)(July, 1963).

(3) Wood, W. W., et al, "Advanced Theoretical Formability Manufacturing Technology", Technical Report, AFML TR 64-411 (Parts I and II) (January, 1965).

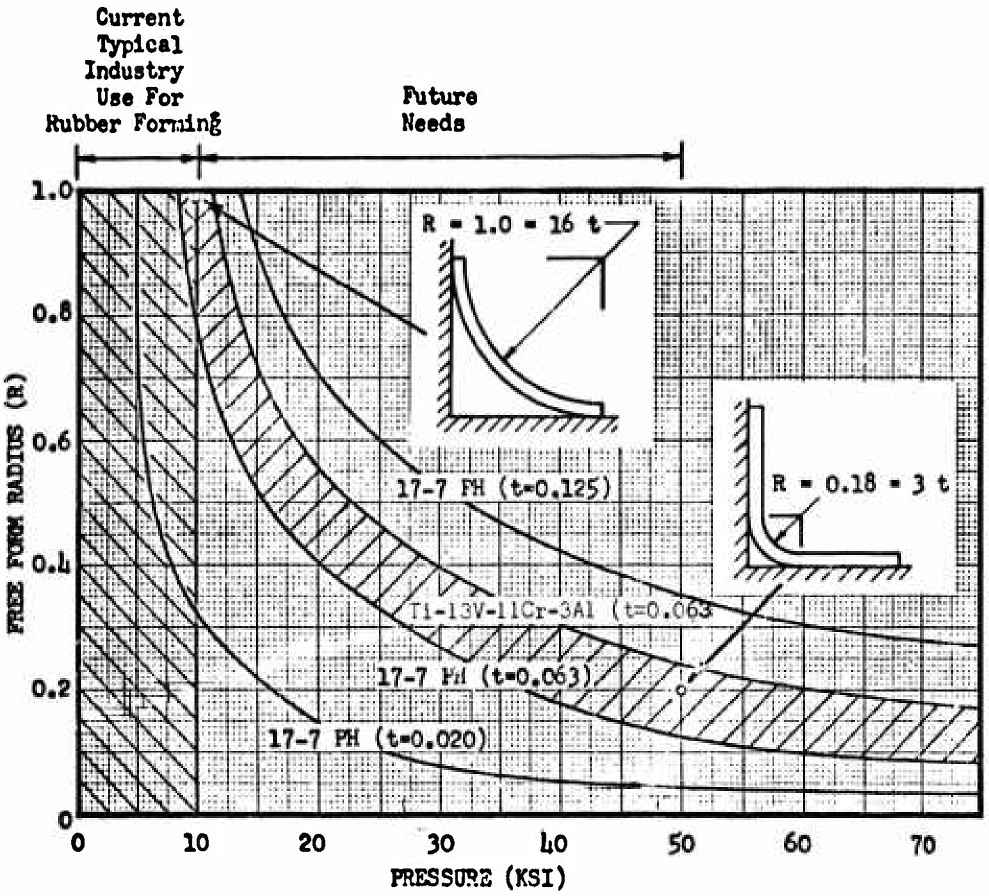

FIGURE 12. EFFECT OF PRESSURE ON FREE-FORM RADIUS

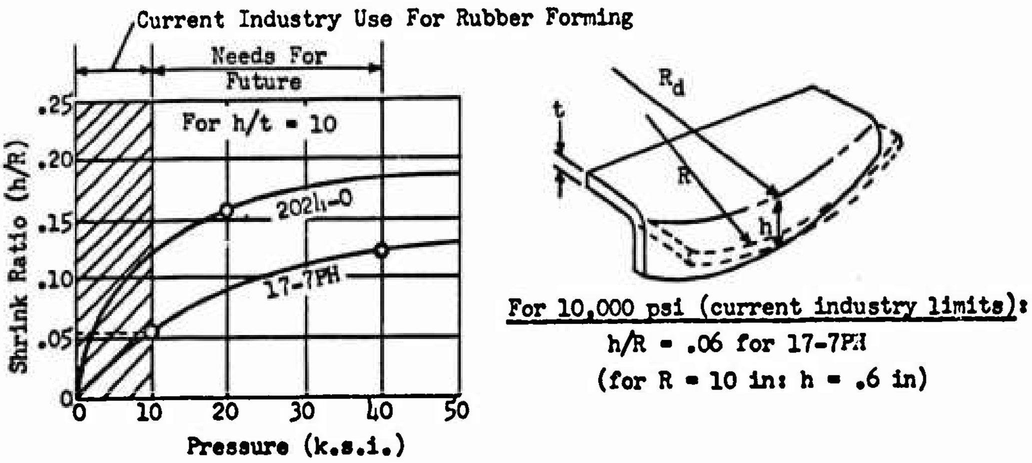

FIGURE 13. EFFECT OF PRESSURE ON SHRINK FLANGE RATIO (h/R)

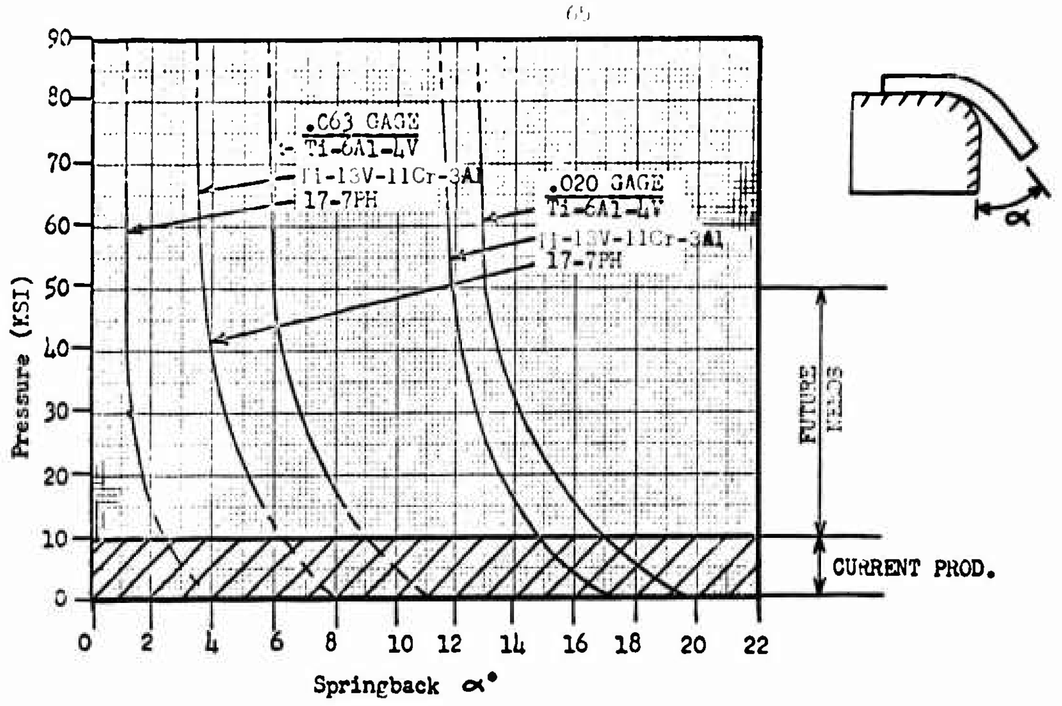

FIGURE 14. EFFECT OF PRESSURE ON SPRINGBACK

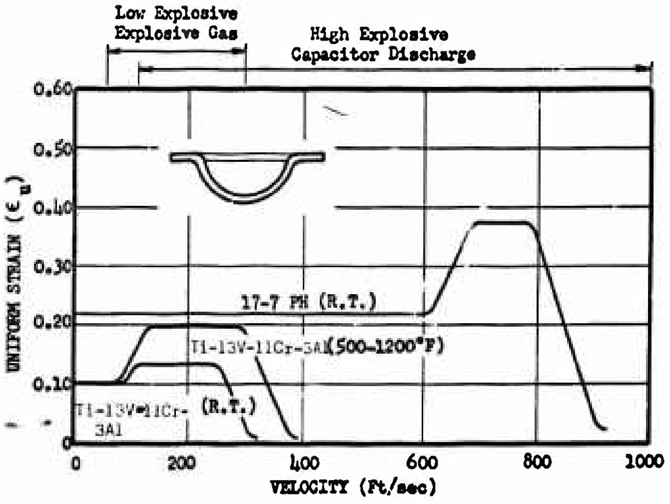

FIGURE 15. HIGH-VELOCITY FORMABILITY OF DOMES

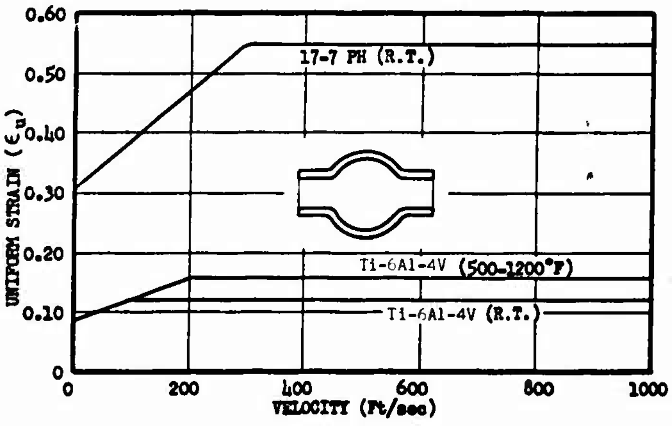

FIGURE 16. HIGH-VELOCITY FORMABILITY OF BULGED CYLINDERS

TABLE 4. PRESSURE CONSIDERATIONS

POTENTIAL HIGH PRESSURE FORMING METHODS	DEVELOPMENT NEEDED
Room Temperature Forming Water Air Solid (Rubber) Elevated Temperature Forming Hot Fluid (Molten Metal) Inert Gas Fluidized Solids (Sand)	High Pressure Press Systems Tonnage to 100,000 Tons Pressure to 50,000 psi Temperatures to 3000°F Sealing Methods Safety Material Behavior of Equipment Effect of High Pressure on Rubber Corrosive and Other Damaging Effects of Hot Fluids Insulation Methods

TABLE 5. HIGH-SPEED-FORMING CONSIDERATIONS

POTENTIAL HIGH-SPEED-FORMING METHODS	DEVELOPMENT NEEDED
Explosive Capacitor Discharge Combustible Gas High Temperature Combinations of these	Mechanized Press to 10 Foot Diameter Cycle Time of 5 Minutes Closed System High Pressure to 50,000 psi Versatile (Form Variety of Part Shapes) Good Safety Features Semi-Mechanized System to 50 Foot Diameter Open System Cycle Time of 1 Hour

THE MACHINING OF TITANIUM

C. T. Olofson*

INTRODUCTION

This presentation concerns the machining of titanium. Subjects closely allied with this method of fabricating include:

Costs
General machining requirements
Planning operations
Safety
Machinability characteristics of titanium
Specific machining processes.

The previous papers have shown that titanium and many of its alloys possess exceptional properties and characteristics. This metal not only has an excellent strength-to-weight ratio but also has good hot strength and unusual corrosion resistance. While these qualities promote strength and reliability at supersonic flight speed temperatures, they also complicate the machining situation.

Fifteen years ago, titanium was considered to be very difficult to machine. Subsequent research and experience, however, have progressively improved this situation. This improvement has resulted from gradual refinements in tool materials, machine tools, tool geometries, and cutting fluids.

COSTS

The strength and chemical reactivity of titanium and its alloys introduce many additional requirements during processing and fabrication. The result is certain increased costs associated with airframe fabrication and assembly, but not necessarily all costs. Very little comparative information on titanium/aluminum machining costs is available. Cost ratios are difficult to establish, and they can vary between machining operations and among investigators.

Machining titanium usually takes more time than machining conventional materials because of lower metal removal rates. On the basis of a survey of different fabricators, and based on equal volumes of metal removed, different machining operations performed on Ti-8Al-1Mo-1V appear to require an overall range of 1.2 to 3.5 times the number of manhours needed for a similar aluminum part. Specific ratios of different machining operations taken from the NASA publication, "Machining and Grinding of Titanium",** are shown in Table 1.

These ratios are not necessarily valid where a titanium part of one design is substituted for an aluminum part of another design to perform the same function at a savings in weight. Furthermore, before these ratios can be converted to labor costs, items such as complexity factors and learning curves should be taken into consideration. Finally, let us not forget the cost of titanium itself. It is relatively expensive when compared with aluminum.

TABLE 1. ESTIMATED DIRECT-LABOR-HOUR RATIOS(a) FOR MACHINING SIMILAR TITANIUM(b) AND ALUMINUM(c) AIRFRAME DETAILS(d)

Machining Operation	Ti to Al Manhour Ratio(e) Probable	Minimum	Maximum
Turning	1.7 to 1	1 to 1	3 to 1
Drilling	2.6 to 1	1.3 to 1	2.7 to 1
End Milling	2.7 to 1	2 to 1	3.3 to 1
Straight Milling	1.2 to 1	1.1 to 1	2 to 1
Profile Milling	1.6 to 1	1.5 to 1	1.8 to 1
Hole Preparation	3.5 to 1	2 to 1	4.5 to 1
Overall Machining	2.7 to 1	1.5 to 1	3.5 to 1

(a) Machining and setup times expected in 1970-1975.
(b) Ti-8Al-1Mo-1V alloy.
(c) 2000 and 7000 series aluminum alloys in 1964-1965.
(d) A production of 100 airframes is assumed.
(e) Ratios do not reflect the rates of improvement that could occur for aluminum by 1970-1975.

It is well known and it was cited in previous papers that precautions must be taken in processing titanium to exclude the interstitial elements - oxygen, nitrogen, and hydrogen. Consequently, processing costs are higher. The basic material costs of titanium mill products are high with pricing increases found for increasing alloy complexity and increasing mill product sophistication. For example, unalloyed titanium bar or billet is considerably less expensive than Ti-8Al-1Mo-1V flat-rolled product. These factors must be taken into consideration when reviewing the costs of machining titanium and in making cost comparisons between titanium and other materials.

GENERAL MACHINING REQUIREMENTS

In view of the high material cost of titanium, the first important requirement in fabrication is to think in terms of minimizing scrap. Closer supervision and inspection are required in the machining of titanium than in the machining of aluminum or stainless steel to prevent scrap, and to assure that all possible precautionary measures are being taken to eliminate errors in cutting methods and in handling the machined parts. Minimizing scrap helps to meet tight schedules and tight budgets.

A proper cutting environment is necessary to minimize scrap. This means high-quality, heavy-duty machine tools, which are snug, well lubricated, and in good condition, are essential for machining titanium. Since titanium is notch sensitive and sensitive to vibration, special setups are required to eliminate chatter. The tool, the work, and the machine setups must be rigid. There should be a minimum overhang between the tool support and the work to eliminate, or at least minimize, tool deflection. Strong, sharp cutting tools are required. Care must be taken to prevent any rubbing of the tool against titanium during the cutting operation, because this causes rapid heat build up and galling. Appropriate feeds, speeds, and depths of cuts must also be used. Titanium is particularly sensitive to cutting speeds, because its rate of heat transfer is low, and high temperatures can build up in the tool if high speeds are used.

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**"Machining and Grinding of Titanium and Its Alloys", NASA Technical Memorandum TMX-53312, NASA/George C. Marshall Space Flight Center, Huntsville, Alabama (August 4, 1965).

Finally, suitable cutting fluids, selected primarily for their cooling ability, are essential. Nitrite amine solutions, potassium nitrite solutions, soluble oil mixtures, and sulfurized oils are all used.

In general, chlorinated fluids and solvents should not be used on alloys if alternate non-chlorinated liquids are available. This is due to the possibility of encountering chloride stress corrosion of the part if residual chlorides remain on its surface, and the part is subjected to subsequent heating. Where chlorinated cutting fluids are used, these should be removed promptly, for example, by using methyl ethyl ketone, popularly known as MEK.

Titanium must be handled carefully "in house" and during shipment to prevent nicks and scratches. It is also a good idea to stress relieve parts after certain machining operations. This applies primarily to turning operations, and to parts which have sharp corners.

Care also must be taken to minimize deflection of titanium during machining operations, since it has a low modulus of elasticity. Stainless steel, for example, has a modulus of elasticity of 29 million psi. The modulus of titanium is about one-half that - or 15 million psi. This means that for the same machining force applied, titanium will deflect about twice as far as stainless steel. Back-up blocks are sometimes used to minimize this. Low-melting filler materials such as Wood's metal may be cast around especially flimsy parts to strengthen them during machining, and then melted away after the operation is complete.

PLANNING OPERATIONS

Close supervision and inspection are needed to prevent scrap, or to facilitate early removal of scrap. Another important step in minimizing scrap is to assure the dissemination of necessary information to the machinists, including all specialized cutting requirements, proper tools, recommended feeds, speeds, depths of cuts, coolants, etc. The operation sheet or planning paper should be clearly marked "Titanium" to call attention to this special material which requires special machining and handling. The sheet should include the part name, part number, and the titanium alloy involved. The machining operation such as turning, profile milling, etc., also should be designated. All pertinent information concerning machine settings, tool materials, and geometry, and any special instructions for the operator should be listed. Special instructions, for example, might require that the tool be examined for flank wear, or the drill for corner wear after so many minutes of operation, or that the part might have to be stress relieved after certain machining operations. The planning systems and procedures used must insure that the operation sheet accompanies the parts to each machine involved, so that the supervisor and operator will have all the required information needed to make satisfactory parts.

SAFETY

The handling and storage of titanium chips is important, since under certain conditions these constitute a fire hazard. Good housekeeping is essential around the machines, since a hot chip could possibly leave the tool and ignite other chips in the area. Accumulated chips should be placed in closed metal containers and stored outside. Care should be taken to assure that chips are not mixed with oil-soaked sludge, oily rags, or other materials susceptible to spontaneous combustion.

The grinding operation can also be hazardous from a fire standpoint. Titanium dust is much more flammable and explosive than the larger size chips resulting from other machining operations. Considerable sparking may accompany grinding. Titanium should never be ground dry. A suitable grinding fluid should always be used, and extra coolant lines should be available to quench out sparking as soon as it occurs. Water-base grinding fluids are safer for the grinding operation, and sparking can be minimized by low wheel speeds. The recommended grinding speeds are 1800 to 2000 feet per minute for titanium as compared with 6000 feet per minute for steel.

Coolant build up around machines should be avoided. Sodium or potassium nitrite which is used in some water-base coolants is an unstable compound and can be a hazard if the solid material is allowed to accumulate around the machines from coolant evaporation. Here again, good housekeeping is important.

Fire extinguishers suitable for metal fires should be readily available. Sand and special proprietary compounds which put out metal fires by smothering are recommended.

In regard to toxicity, titanium metal is considered to be physiologically inert; however, the dust resulting from certain titanium machining operations may be placed in the nuisance category. The metal itself is not harmful to the health in the same sense as toxic metals like beryllium. Any dermatitis or other skin disorder encountered by the operator in machining titanium would probably originate from the cutting oils rather than from the titanium.

MACHINING CHARACTERISTICS OF TITANIUM

The four basic considerations for classifying metals as to machinability are (1) true machinability which relates to the ease of metal removal, (2) abrasiveness, or the tendency of the metal to wear or abrade tools; (3) reactiveness which causes galling or seizing, and (4) finishability, or the ease with which a good chip and a fine surface can be produced.

The abrasiveness of a metal can be (1) inherent, as a result of a metal's original hardness, (2) induced, through strain hardening, or (3) caused by abrasive inclusions in the metal. Titanium is a strong metal - as strong as some steels. However, contrary to some popular opinions, it does not strain harden as rapidly as does stainless steel. Titanium can be abrasive to tools due to abrasive inclusions such as oxides. However, such inclusions are encountered only rarely. The principal reason for tool wear in machining titanium is the relatively high strength of the material over a wide temeprature range.

It has been previously pointed out that titanium will alloy with almost anything. During machining, titanium is extremely reactive to all tool materials at cutting temperatures, and this leads to a tendency to gall and seize on tools. During machining operations, titanium combines with the tool at the hot cutting edge to form a hard, brittle compound which spalls off. For example, during an end milling operation, each cutting edge of the cutter may form this brittle coating during the first cut. As the tool rotates and each cutting edge bites further into the work, the coating may spall off taking part of the tool cutting edge with it.

Ideally speaking, excellent finishes in the range of 20 to 30 microinches rms should be possible with titanium. This metal forms a continuous chip with no built up edge on the tool, and the chip separates cleanly. This should produce a good finish, characteristic of a Type 2 chip, and characteristic of strong metals such as titanium.

True machinability of a metal is generally associated with the basic strength and ductility properties of the metal. However, other factors are involved, and as mentioned previously, the real criterion is ease of metal removal. Pure copper, for example, might be expected to have a high machinability rating, since it has very little strength; however, during machining, copper becomes "gummy" at the tool interface because of high ductility and build up on the edge of the tool. This interferes with the removal of metal and accordingly, copper has a very low rating in the machinability spectrum. On the other hand, leaded brass, a copper alloy, has an excellent rating.

The true machinability rating indicates a comparative rate of metal removal that can be achieved in a machining operation at constant tool wear as compared with a standard metal of known machinability. AISI B1112 steel has been selected in industry as a standard and assigned a rating of 100. This particular alloy is well known for its ease of machining, since it has been resulfurized to make it suitable for screw machine production. This rating system indicates that other metals rated at 100 would be equally machinable as B1112 steel. A rating of 200, as shown for leaded brass, in Table 2, means that the metal can be machined at twice the rate of machining B1112 steel. If, for example, B1112 steel can be turned at a cutting speed of 180 feet per minute using 0.009-inch feed per revolution and a 0.1-inch depth of cut; and if this results in 0.015-inch wear land on a carbide tool flank in one hour, then leaded brass can be cut at twice the rate or 360 feet per minute, to obtain the same rate of tool wear with the same feed and depth of cut. For a rating of 60, as shown for 1045 steel, this system means that 1045 steel can be cut at only 60 percent of the speed used for B1112. Other conventional metals rated in the table are AISI 4340 steel (annealed) at 45, and AISI Type 302 stainless steel at 35. Unalloyed titanium is rated at 40, or a little better than Type 302 stainless steel. The titanium alloys shown are all rated considerably lower than stainless steel. The toughest titanium alloy to machine is the all-beta alloy, Ti-13V-11Cr-3Al, with a rating of only 16.

Several of the properties of titanium noted previously contribute to its low rating in the machinability spectrum. Excessive cutting temperatures develop at the tool/chip interface due to the metal's low specific heat and its low thermal conductivity. Temperatures up to 1800 F can develop with carbide tools, and up to 1000 F with high-speed steel tools. Titanium is a light metal having a combination of properties which tends to confine the heat to the tool-chip interface. It is possible to get a red hot chip of titanium from the turning operation if the machine is run fast enough, and if no coolant is used. The other properties affecting titanium machinability are chemical reactivity and relatively low modulus of elasticity. Both contribute to the difficulties experienced in machining titanium and affect machinability ratings.

TABLE 2. TITANIUM MACHINABILITY RATINGS COMPARED WITH OTHER METALS

Titanium Alloys		Conventional Metals	
Metal	Rating	Metal	Rating
Unalloyed Titanium	40	Brass, leaded	200
Ti-8Mn	25	B1112 Steel	100
Ti-4Al-4Mn	22	1045 Steel	60
Ti-6Al-4V	20	4340 Steel	45
Ti-13V-11Cr-3Al	16	Type 302 Stainless	35

SPECIFIC MACHINING PROCESSES

The machine and tool requirements for turning, milling, drilling, and tapping titanium are summarized in Table 3. The requirements are discussed separately as follows:

As previously noted, heavy-duty, high-quality machine tools, in good condition should be used for machining titanium. This means that they should be strong, snug, well lubricated, "overpowered", and free from vibration. When the tool takes a cut, sufficient power and rigidity should be available to keep the tool moving at its required cutting speed. The tapping operation requires machinery with extra sensitivity, since taps are easily broken when used on titanium.

Three types of tool materials used for machining titanium are (1) the stellite or cast alloy type, (2) the carbides, including the cast iron grades, C-2, C-3, and C-4, and (3) the high-speed steel grades, T-5, T-15, and M-10. The T-5 and the T-15 are cobalt grades for high-speed steel. The molybdenum high-speed steel, M-10, is used in drills and taps for titanium. The high-speed steel tools can be used for tool-chip interface temperatures up to 1000 F.

In addition to the regular high-speed tools and brazed carbide tools, a new type called "throw aways" seems to work very well for turning titanium. These are small insert-type tools with multiple cutting edges. They are clamped in tool holders of specific rakes, and when a cutting edge is worn out, the insert is rotated to its next cutting edge and cutting is resumed. The insert is discarded when all cutting edges are used up.

A multi-tooth, helical type tool is preferred for the milling operations including peripheral, face, and end milling. The tool should have as many teeth as the chip space will allow for smooth cutting.

A heavy-duty stub drill is used for rigidity in drilling titanium. Both low helix and high helix types are used, and they usually are ground with a crank-shaft type point.

TABLE 3. REQUIREMENTS FOR MACHINING TITANIUM

Item	Description	Operation			
		Turning	Milling	Drilling	Tapping
Machine tool	Strong, over powered, vibration free	X	X	X	Lead screw
	Sensitive	--	--	--	X
Tool materials	Carbide C-2 Carbide C-3 Carbide C-4	X	X	Deep holes	--
	High speed steel T-5, T-15, M-10	X	X	X	X
Tool types	--	Throwaways, brazed, regular	Multitooth helical, face, end	Heavy duty stub, helix, crankshaft point	Chip-driving spiral point
Tool design	Rake angles	+(finish) ±(rough)	Not critical	Low or high helix	+6 to +10
	Lead angles	Use	Use	--	--
	Relief angles	7°	10°	10°	3°
Set up rigidity	Work support	Minimum overhang	Close to table	Support thrust	Support thrust
		Steady rest	Back-up block	--	--
		Follow rest	Filler metals	--	--
	Tool overhang	Minimum	Minimum	Short drills	Short taps
Cutting techniques	--	Cut on dead center	Climb mill	Drill to size	--
Feed, in.	Positive	To 0.020	To 0.015	To 0.009	--
Cut depth, in.	--	To 0.250	To 0.100	--	--
Speed, ft./min	High speed steel	To 170	To 110	To 50	To 50
	Carbide	To 300	To 190	To 200	--
Cutting fluids	Sodium nitrite, five percent	X	--	--	--
	Soluble oil, 1:20	X	X	X	--
	Sulfurized chloronated oil	X	X	X	--
	Lithopone paste	--	--	--	X

A chip driving, spiral point tap is used for tapping titanium. Special precautions must be taken in relieving taps as they are easily broken when working with titanium.

Tool geometry including rake angles, lead angles, and relief angles are important in specific machining operations. Positive rakes are used almost exclusively for finishing operations in turning; however, both positive and negative rake angles are used with carbide tools for rough turning cuts. The rake angles do not seem to be too critical in milling since a wide variety of rake angles are used successfully with titanium. Both low and high helix angles are used in drilling. Positive rake angles of six to ten degrees are used for tapping.

Lead angles are normally used in turning and milling. This angle provides a longer cutting edge which distributes the heat of cutting and gives longer tool life.

Relief angles on tools used for titanium are a little higher than those used for more conventional metals, because, as mentioned before, it is important for the tool not to rub on titanium since this would cause galling and seizing. On the other hand, if the angle were too large, the tool would break more easily. A seven degree relief angle is used in turning, ten degrees for milling and drilling and only three degrees for the more critical operation - tapping.

Tool and work set-up rigidity is extremely important in machining titanium. There should be a minimum overhang of both tool and work to prevent deflection and rubbing. In a turning operation, the work should be placed in the lathe chuck in such a manner as to minimize overhang, and to support the work close to the cutting tool. Steady rests, follow rests, or back-up blocks should be used to help support long pieces. In milling, the cut should be made close to the table for maximum support, and back-up blocks should be used if needed. Especially flimsy parts may be reinforced with low melting filler materials which are cast around the part and later melted away after the machining operation is complete. For drilling and tapping, the work piece should be supported at the point of thrust, and short drills and taps should be used.

Positive feeds should always be used for cutting titanium. Once a cut is started it should be continued. The tool should not be allowed to stop, or to dwell in the cut. In turning, the cut is made on dead center. In milling, climb milling is recommended. Since the milling cutter tends to pick up a titanium chip on its cutting edge, this chip may fuse fast and then break the cutting edge on its second pass as mentioned previously. In climb milling, the cutter takes a deep cut as it enters the work, but picks up only a thin chip at the exit of the cut. This minimizes the damage to the tool. However, sturdy machine tools which can take a heavy load without deflecting are required for climb milling. Care should be exercised to retract the cutter from the work at the end of a milling cut. In drilling, the operator usually should not attempt to drill a small hole and then enlarge it. The hole is drilled to size the first time, and once the drill is started the operation should not be interrupted until the hole is completed.

Feeds, speeds, and depths of cuts are critical in machining titanium. The general rule is to use a heavy feed and a low speed. In turning, feeds up to 0.020 inch per revolution are used for rough cuts. Feeds up to 0.012 inch per tooth are used in milling, depending on the operation. In drilling and end milling, the feed depends on the tool diameter and is usually limited to maximums of 0.015 inch per revolution and 0.006 inch per tooth, respectively.

As shown in Table 3, depths of cuts are limited with titanium to a maximum of 0.250 inch in turning and 0.100 inch in milling.

Speeds are very important in machining operations and depend on the type of tool used and the material being cut. For example, when turning unalloyed titanium, high-speed steel tools may cut at 125 feet per minute and carbide tools at better than 300 feet per minute. Titanium alloys must be cut at considerably lower speeds. When face milling unalloyed titanium, speeds up to 150 feet per minute can be used with high-speed steel tools, and up to 400 feet per minute with carbide tools. Since heat is confined at the drill point in the drilling operation, speeds must be reduced below 80 feet per minute for high-speed steel tools, and to 200 feet per minute for the carbides.

Cutting fluids for machining titanium are selected primarily for their cooling ability. Three types of fluids are generally used. Both the five percent sodium nitrite water solution and the 1:20 soluble oil-water solution are used and have excellent cooling properties. The third type used, sulfurized chlorinated oil, does not have quite the cooling ability but does supply more lubricity. This type is used at lower speeds. A lithopone paste, on a heavy sulfurized mineral oil, can be used for tapping.

SUMMARY

Problems in machining titanium originate from three basic sources: high cutting temperatures, chemical reactions with tools, and a relatively low modulus of elasticity. Unlike steel, titanium does not form a built-up edge on tools, and this behavior accounts for the characteristically good surface finishes obtained even at low cutting speeds. Unfortunately, the lack of a built-up edge also increases the abrading and alloying action of the thin chip which literally races over a small tool-chip contact area under high pressures. This combination of characteristics, and the relatively poor thermal conductivity of titanium results in unusually high tool-tip temperatures.

Titanium's strong chemical reactivity with tool materials at high cutting temperatures and pressures promotes galling and tool wear.

Mechanical problems result from titanium's relatively low modulus of elasticity, half that of steel. The low modulus coupled with high thrust forces required at the cutting edge can cause deflections in slender parts. Distortion of that kind creates additional heat, because of friction between the tool and workpiece; and creates problems in meeting dimensional tolerances. Because of differences in thermal and mechanical properties, titanium parts may "close in" on steel drills, reamers, and taps.

These difficulties can be minimized by following machining recommendations for titanium. When proper techniques are employed, machining of titanium is not an unusually difficult or hazardous operation.

WELDING OF TITANIUM ALLOYS

K. C. Wu*

INTRODUCTION

The joining of metals is a most important consideration in the manufacture of structure for aircraft. It is quite common for metallic joints to be the limiting link in the structure from a mechanical properties viewpoint, especially from a fatigue endurance consideration. Frequently, the metallic members of a structure can be designed to an optimum configuration on the basis of maximum strength at minimum weight and with optimized physical stability, only to find that strength, weight, or stability considerations at the joints impose penalties. On this basis, the importance of metallurgical joining processes is readily appreciated. The importance of choosing the optimum joining method because of manufacturing cost effectiveness considerations, is apparent. In Figure 1, the numerous methods available to the joining specialist are shown.

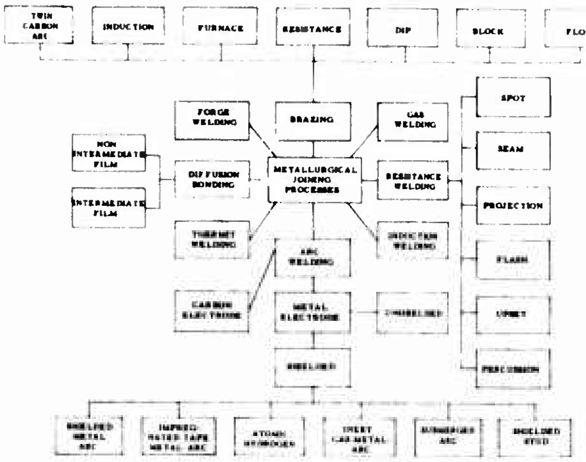

FIGURE 1

Welding is a major joining process for fabrication of structural aircraft members. The most commonly used welding processes for titanium alloys are inert-gas metal-arc welding and resistance spot welding.

In the arc welding processes, the arc is established between an electrode (consumable or nonconsumable) and the workpiece by ionization of the shielding gas using either direct current or alternating current. The welding current is supplied by an appropriate power supply, generator, or rectifier. A molten pool is formed under the moving arc and resolidifies behind it. Thus, a welded joint is formed. Filler metal is used either as a consumable electrode or added into the molten pool through a feed mechanism for the nonconsumable electrode process. An arc fusion welding setup is schematically shown in Figure 2.

A photograph of typical equipment used for arc fusion welding is shown in Figure 3. Note the inert-gas trailing shield in the photo which must be used in the welding of reactive metals such as titanium. This will be discussed in detail later. A cross section of a butt weldment in titanium flat-rolled product formed by an arc fusion welding operation is shown in Figure 4.

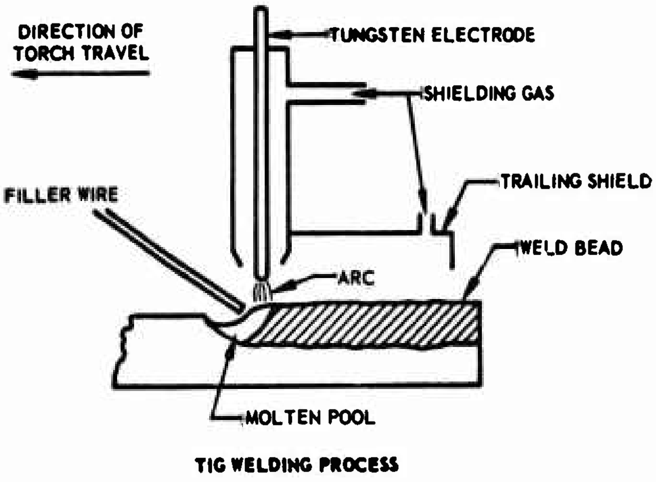

FIGURE 2 INERT GAS SHIELDED ARC WELDING PROCESS

FIGURE 2

FIGURE 3

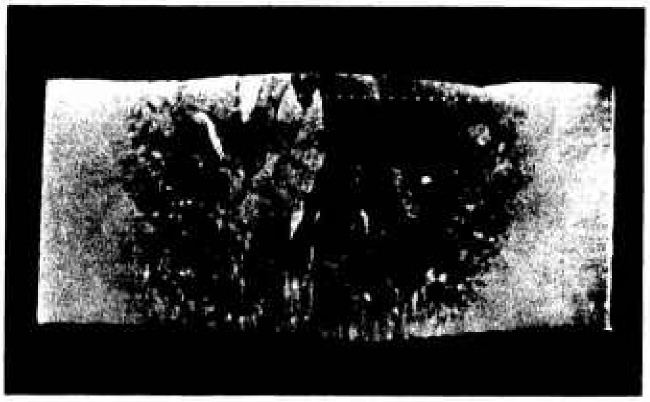

FIGURE 4

Resistance welded joints are formed by resistance heating at the faying surface due to the existence of contact resistance and application of electric current. The fusion zone is located between the sheets (or plates) and is not visible except in section. It can be formed as an individual spot (spot welding) or overlapped spots (seam welding) depending upon the joint design. A schematic drawing of a spot welding machine is shown in Figure 5.

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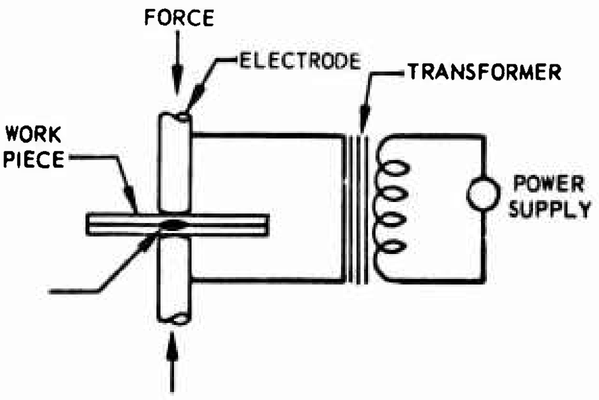


FIGURE 5. SCHEMATIC DRAWING OF SINGLE-PHASE AC RESISTANCE SPOT-WELDING PROCESS

A photograph of typical equipment for spot welding is shown in Figure 6. The power supply for resistance welding can be single-phase AC, three-phase frequency converter, or three-phase rectified DC current. An electronic sequencing device is an integral portion of a modern resistance welding machine. A cross section of a typical spot weld in titanium alloy is shown in Figure 7.

The selection of a welding process depends on the material, joint geometry, material thickness, accessibility, and distortion and weight considerations. In general, arc fusion welding is used to make butt joints and resistance welding is for lap joints.

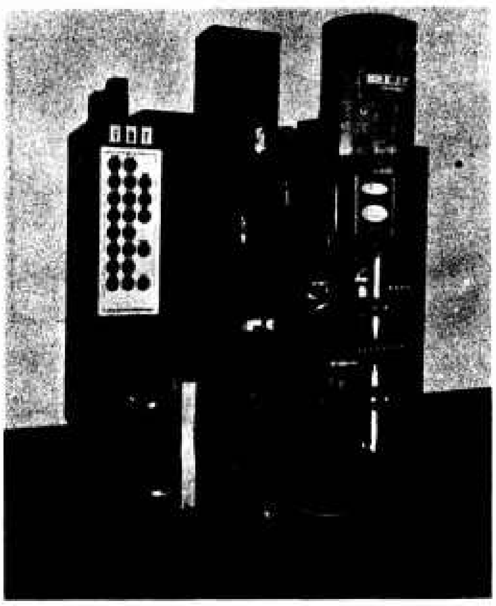


FIGURE 6

FIGURE 7

WELDING PROCESSES

TIG Welding

Inert-Gas Shielding

When welding titanium alloys with the TIG process, shielding gas is required, not only for the molten pool but also above the hot weld bead through the use of a trailing shield and the back side of the sheet by using back-up shielding. The reason for this is that (1) the thermal conductivity of titanium alloys is relatively low and the weld bead remains hot, above 1000 F, for a significant length of time and (2) the interstitial elements diffuse into titanium rapidly above 1000 F and embrittle titanium even when only a few parts per million are present.

The flow rate of the shielding gas depends on the other welding parameters. The backup gas flow rate should not be so high that it causes the formation of a concave weld bead on the root side. The gas flow rates of the torch and trailing shields should be adjusted individually according to nozzle size, nozzle-to-work distance, trailing shield construction, and, particularly, travel speed such that no turbulence occurs in the shielding gas. For titanium welding, both argon and helium are used. Argon has a higher atomic weight than helium (40 versus 4); therefore, argon shielding is less affected by air currents in the welding area. When the electrode-to-work distance is held constant, an argon arc is of lower voltage than helium due to the difference in ionization potential; that is, for a given arc length and amperage, an argon arc produces less heat than helium. Therefore, helium is more advantageous for welding thick materials which require deep heat penetration.

Electrode Geometry

Tungsten has high electrical resistivity and low thermal conductivity. In order to have a constant electrode-tip-to-work distance for a certain arc voltage, the distance that the electrode protrudes from the collet, called the electrode extension, has to be kept constant. The influence of electrode geometry on the shape of the weld bead has been demonstrated by Savage and his associates.(1) A blunt tip causes arc wandering, while a sharp tapered tip increases voltage drop, current density, and, in turn, causes tip melting. The desired tip geometry depends on the welding variables. In general, a spherical tip or 60° to 120° included angle with approximately a 0.020 inch diameter flat at the tip is acceptable.

Back-Up Bar Materials

For a given set of welding parameters, the cooling rates in a weldment are controlled primarily through the selection of the proper back-up bar material. The cooling rate required for titanium weldments depends on the type of titanium alloy employed. Therefore, selection of proper back-up bar material should not be neglected. For instance, a fast cooling rate increases the amount of alpha-prime, which reduces toughness in a Ti-8Al-1Mo-1V weldment.(2) In this case, a slow cooling rate is preferred in order to retain fracture toughness. A slow cooling rate may be achieved by using a back-up bar having low thermal conductivity, such as stainless steel. On the other hand, the titanium alloy Ti-6Al-4V requires a rapid cooling rate for the best subsequent aging response, suggesting the use of a high thermal conductivity material for the back-up bar, such as copper.

The cooling rate may be further reduced by manipulating the welding parameters to give a high energy input and/or by using a preheat.

Energy Input and Thermal Cycle

To cause the melting and flow of the metal during welding, energy, in the form of heat, has to be delivered to the joint. The electrical energy of the arc is converted into kinetic energy in the form of high-velocity free electrons and positive ions that bombard the workpiece and create heat. This heat, called the energy input, is measured in joules per inch. Energy input is a function of the welding variables and is as follows:

$$\text{Energy Input} = \frac{E \times I \times 60}{V} \text{ Joules per inch}$$

where

E is the voltage in volts

I is the current in amperes

V is the travel speed in inches per minute.

The energy input is also a controlling factor for the heating and cooling rates in a weld, thereby affecting the solidification parameters, transformation products, residual stress levels, and mechanical properties.

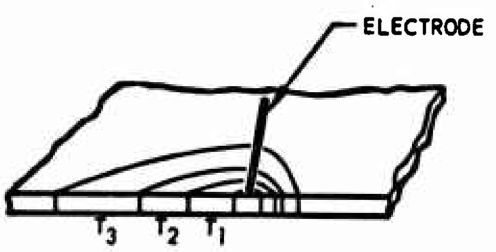
The metal surrounding the joint serves as a heat sink during welding. Therefore, the cooling rate in a thin sheet (a small heat sink) is slower than that in a thick plate (a large heat sink) for the same energy input.

The temperature gradient from the fusion zone to the base metal in a weldment varies in direct proportion to the diffusivity of the material. The thermal diffusivity for titanium alloys (0.091 cm^2/sec) is approximately one-half that of low-carbon steel (0.208 cm^2/sec); therefore, the temperature gradient when welding titanium alloys is much smaller than that for low-carbon steel. The temperature distribution in a typical welded plate is sketched in Figure 8.(3)

The shape of the isotherms changes with the travel speed. Figure 9 shows the isotherms for a stationary heat source and for a moving source. As the travel speed of the heat source increases, the temperature gradient ahead of the source increases and the temperature gradient behind the source decreases.

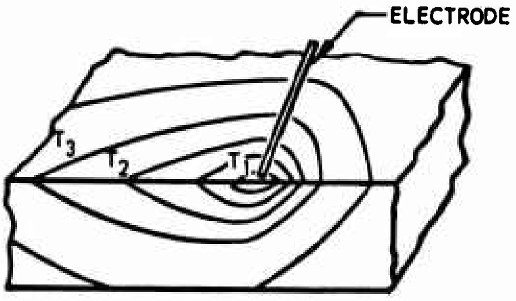
The thermal cycle experienced at various locations in the weld heat-affected zone is a function of distance from the heat source, thermal diffusivity of the material, energy input, etc.(4) The results of a mathematical analysis of the thermal characteristics of a weld heat-affected zone yielded the following relationship:

$$T - T_o = f(s,d)\ \frac{\text{Energy Input}}{1000} \times \text{preheat factor}$$



$T_1 > T_2 > T_3$

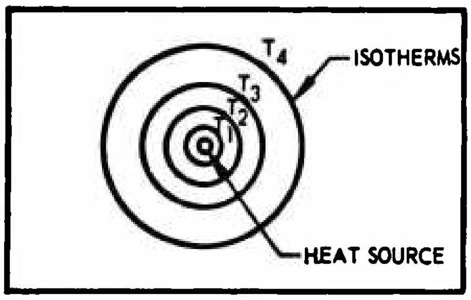
(A) ISOTHERMS IN A THIN SHEET



(B) ISOTHERMS IN A THICK PLATE

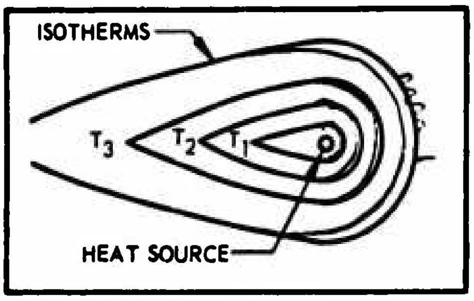
$T_1 > T_2 > T_3$

FIGURE 8. TYPICAL TEMPERATURE DISTRIBUTION IN WELDED PLATES



$T_1 > T_2 > T_3 > T_4$

A. STATIONARY HEAT SOURCE



$T_1 > T_2 > T_3$

B. MOVING HEAT SOURCE

FIGURE 9. ISOTHERMS PRODUCED BY STATIONARY AND MOVING HEAT SOURCES

where,

T = temperature (°R) at any point a distance, d, from the arc

To = initial plate temperature (°R)

f(s,d) = a mathematical expression which i function of time and distance

Energy Input = in Joules per inch

Preheat Factor = 1 (no preheat) or greater (with preheat)

A typical thermal cycle in the heat-affected zone is shown in Figure 10. The greater the distance from the fusion line, the lower the heating rate, cooling rate, and peak temperature. Also shown is the microstructural change in a Ti-8Al-1Mo-1V weld heat-affected zone due to the different thermal cycles experienced.

Resistance Spot Welding

Contact Resistance

In resistance spot welding, the heat which actually produces fusion is generated at the faying surface due to resistance heating. Microscopically, the metal surface has hills and valleys and a thin layer of oxide. The metal-metal contact, even under force, is limited to small areas. When welding current passes through these contact points from one sheet to another, the restricted current passage increases the electrical resistance, as shown in Figure 11. In this manner, then, resistance heat causes melting at the faying surface and forms the weld. Applying the electrode force or chemical pickling, which increases contact area, therefore, reduces contact resistance.

The contact resistance is normally not very consistent from point-to-point on the same surface. In order to obtain reproducibility in weld quality, low contact resistance is required. For titanium welding, the surface condition is critical, not only because of the desire to maintain consistency of weld strength, but also because of the nugget embrittlement caused by solution of surface oxides.

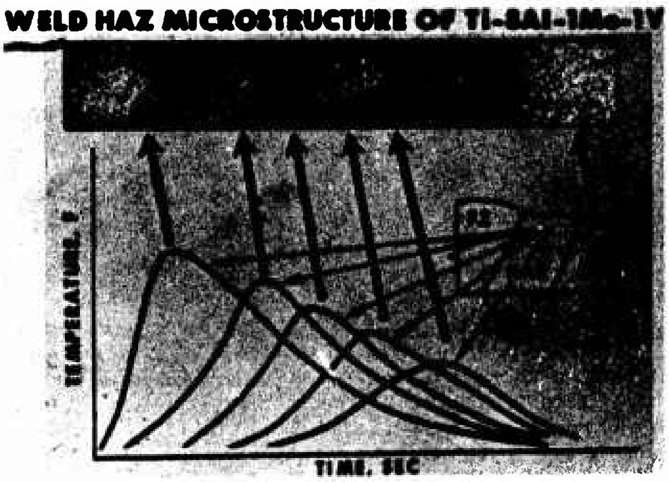


FIGURE 10

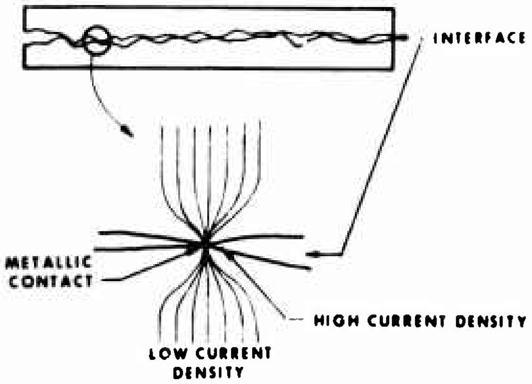


FIGURE 11. POINT CONTACT IN A METAL-METAL CONTACT SURFACE

Surface Treatment

The contact resistance can be reduced either mechanically or chemically. Brushing with a stainless-steel wire brush can produce an acceptable surface condition (about 100 microhms). However, for a large surface area, chemical cleaning is most efficient. A commonly used pickling solution for titanium alloys contains 30% HNO_3 (70 percent concentration), 3% HF (49 percent concentration, and 67% water.

The effect of pickling time on contact resistance for Ti-8Al-1Mo-1V is shown in Figure 12. For practical reasons, a one-minute pickling time was used in the Titanium Producibility Program.(2) The strength of the pickling solution decreases with use. Therefore, the pickling time should be increased as the solution strength decreases in order to obtain the required contact resistance over a period of time of solution use. The efficiency of the pickling solution can be restored by adding an adequate amount of HF.

Since titanium has high affinity for oxygen, the contact resistance increases with increase in storage time after pickling. This effect is shown in Figure 13. It is recommended, therefore, that welding be conducted immediately after pickling to obtain consistently reproducible welds and to avoid the necessity for recleaning.

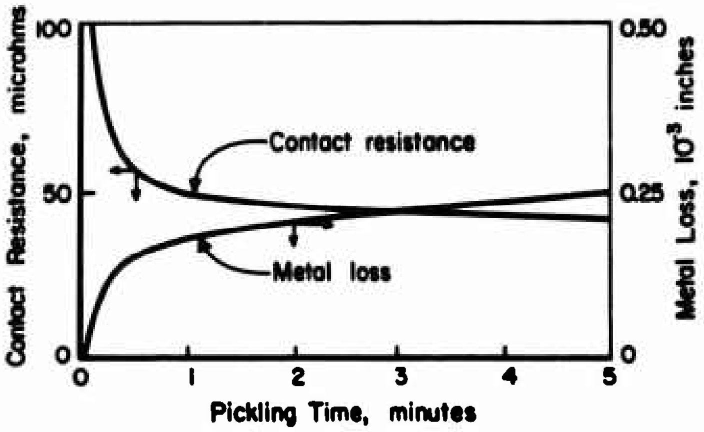


FIGURE 12. EFFECT OF PICKLING TIME ON CONTACT RESISTANCE AND METAL LOSS (Ti-8Al-1Mo-1V)

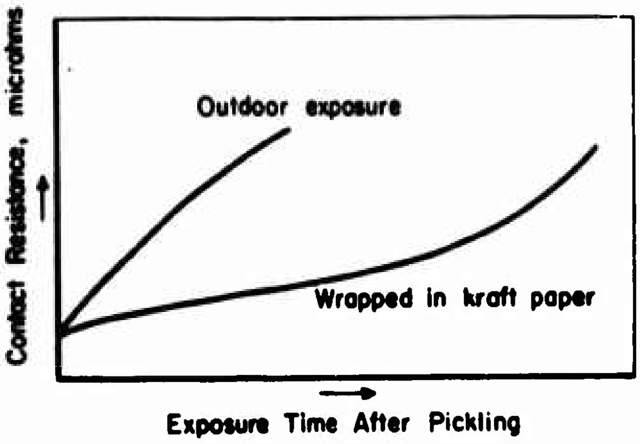


FIGURE 13. EFFECT OF EXPOSURE TIME AND ENVIRONMENT ON CONTACT RESISTANCE OF TITANIUM SHEET

Electrode Geometry

Electrodes serve three functions: (1) they maintain proper position of the workpieces; (2) they conduct the welding current; and (3) they conduct heat away from the workpieces. They are made of copper alloys or tungsten-copper composites. The high-alloy copper or tungsten-copper composite electrodes have high wear resistance and low thermal and electrical conductivity. On the other hand, the low-alloy copper electrodes wear easily and give high thermal and electrical conductivity. Wear resistance of the electrode and heat balance in the weld are the basis for selecting electrode materials for a particular welding application.

The electrode geometry influences the nugget size and electrode indentation. A domed electrode tip is recommended since the spherical shape minimizes the alighment problem and concentrates the welding current. The spherical radius of the dome controls the electrode indentation and limits the size of the nugget. In order to obtain a "plug" failure (that is, failure around the nugget rather than through it in tension-shear and normal tension tests), the diameter of the nugget should be at least four times the sheet thickness. This is found from the relationship obtained by equating

πDt (circumferential area of the nugget =

$\frac{\pi D^2}{4}$ (surface area of the nugget).

Then $D = 4t$

D is the minimum diameter of the nugget, in inches

t is sheet thickness, in inches.

The radius of the domed tip is determined by the permissible indentation when the electrode tip diameter produces an optimum size of weld nugget.

Electrode Force

Electrode force is employed to make intimate contact between the weld sheets by breaking up the oxide film and causing plastic deformation at contact points in the faying surface. As a general rule, the required electrode force is proportional to the strength and thickness of material to be welded and inversely proportional to the welding time. A properly selected electrode force produces minimum amount of indentation and sheet separation and wide optimum welding current range. High electrode force causes excessive distortion, indentation, and sheet separation. Low electrode force causes early interface expulsion and pitting between the electrode and workpiece. The proper electrode force is then selected based on other welding parameters and requirements.

Welding Time

In resistance welding, welding time is measured in cycles, defined to be one-sixtieth of a second. The initial fusion is obtained within the first half-cycle as stated by Kouwenhoyen and Little.(5) During this half cycle, contact resistance decreases to a minimum value. As welding current continuously flows through the specimen, the nugget propagates and the temperature of the specimen increases. The resistance in the specimen raises slightly due to increase in temperature. Welding time also increases with increase in sheet thickness. Short welding times give less heat dissipation and, therefore, higher thermal efficiency. This is particulary true when a high conductivity material is welded, such as aluminum. However, a short welding time does not necessarily indicate an optimum welding schedule. Since it requires a certain amount of heat to make a weld, the shorter the welding time used, the higher the welding current needed. In order to keep the molten metal from expelling when using a high welding current, a high electrode force is required. However, it has previously been shown that a high electrode force tends to increase distortion. An optimum set of welding parameters is obtained by using the appropriate electrode force, welding time, and a wide range of welding currents that do not noticeably affect joint strength.

WELDING METALLURGY OF TITANIUM ALLOYS

The welding process produces a fusion zone and a heat-affected zone. The fusion zone is a result of melting under the arc and is a continuous arc casting process with the base metal acting as a "mold". The portion of the "mold" adjacent to the fusion zone which is exposed to the welding thermal cycle and is "heated treated" in a relatively short time is defined as the heat-affected zone. The maximum or peak "heat treatment" temperatures in this zone vary exponentially with the distance from the fusion line. The microstructure in the fusion zone is dependent upon the mechanics of solidification and the influence of thermal cycles. The microstructure in the heat-affected zone results from the initial microstructure and weld thermal cycle.

The metallurgy of the following titanium alloys will be discussed: Ti-5Al-2.5Sn, Ti-8Al-1Mo-1V, Ti-6Al-6V-2Sn, Ti-6Al-4V, and Ti-13V-11Cr-3Al.

Weld-Fusion Zone

A pure metal solidifies entirely at one temperature. In an alloy, solidification occurs over a range of temperatures. These phenomena can be illustrated by using a binary eutectic phase diagram as shown in Figure 14.

If metal A contains none of metal B, metal A solidifies entirely at T_1. An A-base alloy containing X% of B begins to solidify at T_2 on cooling. At this

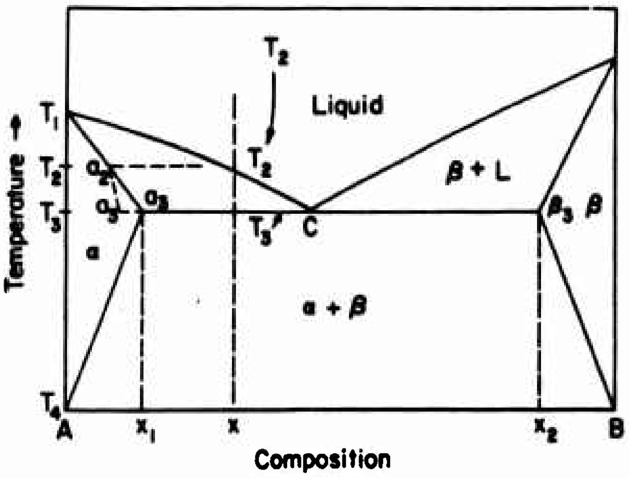


FIGURE 14. TYPICAL BINARY EUTECTIC PHASE DIAGRAM OF ELEMENTS A AND B

instance, solid phase α containing a_2% of B precipitates from the liquid. As the alloy cools slowly to T_3, the composition of the α-phase adjusts by diffusion from a_2 to a_3. At the same time, the composition of the liquid changes along the liquidus to C at T_3. At this temperature, T_3, the remaining liquid solidifies and contains the α and β phases. The composition of the α and β phases are X_1 and X_2, respectively. If the cooling rate is rapid, diffusion in the solid α-phase will not be extensive enough to allow the composition of the α-phase to reach a_3; rather, the composition a'_3 will be obtained. The faster the cooling rate, the greater is the deviation in composition from equilibrium conditions.

The cooling rates inherent to a welding process are, in fact, far from equilibrium conditions. This is one of the reasons why segregation is always more severe in the weld-fusion zone than in a normalized material. Since the number of components in a commercial titanium alloy is more than two, it solidifies in a more complex fashion than the example cited above. Fortunately, in titanium alloys, the solid solubility of major alloying elements, such as aluminum and vanadium, is fairly high. Therefore, severe segregation in the fusion zone of titanium alloys is seldom experienced.

Solidification in the fusion zone is due to the loss of heat by conduction through the cold base metal. The direction of crystal growth during solidification in the fusion zone is opposite to the direction of heat dissipation. The solidification front coincides with the isotherm of the solid liquid interface (isotherms shown previously in Figures 8 and 9). Crystal growth in the fusion zone is three dimensional; i.e., from the surrounding base metal toward the centerline of the fused metal and in the direction of the moving arc. The morphology (physical appearance) of the growing crystal is controlled by the degree of constitutional supercooling, temperature gradient, and rate of growth. Within the fusion zone produced by the arc welding process, a columnar structure is usually found growing in from the heat-affected zone to the center of the fusion zone. In the fusion zone of a resistance spot weld a similar columnar structure is found, but, in some materials, equiaxed grains can be found at the center of the fused metal. However, equiaxed grains are not found in titanium-alloy spot welds.

Formation of the equiaxed grains is due to the high concentration of rejected alloying elements being pushed ahead of the growing grains. The high concentration of solute, along with the proper temperature gradient, causes a high degree of constitutional supercooling which, in turn, increases the rate of nucleation of the solid. The high rate of nucleation creates numerous nucleation sites, thereby forming smaller, equiaxed grains.

Large, elongated grains in a fusion zone are undesirable because of the increased concentration of grain boundary impurities and, possibly, directional properties. Attempts to refine these large grains through mechanical vibration and magnetic stirring have been used in the welding of titanium alloys. It was found that grain refinement by magnetic stirring improved strength and ductility in the fusion zone of Ti-13V-11Cr-3Al welded in the aged condition.(6)

Numerous theories have been postulated for the solidifcation mechanisms of pure metals. However, these theories have not been extensively applied toward improving the microstructure and mechanical properties in the fusion zone of the titanium alloys.

Weld Heat-Affected Zone

As mentioned above, the heat-affected zone is a result of a short-time heat treatment caused by the welding heat conducted from the fusion zone. The duration of this "heat treatment" is rather short, when compared to a nominal heat treatment, ranging from seconds (resistance welding processes) to minutes (arc-welding processes). The peak temperature of the welding thermal cycle in this zone decreases exponentially with the increase in distance from the fusion line. The heating and cooling rates increase with increasing peak temperature and, in turn, decrease with increase in distance from the fusion line. As a result, the final microstructure varies from the fusion line to the unaffected base metal due to the different time-temperature effects of the thermal cycle. Since mechanical properties are structure sensitive, the mechanical properties in the heat-affected zone change gradually from the fusion line to the unaffected base metal. A photomicrograph of the weld heat-affected zone of Ti-8Al-1Mo-1V and the typical welding thermal cycles experienced in the various areas in this zone have been shown in Figure 5.

TITANIUM WELDMENTS

Most of the titanium alloys have been welded by using the TIG and resistance spot welding processes. The MIG process has been used for welding plate, one inch or thicker.(7) The submerged arc welding process is seldom, if ever, used in the United States, but its use is not uncommon in Russia.(8)

Lewis, et al, studied the effect of vanadium, manganese, and aluminum additions in iodide and sponge titanium on the mechanical properties of weldments produced with the manual TIG welding process.(9) It was concluded that the addition of alloying elements improved the strength but decreased notch toughness and bend ductility in welds of these alloys. The notch toughness and bend ductility were lower in sponge titanium welds than iodide titanium welds due to the higher oxygen and carbon content of the former.

Fusion welding of Ti-5Al-2.5Sn does not present mechanical property problems, since the ductility in this alloy is excellent. The resistance spot welding schedules for Ti-5Al-2.5Sn of 0.062-inch-thick sheet was established.(10) The tension-shear and normal-tension strengths under the optimized welding conditions were 5750 and 1250 lbs, respectively. The ductility ratio was 0.21.

Welding development of Ti-8Al-1Mo-1V has been conducted extensively throughout the aerospace industry and Government agencies. In the TIG process, filler wire of similar composition was normally used for this alloy. The notch-tension strength (K_t = 7.5) in the fusion zone of 0.060-inch sheet with matching filler wire was superior to that in the base metal (157.7 versus 155.9 ksi).(11) By using Ti-75A filler wire for welding of 0.060 inch sheet, the room temperature subsize V-notch impact strength was increased from 1300 in.-lb per square inch for matching filler wire to 1900 in.-lb per square inch for the Ti-75A wire. The heterogeneous welding technique not only improved notch toughness in 0.060-inch TIG weldments, but also extended the fatigue life in spot welds. When Ti-75A was added to the spot-weld nugget by placing a 0.003 inch foil in the joint, the fatigue life in the single- and three-spot specimens was at least doubled.

The spot-weld strengths in 0.060-inch sheet were 4550 lbs for tension-shear and 1010 lbs for normal-tension when tested at room temperature. The tension-shear and normal-tension strengths were increased about 10 percent by using Ti-75A intermediate foil.

Wu and Krinke(12) also conducted residual stress measurements in Ti-8Al-1Mo-1V spot welds, the effect of the welding schedule and spot spacing on the residual stress and the effect of residual stress on fatigue life. The results indicated that decreasing the spot spacing from 1.5 to 0.5 inch increased residual stress and reduced fatigue life.

Stress-corrosion and thermal-stability tests were also conducted in that investigation. Alternate heating and salt-water spray did not cause cracking. The effects of salt-spray stress-corrosion tests and thermal exposure were a decrease in tension-shear strength for spot welds and an increase in tensile strength and decrease of elongation of TIG-welded specimens. Ordering was a result of both test environments for both types of specimens. Stress-corrosion cracking was found only in spot welds exposed in hot salt at 500 F for 1000 hours, as shown in Figure 15.

Spot welding schedules for Ti-8Al-1Mo-1V in other sheet thicknesses have been established.(13) It was reported that difficulties were not encountered in welding Ti-8Al-1Mo-1V. However, the ductility ratio (normal-tension strength/tension-shear strength) could not meet military specifications for thicknesses up to 0.062 inch. It was also indicated that spot-welded assemblies of the Ti-8Al-1Mo-1V alloy had the best short-time elevated-temperature properties.

TIG welding of the aforementioned alloys was conducted by Mitchell and Day.(14) Good creep resistance was found in welded Ti-8Al-1Mo-1V sheet. Notch-tension strength was higher than the unnotched tension strength in the weldment of all three alloys tested.

Weldability of Ti-6Al-4V is claimed to be good. However, cracking was found in 2-inch-thick weldments with matching filler wire.(15) By using preheat and an interpass temperature of 175 F, cracking was eliminated. When commercially pure titanium filler wire was used, no cracks were found even without preheat. One-inch-thick Ti-6Al-4V plate was reportedly welded by using the manual short-arc process, with matching filler wire and 75 percent helium and 25 percent argon shielding gas.(16) Manual TIG welding(17) was used to weld 0.025-inch-thick Ti-6Al-4V sheet for rocket-motor case with matching filler wire. Although the hydrostatic test standard was met, porosity could not be eliminated.

Daley and Hartbower(18) reported that a 100 percent tensile joint efficiency at an ultimate tensile strength of 150 ksi and 10 ft-lbs V-notch Charpy impact energy at -40 F could be obtained in an automatic TIG-welded Ti-6Al-4V welded fusion zone with matching filler wire.(19)

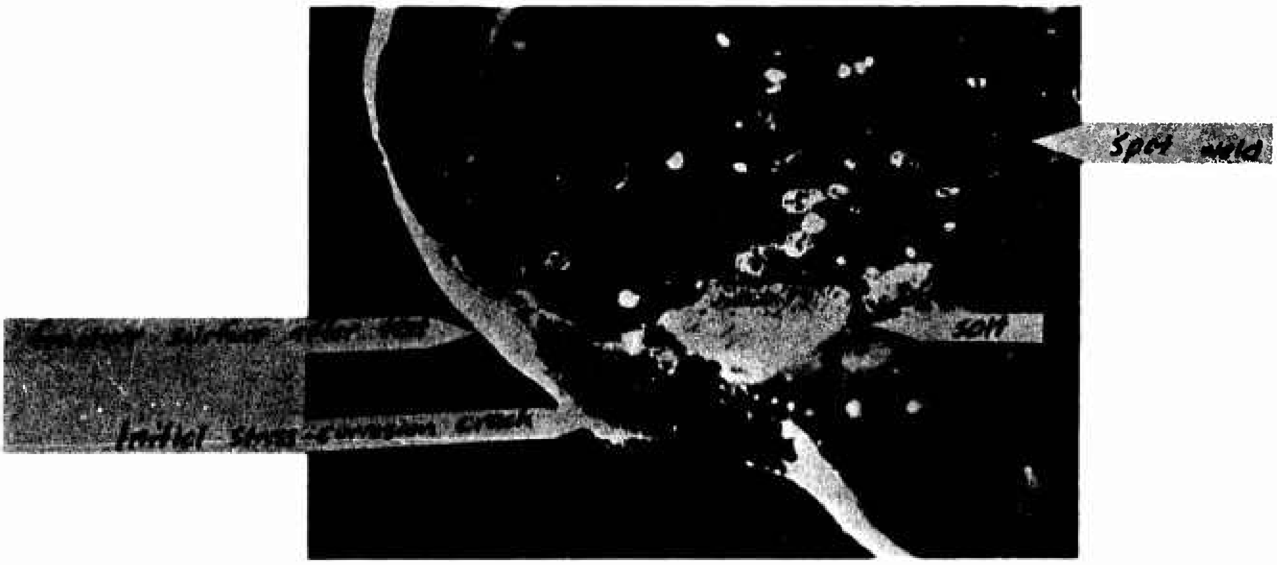


FIGURE 15. STRESS-CORROSION CRACKING IN Ti-8Al-1Mo-1V SPOT WELD EXPOSED IN HOT SALT AT 600 F FOR 1000 HOURS

The effect of interstitials on the mechanical properties of Ti-6Al-4V weldments was studied.(20) The results indicated that the properties of the base alloy were not impaired by oxygen contents of 0.20 percent on nitrogen contents of 0.10 percent. Hydrogen up to 150 parts per million did not appear to have a marked embrittling effect.

Resistance spot welding schedules for 0.035 to 0.093-inch-thick Ti-6Al-4V were established.(21,22) The resulting data were comparable to recommendations for similar gages of stainless steel. The in-machine post-weld heat treatment increased the ductility ratio and was considered to be a practical operation for quench-and-age type alloy.

The weldability of Ti-6Al-6V-2Sn is the lowest of all titanium alloys discussed. Fusion-zone cracking can be eliminated by using commercially pure titanium filler wire. However, ductility is gained only at the expense of the tensile strength. The real problem of welding this alloy is in the heat-affected zone. In addition to the remedial method discussed in the preceding section, improved joint design would help to eliminate heat-affected zone cracking.

A 100 percent joint efficiency and good ductility can be obtained in an annealed Ti-13V-11Cr-3Al weldment.(23) Since the strength in this alloy is developed by aging, the annealed Ti-13V-11Cr-3Al is not very attractive from the point of view of strength/weight ratio. Post-weld solution annealing lowered ductility due to precipitation, possibly alpha, in the grain boundaries. Aging after welding reduced tensile ductility considerably. It was concluded that various combinations of sequences of welding, aging, cold work, flash anneal, and magnetic stirring could improve the tensile ductility in the weld by a certain degree.

SUMMARY

Most of the titanium alloys can be welded with all welding processes without much difficulty. Since titanium alloys are relatively easily contaminated and embrittled by solution of interstitial elements, cleaning and shielding should be carefully employed.

Titanium alloys are used for either high-strength applications and/or high-temperature service. For high-strength applications, the joint efficiency cannot be used as the sole criterion for judging weld quality since the toughness is also of great importance. The fusion-zone properties can be improved by adding dissimilar filler metals and the heat-affected zone properties can be adjusted by knowing the continuous cooling transformation kinetics. Post-weld heat treatment could improve ductility, but in some cases, it presents practical problems. For high-temperature applications, microstructural stability is of primary importance. The heat input from the welding process has an accumulative effect on the thermal exposure which causes microstructural instability. In addition to this, residual stress distribution in a weldment, particularly in a thick member, should be evaluated because it may accelerate the reaction of stress-corrosion cracking.

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DIFFUSION BONDING AND BRAZING

R. R. Wells*

DIFFUSION BONDING

It has been stated that solid-state diffusion bondments are as strong as the base alloy. In reality, this strength is seldom realized in the fabrication of aerospace structures. Why? The answer lies in the knowledge that the joint strength is dependent upon the number of voids which remain after the bonding process. Let us look at some of the details of making these joints, then return to the above question.

Figure 1 illustrates the voids which are present at two "smooth" surfaces are brought into intimate contact. Note that the hills or surface asperities come in contact first. A light force deforms these hills to rapidly increase the surface contact area. However, the effect of successive incremental increases of force decreases as the total contact area increases (Figure 2). This results from the change in stress per unit area as the contact area increases per unit increase in force. Forces large enough to cause complete surface contact result in deformed base alloy (Figure 2).

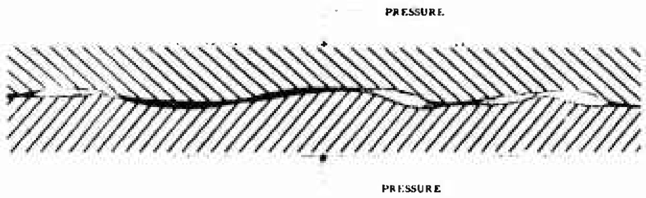

FIGURE 1

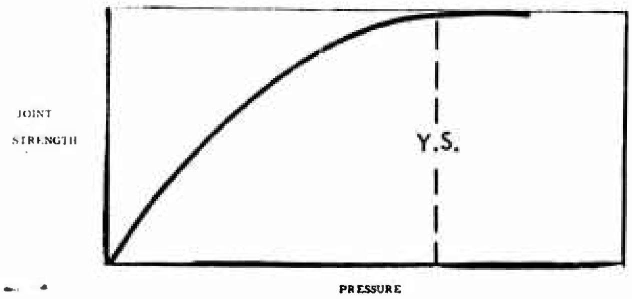

FIGURE 2

Temperature is used to aid atom interchange across the contact areas, and in the case of titanium, to dissolve the surface oxides at temperatures in excess of 1400 F. In addition, increases in temperature lower the yield strength of the base alloy, and if raised sufficiently, allow creep to occur in the base alloy. The latter two processes allow further surface deformation, thus increasing the total surface contact area. The approximate effect of temperature is shown in Figure 3.

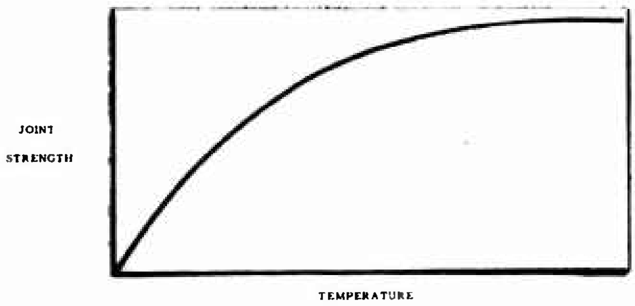

FIGURE 3

Increasing the diffusion bonding time results in additional creep deformation of the base alloys, and if an intermediate is used, additional atom interchange between alloys (Figure 4). Now, let us return to the question of why many solid-state diffusion-bonded joints are not perfect. Roll bondment products may have perfect bonds due to the large pressures used resulting in deformation of the entire structure. However, in fabricating aerospace structures such as honeycomb joints, deformation cannot be tolerated. As high pressures cannot be utilized, there is a tendency to either creep the parts together with small deformations or settle for voids, thus accepting a poorer joint. Frequently, a near perfect, that is voidless joint, can be achieved by recrystallizing the base alloy (Figure 5). Unfortunately, while this joint has base-alloy strength, it is usually undesirable to recrystallize the titanium-base alloy. For example, in the case of alpha-beta titanium alloys, recrystallization results in a loss of fracture toughness. Thus, in either of the above cases, the joint does not have the desired combination of strength, ductility, etc.

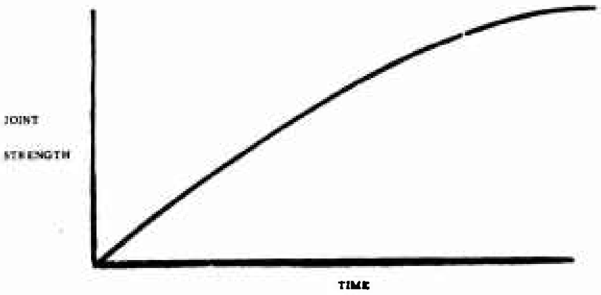

FIGURE 4

FIGURE 5

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For the above reasons, most investigators have used intermediate materials for forming solid-state diffusion bondments. A good intermediate must deform to fill all voids and be compatible with the base alloy. As the service conditions may dictate high temperatures, high stresses, and long exposure times, then the intermediate joint must be creep resistant. This poses a diffusion problem, since the intermediate must exhibit a low yield strength to affect a sound joint and later the intermediate is required to exhibit a high yield strength in order to produce a joint having a high lap-shear strength. With titanium alloys, the compatibility factor is also quite important due to corrosion and stability problems.

The best solid-state diffusion bonding intermediate for titanium alloys which has been investigated at Northrop is pure titanium. At the bonding temperature of 1700 to 1800 F, the pure titanium is softer than the base alloy; therefore, it deforms and fills the voids without deforming the base alloy. Diffusion cycles can then render a composition change to produce a satisfactory joint. However, base-alloy properties are not developed by this joining technique.

Practical limitations applicable to solid-state diffusion bonding of foil-gage titanium sandwich panels are:

(1) Close tolerance machining of core

(2) Close fit up required of all component parts

(3) Low creep strength resulting in crushed core if careful control not exercised

(4) Requirement of long time at temperature to achieve joints, thus adding to costs.

A technique for forming corrugated-type sandwich panels with excellent bonds has been developed and patented by Battelle Memorial Institute. This process involves placing steel shapes in what is to be the open area of the final titanium panel (Figure 6). After hot rolling in a rolling mill, the steel is etched away leaving the open corrugated structure. The advantages are:

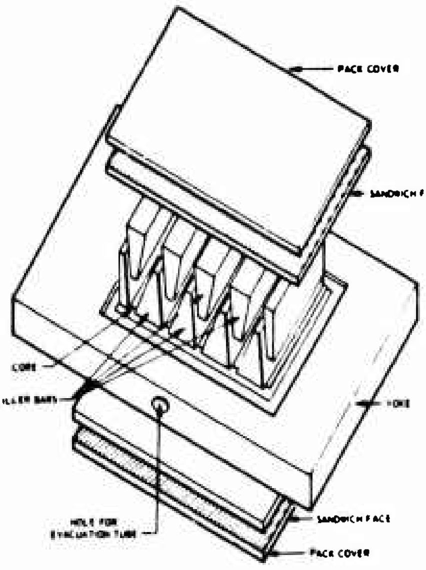
(1) Capability of making certain types of sandwich panel materials

(2) High-integrity joints.

Disadvantages are:

(1) Cost of etching the steel away

(2) The process is limited to shapes in which the acid may reach the steel in order to remove it.

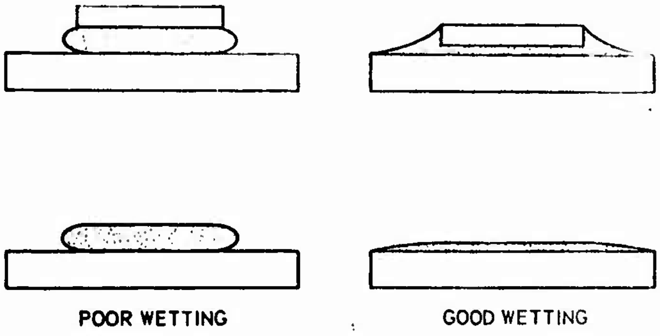


Exploded View of Roll-Welded Pack Ready for Hot Rolling

FIGURE 6.

CONVENTIONAL BRAZING OF TITANIUM

The conventional process of brazing involves the use of an alloy with a melting point below that of the material being brazed. The liquid braze alloy must "wet" the material and flow along the capillary joints. Wetting is illustrated in Figure 7. On the left is a liquid which tends to ball rather than wet the material as shown on the right. This is similar to water on a waxed car.



CONVENTIONAL BRAZING

FIGURE 7

Once a braze alloy has been found which melts, wets, and flows satisfactorily, mechanical and physical-property data may be generated.

Investigators have been searching for good brazing alloys for titanium alloys for approximately 15 years. Despite articles such as "It is Easy to Braze Titanium"[a] which appeared in 1953, the search for braze alloys continues today.

The best braze alloy developed to date for titanium is based on the silver-5 aluminum composition. This alloy flows on titanium at 1790 F. Advantages of this alloy are that it is available in foil form and works satisfactorily for many applications. Disadvantages are its high cost, weight, and lack of salt stress-corrosion resistance.

THIN-FILM DIFFUSION BRAZING OF TITANIUM

A process for thin-film diffusion brazing of titanium alloys has been developed at Norair. This process depends upon the formation of small quantities of liquid which behave as a braze alloy. Subsequent diffusion then drastically alters the alloy composition, resulting in a metallurgical compatible titanium joint. The process is a combination of diffusion bonding and conventional brazing. The general details of this process may be illustrated by viewing a simple eutectic phase diagram

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(a) Meridith, H. L., "It is Easy to Braze Titanium", American Machinist, 97 (March, 1953).

(Figure 8). Initially, a thin layer of Element B is deposited on the titanium surfaces to be joined. Titanium component parts are assembled, light pressure is applied, and they are placed in an inert or neutral atmosphere to protect the titanium. The parts are then heated above the eutectic temperature.

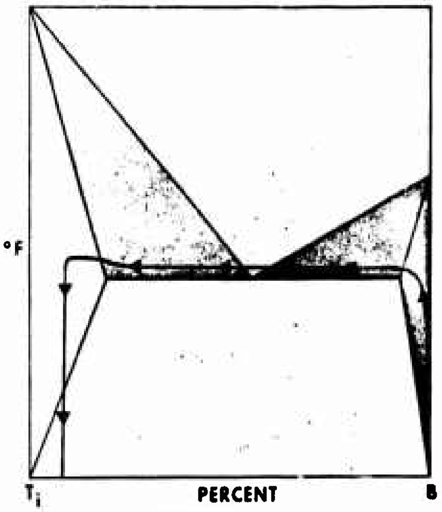

FIGURE 8

As seen on the phase diagram, the Element B and the titanium interdiffuse prior to the eutectic temperature to form a solid-solution alloy of titanium and Element B. This occurs due to the chemical gradient present. After sufficient solid diffusion occurs, eutectic composition, liquid, metal is formed. This liquid wets and flows much as a braze alloy, thus forming a liquid interface between the titanium components. Since the chemical gradient still exists, diffusion between the Ti-B eutectic alloy and titanium continues. Eventually, solidification occurs. With additional holding time, solid-state diffusion continues. This process requires that the components be diffusion treated until the desired final composition is reached in the joint.

The above treatment has now generated a B-containing, beta-phase titanium joint. Controlled cooling transforms this B-containing beta titanium to alpha-phase titanium and compounds (Figure 9).

FIGURE 9

Advantages of this process are low-cost braze material, light weight, extremely high strength, thermal stability, and stress-corrosion resistance. Disadvantages are the close fit-up requirements and control of the intermediate content needed.

COMPARISON OF JOINING SYSTEMS

One difference between these three joining systems becomes apparent when it is desired to form "Tee" joints such as honeycomb core to face sheets (Figure 10). Note the large fillet associated with conventional brazing and the complete lack of fillets with diffusion bonding. The fillet size is a significant factor in these joining systems inasmuch as low-strength joining material requires a large fillet to produce a strong joint. While large fillets aid in distributing stress, especially with regard to fatigue, they also add considerable weight to the structure (Figure 11). From the fabrication viewpoint, the smaller the fillet size the tighter must be the fit up.

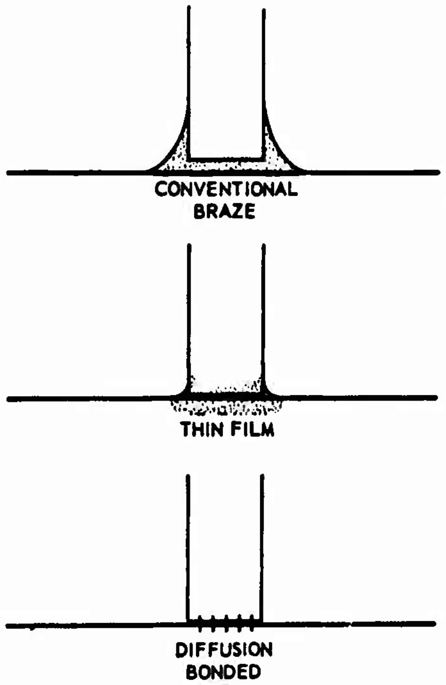

FIGURE 10

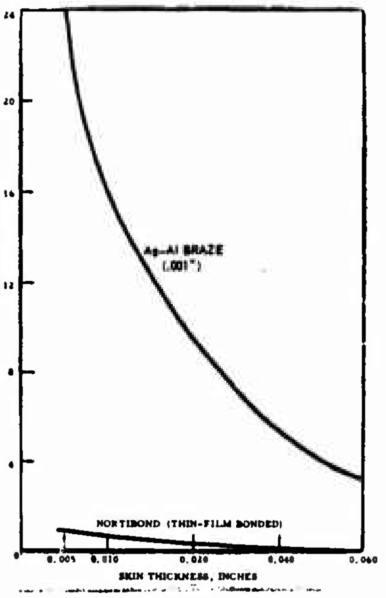

FIGURE 11

Another comparison among the three systems is lap strength as a function of temperature (Figure 12). These curves show the relative strength levels for the three methods of bonding titanium. Note the Ag-Al braze alloy is not as strong as the thin-film bond. However, this strength difference may be overcome by utilizing larger fillets or overlaps.

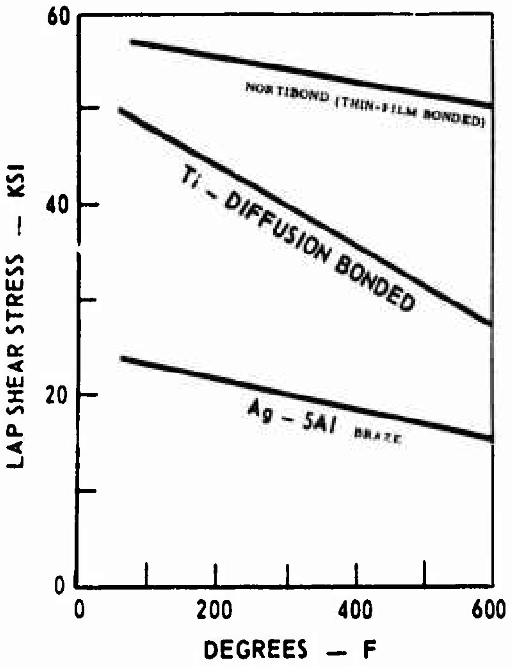

FIGURE 12

Comparison of the resistance to stress corrosion is yet another indicator of the relative merits of these systems. These tests were performed by stressing the specimens in NaCl at 600 F. Each type of joint was loaded to 33 percent of the yield strength at 600 F. The Ag-Al brazed specimens failed after only 168 hours in the hot salt. Microstructure studies showed general corrosion surrounding all of the braze areas. Specimens which did not fail were then tested at room temperature. Figure 13 shows the decrease in lap-shear strength due to the effects of stress corrosion.

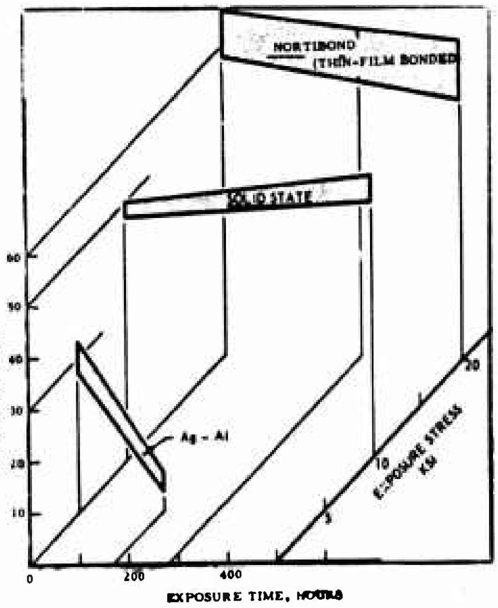

FIGURE 13

Neither the solid-state diffusion-bonded nor the thin-film-bonded specimens failed after 500 hours' exposure. These specimens were then tested in lap-shear. The test results indicated slight changes in the joint strength. Normal scatter probably accounts for the differences in strength.

The advantage of the thin-film bonding process for fabrication of titanium honeycomb should be fairly obvious. Therefore, let us take a closer look at the properties and advantages of this joining method.

Two types of tests were performed in order to establish the applicability of this joining system to titanium honeycomb. The first test was used to establish thermal stability of thin-film bonds with regard to long-time service-temperature exposures. After preliminary tests indicated that the system was relatively stable at 1000 F, it was decided to conduct further tests at 1000 F. Therefore, a series of lap-shear specimens were prepared, sealed in argon, and exposed at 1000 F for times of 100 and 1000 hours. Figure 14 shows the small decrease in strength as a result of these exposures.

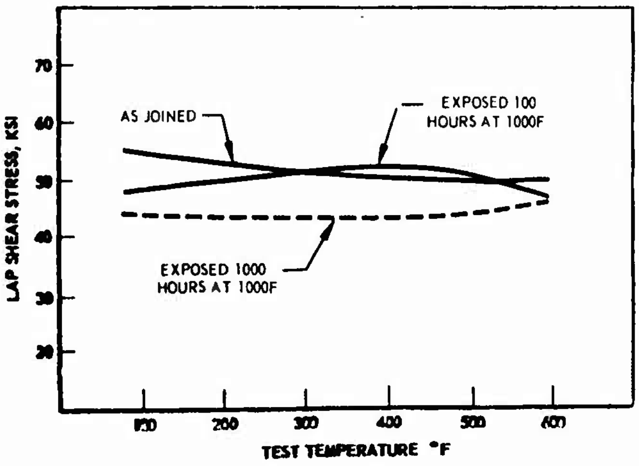

FIGURE 14

Secondly, assurance was needed that the thin film did not degrade the titanium sheet with respect to fracture toughness. Once again, preliminary tests were conducted before the fracture-toughness evaluations were made. A series of bend specimens were tested at temperatures of -320, -165, and 75 F. These specimens were loaded with the thin-film-coated surface in tension. While the bend angle was less than that of Ti-8Al-1Mo-1V, the results indicated that the material did possess ductility of the same order as TIG weldments. Finally, sheet Ti-8Al-1Mo-1V alloy was thin-film processed and tested in notched and unnotched tension. These results (Table 1) show that the thin-film-coated sheet exhibited notch toughness approaching that of duplex-annealed Ti-8Al-1Mo-1V. In fact, had it been possible to cool the test specimens faster, the toughness values might have been equal.

Salt stress-corrosion susceptibility of this joining system has been evaluated at 600 F. These tests have indicated that the salt stress-corrosion properties are slightly better than the Ti-8Al-1Mo-1V duplex-annealed alloy.

TABLE 1

	NOTCHED UNNOTCHED YIELD	NOTCHED UNNOTCHED ULTIMATE
0.020 INCH DUPLEX ANNEALED Ti-8-1-1	1.1	--
0.010 INCH NORTIBOND Ti-8-1-1	1.05	0.93
0.020 INCH MILL ANNEALED Ti-8-1-1	0.85	--

THIN-FILM-BONDED HONEYCOMB PANELS

There are several tests which can be conducted in order to determine honeycomb panel properties. A few of these tests are described below, along with a description of the test panels.

A. Panel Configuration

Ti-8Al-1Mo-1V face sheets, 0.010 inch thick
Ti-75A titanium core, 3/16-inch cell x 0.0015-inch foil x 1/2-inch thick

Density: Theoretical component density plus 0.00352 lbs/ft^2 of panel or 1.6 g/ft^2 of panel

B. Core Shear Test

Performed as plate shear test at room temperature
Value 354 psi
Failure by core shear

C. Beam Flexure Test

Test beam simply supported on 8-inch span loaded with 2-point ram.

Test Temp, F	Core Shear, psi	Face Sheet Stress, psi
RT	300	89,900
450	166	49,800

Failure by core shear

D. Peel Test

Vertical peel conducted at room temperature
Load 29 in.lb/3 in. width
Failure in core

E. Acoustic Fatigue

Tested 6 in. x 9 in. x 1/2-in. panel at:
1-1/2 hr at 170 DB
16-1/3 hr at 173 DB
100 hr at 176 DB
No failure

Note: No failures occurred in the joints during any of the above tests.

The most extensive honeycomb testing was performed by compressively loading the core (flatwise compression) or the face sheets (edgewise compression). These results are shown as a function of temperature in Figure 15. Edgewise compression specimens tested below room temperature failed due to core failure near the yield strength of the face sheets indicating an optimum design. However, as the test temperature was increased to room temperature, the failures occurred below the yield strength of the face sheets by face-sheet buckling into the core.

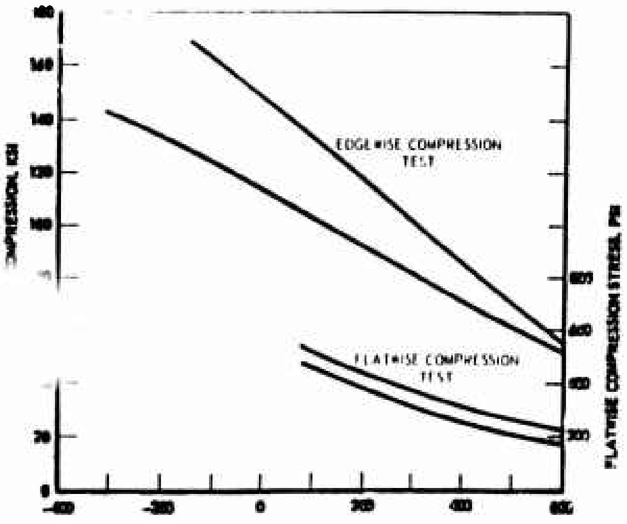

FIGURE 15

Based upon the above data, comparisons of several types of panels were made. Figure 16 shows a strength-to-density plot comparing thin-film-bonded titanium, adhesively bonded aluminum, and brazed steel panels between 75 and 600 F. Thin face sheets were used as this is the realm of maximum usefulness for the thin-film-bonding system.

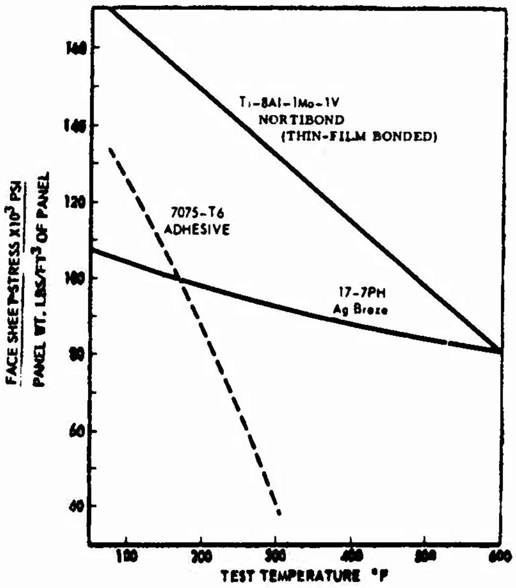

FIGURE 16

SUMMARY

Three methods of joining titanium sandwich panels have been described here:

(1) Solid-state diffusion bonding
(2) Brazing
(3) Thin-film diffusion brazing.

Of these, the authors believe that the thin-film diffusion-brazing process appears to be the most applicable to the fabrication of titanium honeycomb panels. Furthermore, comparisons of thin-gage titanium panels with aluminum show that by proper application, thin-film-bonded titanium panels could be used to reduce the weight of an airframe by replacing aluminum components.

ADHESIVE BONDING OF TITANIUM

S. R. Breshears*

INTRODUCTION

Adhesive bonding of load-carrying structures has been in common use in the United States since 1946, and has been proven as an effective and efficient means of joining two metal surfaces to form a strong structural bond. Examples of advantages of adhesive bonding in aerospace applications are discussed in the following sections.

Adhesive bonding of metal-to-metal laminates or stiffeners or splice plates in shear webs permits increased tension field allowable stress, compared to a riveted stiffener design since effective skin and web panel width is reduced.(1) By this method, wrinkles in the skin or web panel will progress only to the edges of the stiffener flanges rather than to the riveted lines in the stiffener flanges. Within limits, the full tensile strength of primary tension skins can be developed with bonded splices because reduction in cross-section area does not occur as in rivet and bolt holes. Bonding of splice plates and doublers results in a reduction of weight since the loads are transmitted as shear stresses.

The ability to fabricate structural components from sandwich composites also offers important competition to integral machining and chemical milling of slabs. The adhesive-bonded honeycomb-sandwich construction offers high panel stiffness-to-weight ratio and at a cost approximately ten times lower than the cost of comparative brazed panels. With proper selection of skin thickness and core cell size, the allowable buckling stress of the sandwich panel can be made equal to, or slightly greater than, the compressive yield stress of the facing material. The primary buckling strength of a sandwich panel is higher than that of an equivalent-weight stringer-skin panel because the compressive stress is carried by the entire skin rather than by the stiffener in a locally unbuckled skin.

Adhesive bonding of sandwich constructions can greatly increase fatigue life by providing (1) a more even stress distribution in the structure, (2) better local support for the skins, and (3) because of the visco-elastic nature of the adhesive, reduce the amplitude of the exciting forces at the interfaces between the more rigid metals.

The use of adhesives in aircraft can improve the aerodynamic characteristics of the flight vehicle as follows:

(1) Bonded sandwich provides excellent support for sheet skins, resulting in smooth surfaces and reduced waviness

(2) Bonding permits increased stiffness and improved definition of trailing edges

(3) In semimonocoque construction, bonded stiffeners make possible smoother and truer contours free from local deformations and wrinkles

(4) In lightly loaded components, bonding permits light designs with less deflection.

Fundamentally, adhesive bonding permits the assembly of complex parts and structures from relatively small numbers of simple-to-produce details. With properly designed fixtures and with versatile equipment such as autoclaves, presses, and control ovens, large assemblies can be fabricated with fewer operations. Cost figures available from large production users of adhesives show approximately 40 percent savings in manhours per square foot of adhesive-bonded structures as compared to conventional attachments.(2) Probably the largest manufacturing economy from use of adhesive bonding is the ability to control and produce a small or large quantity of bonded parts in the same basic equipment.

The major advantages of using adhesive bonding in aircraft are summarized below:

(1) Large weight savings for equal stiffness

(2) Increased damping characteristics, resulting in increased fatigue life

(3) Ability to seal off liquids, gases, and pressurized compartments

(4) Improved aerodynamic characteristics through smoothness of exterior surfaces, i.e., rivets are eliminated and surface waviness is reduced

(5) Low material and manufacturing costs

(6) High contact area for attachment and load transmittal

(7) Excellent thermal insulative properties

(8) Improved acoustical resistance and reduction of noise levels within vehicle

(9) Adaptability to form complex composite structures

(10) Greater resistance to corrosion attack.

ADHESIVE BONDING OF TITANIUM - THE GENERAL CASE

Advanced design studies of Mach 3 supersonic aircraft indicate that wing and fuselage surface temperatures will range from 600 F at the leading edges to about 450 F in other areas. The metal selected to meet these temperature regimes is titanium because of its high strength-to-weight ratio at elevated temperatures. To adhesively bond titanium subjected to these temperatures, an adhesive capable of withstanding temperatures of 600 F for 1000 hours and 450 F for much longer time periods, say 30,000 hours, is required.

The state of the art in adhesive bonding consists of aluminum bonded with adhesives which are subjected to a maximum of about 250 F for long periods of time. With the advent of the Mach 3

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aircraft, new technology must be developed to bond titanium metals with newly developed high-temperature adhesives. The technologies to be developed include:

(1) Titanium surface treatments

(2) High-temperature adhesive development

(3) Application and bonding of high-temperature adhesives

(4) Testing of adhesively bonded structures at elevated temperatures.

Titanium Surface Treatments

Titanium can be readily cleaned and etched preparatory to bonding by solvent cleaning and hydrofluoric acid-nitric acid etching. However, the clean titanium surface oxidizes very rapidly even after an adhesive or adhesive primer has been applied to the surface, dried, and/or cured. The resulting oxide film acts as a release agent, thereby causing complete adhesive failure. To prevent this rapid oxidation, a conversion coating or other protective coating must be applied to the titanium surface. The coating must prevent oxidation, must be hard, must be stable in all environments, and must adhere tenaciously to the titanium metal.

Numerous conversion coatings are available that will protect titanium metal from further oxidation and present a surface suitable for bonding. The best conversion coating evaluated in this laboratory consists of a phosphate-fluoride treatment. A chromic acid-fluoride coating rates as a close second.

In addition to the conversion coatings, a controlled oxide surface presents an excellent surface for bonding. The oxides of titanium are numerous and range in color from a white to straw color, gold, green, various shades of blue to purple, and finally black. These oxides can be formed by (1) heat, (2) anodic treatments, and (3) chemical treatments. The oxides formed by heat have not given good adhesive bonds, whereas those from certain anodic and chemical treatments have been very successful. The best chemically formed oxide is the black oxide via a proprietary chemical treatment. This treatment can provide a complete spectrum of oxide colors, but only the black oxide gives satisfactory bonds. Lap-shear strengths 50 percent higher than those attainable by the phosphate-fluoride method have been obtained.

Adhesive Development

To be useful as a high-temperature structural adhesive, a material must have both chemical and phase stability. Chemical stability by definition includes (1) resistance to thermal and oxidation degradation, (2) no chemical change within the material as a result of chemical reaction with fillers, carriers, and by-products, or unreacted starting materials, and (3) inertness to metal surfaces. Phase stability is required to provide continuing strength at elevated temperature, since a phase change upon high-temperature exposure will show a generally undesirable variation in physical properties.

Decomposition of organic polymers serving as binding resins for adhesives at elevated temperatures is a complicated process consisting of (1) thermal degradation, (2) reaction of the polymers with the surrounding environment (atmosphere and adherent surface), and (3) reaction of the polymer with additives within the bulk adhesive structure.

Thermal Degradation Mechanisms

Thermal degradation is a rate process dependent upon the temperature. For degradation processes, the decomposition is assumed to be a first-order chemical reaction:

$$A \rightarrow B + C + D + \ldots \qquad (1)$$

The rate can be described by the expression:

$$-\frac{dC_A}{dt} = -kC_A \qquad (2)$$

where

C_A = concentration of Reactant A
t = time elapsed
k = degradation rate constant.

Separation of the variables and integration of Equation (2) becomes

$$\ln C_A = -kt + \text{constant} . \qquad (3)$$

By normalizing the concentration term, it is possible to convert Equation (3) to a form suitable for describing any degradation or loss phenomenon as a first-order model

$$\ln(1-R) = -kt + \text{constant} \qquad (4)$$

where

$(1-R)$ = fraction of tensile strength or weight remaining after time t

R = fraction of tensile strength or weight lost during time t

k = degradation rate constant

t = time elapsed.

Since thermal degradation is a rate process dependent upon the temperature, degradation rates can be correlated satisfactorily as a function of temperature by an expression of the Arrhenius type

$$\log_{10} k = \frac{-\Delta E}{RT} + \text{constant} \qquad (5)$$

where

k = first order rate constant for degradation
ΔE = activation energy
R = universal gas constant
T = temperature in degrees absolute.

Experimental data are correlated by plotting k versus $1/T$ (°R). When carried out on semi-log paper, the plot of log k versus $1/T$ is a straight line, which makes the plot additionally useful for extrapolating the degradation into data outside of the ranges for which experimental values have been obtained. By this method, it is convenient to obtain short-term aging data of adhesives at elevated temperatures, and then, by extrapolation, obtain the long-term aging life at lower temperatures. An example of this are the plots in Figure 1 of the aging data for 422J and Imidite 850 adhesives (data from Tables 1 and 2).

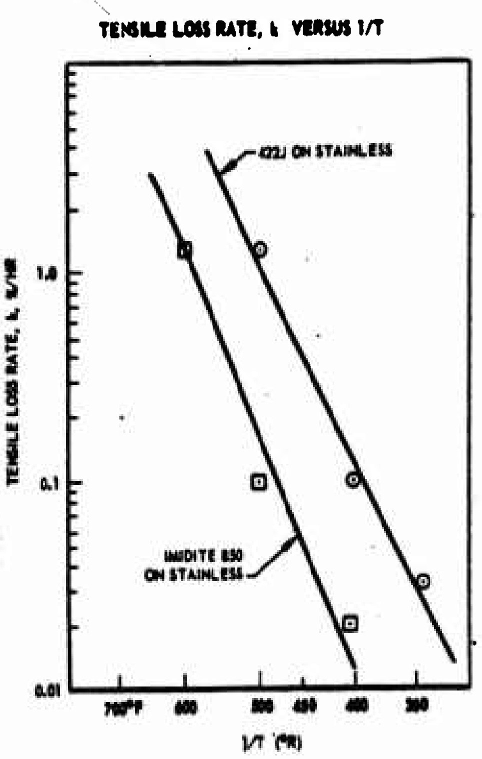

FIGURE 1

TABLE 1. AGING DATA - SHELL 422J ADHESIVE IN AIR, LAP-SHEAR SPECIMENS

Temp, F	Exposure, hrs	Tensile, psi	k %/hr	Reference
	On Aluminum			
250	0	2000	--	5
	4380 (6 mo)	1500	0.0064	
	8760 (12 mo)	1350	0.0045	
350	0	1700	--	5
	4380	400	0.0333	
	8760	200	0.0244	
400	0	1700	--	6
	200	1400	0.095	
500	0	1600	--	6
	200	600	0.490	
	On 17-7PH Stainless Steel			
350	0	1870	--	7
	1000	1302	0.036	
400	0	2200	--	6
	200	1800	0.100	
500	0	1900	--	6
	50	1000	1.280	

TABLE 2. AGING DATA - IMIDITE 850 IN AIR, PH15-7Mo STAINLESS STEEL LAP-SHEAR SPECIMENS

Temp, F	Exposure, hrs	Tensile, psi	k %/hr	Reference
350	0	2685	--	8
	2000	2930	--	
	4000	3367	--	
	5000	2910	0.0015	
400	0	2570	--	8
	500	3585	--	
	1000	2817	0.0486	
	4000	1825	0.0145	
500	0	2690	--	8
	240	2590	--	
	500	2650	--	
	1250	1480	0.078	
	1500	955	0.098	
600	0	2895	--	8
	65	1190	1.370	
	100	1293	--	
	150	396	1.320	
700	0	2405	--	8
	8	1580	5.250	
	16	1235	3.080	
	24	750	6.230	

Effect of Oxygen on Degradation

It has been reported that the major cause of strength losses of high-temperature adhesives in air is the air-oxidation of the organic material within the adhesive bond.(3,4) Data presented in these references for the aging of high-temperature adhesives on 17-7PH stainless steel under nitrogen and in air at 600 F are comparable with data generated for the aging of similar structural adhesives under 0.1 atmosphere absolute total pressure on PH15-7Mo stainless steel. These data are listed in Table 3 for AF31, Metlbond 311, and Imidite 850. A comparison of the tensile strengths versus aging time for Metlbond 311 and Imidite 850 and the degradation rates of Imidite 850 in air at 1.0 and 0.1 atmosphere are plotted in Figures 2 and 3, respectively.

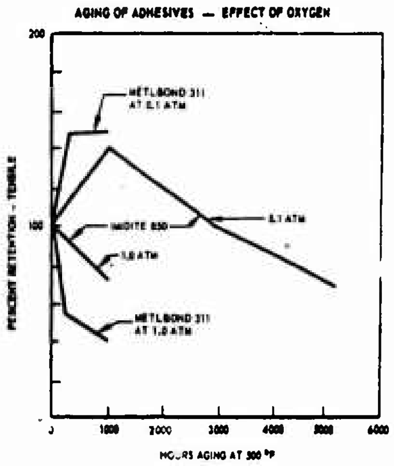

FIGURE 2

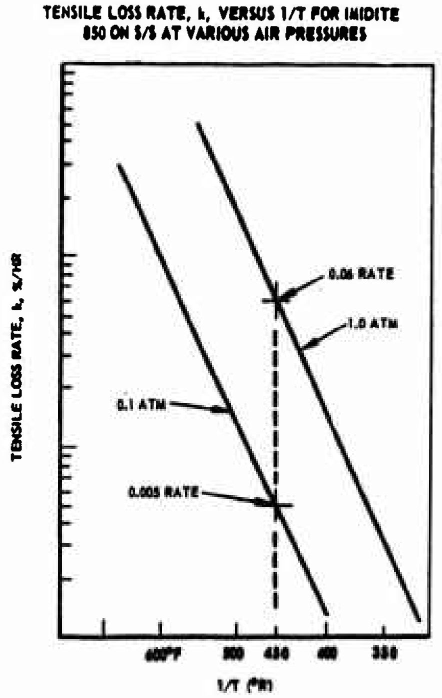

FIGURE 3

TABLE 3. LAP-SHEAR TENSILE DATA FOR HIGH-TEMPERATURES ADHESIVES - EFFECT OF 0.1 ATMOSPHERE AIR ON PH15-7Mo STAINLESS STEEL

Adhesive	Temp, F	Exposure, hrs	Tensile Strength, psi 1.0 atm	Tensile Strength, psi 0.1 atm	Reference
AF31	500	0.167	--	654	9
		200	--	540	
		500	--	588	
		1000	--	1400	
	600	0.167	--	508	9
		200	--	202	
		500	--	149	
Metlbond 311	500	0.167	1340	806	9
		200	720	1208	
		1000	530	1210	
	600	0.167	1240	703	9
		200	720	1158	
		500	--	278	
Imidite 850	400	0.167	2318	2318	8
		4000	1825	3472	
		10,000	--	3184	
	500	0.167	2202	2202	8
		1000	1600	3080	
		3000	--	2219	
		5000	--	1670	

Contact Catalytic Effect of Metals on Degradation

For organic resins in contact with stainless steels and titanium in air, a contact catalytic effect occurs which serves to greatly increase the degradation rate. In general, the aging performance of a structural adhesive in air on stainless steel at elevated temperature is much inferior to its performance on aluminum or titanium with a conversion coating, as data in Tables 4 and 5 and Figure 4 indicate. The very marked difference in the performance of the same adhesives on aluminum, stainless steel, and titanium, strongly indicates that certain metal surfaces have an important catalytic effect on the deterioration of organic materials at elevated temperatures in air.

TABLE 4. AGING DATA FOR 422J IN AIR ON ALUMINUM AND STAINLESS STEEL(10)

Material	Temp, F	Exposure, hrs	Tensile, psi
2024-T3	500	0	2400
		100	1100
17-7PH	500	0	2400
		100	400

TABLE 5. AGING DATA FOR IMIDITE 850 IN AIR ON STAINLESS STEEL AND TITANIUM(8)

Material	Temp, F	Exposure, hrs	Tensile, psi
PH15-7Mo	500	0	2200
		500	2657
		1000	1600
		1500	955
Ti-8Al-1Mo-1V	500	0	2008
		500	2195
		1000	2280
		1500	2034

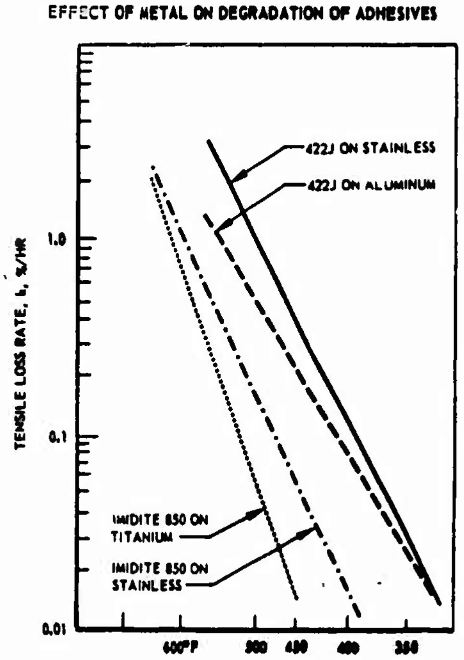

FIGURE 4

Adhesive State of the Art

A review and evaluation of the available high-temperature resistant adhesives indicates that adhesives meeting supersonic aircraft requirements are available. These adhesives are formulated from organic polymers containing the aromatic and/or heterocyclic ring systems possessing high resonance energy. (The epoxy or epoxy-phenolic types will not meet SST requirements.) Three aromatic or heterocyclic polymer types presently being used in high-temperature adhesives are (1) polybenzimidazoles, (2) polypyromellitimides, and (3) modified polyphenyl ethers (see Figure 5). Lap-shear tensile strengths before and after aging at elevated temperatures are given in Table 6 for Imidite 850 (a polybenzimidazole), FXM-34B-25 (a polypyromellitimide), and PPE 27A (a modified polyphenyl ether). A plot of tensile strength versus temperature for these adhesives is shown in Figure 6, while an Arrhenius plot of degradation rates is given in Figure 7.

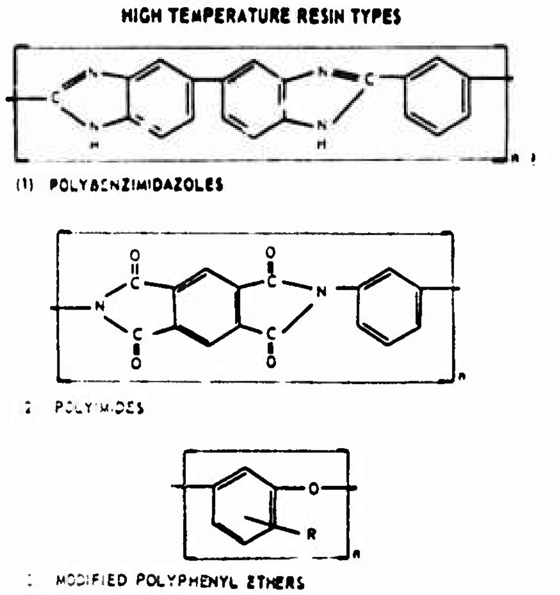

FIGURE 5

TABLE 6. LAP-SHEAR TENSILE STRENGTHS FOR HIGH-TEMPERATURE ADHESIVES ON TITANIUM[8]

Temp, F	Exposure, hrs	Tensile, psi Imidite 850	 FXM-34B-25	 PPE 27A
RT	0	2130	2570	2940
400	0	1789	2278	1100
	4000	2683	1623	1480
500	0	2008	1758	1283
	2000	1807	1916	1057
600	0	1672	1192	1248
	300	155	1815	943

TABLE 7. STORAGE STABILITY OF PPE ADHESIVE[8]

Adhesive Storage	Lap-Shear Tensile, psi* RT	 450 F	 600 F
0	2715	1198	827
1 yr	2940	1290	940

*On Ti-8Al-1Mo-1V alloy.

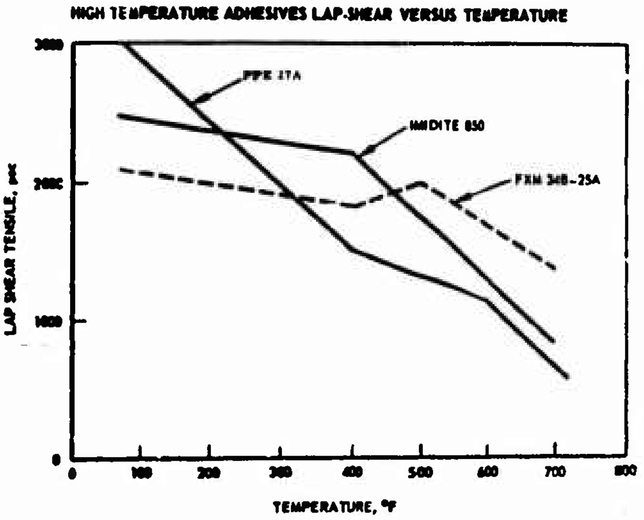

FIGURE 6

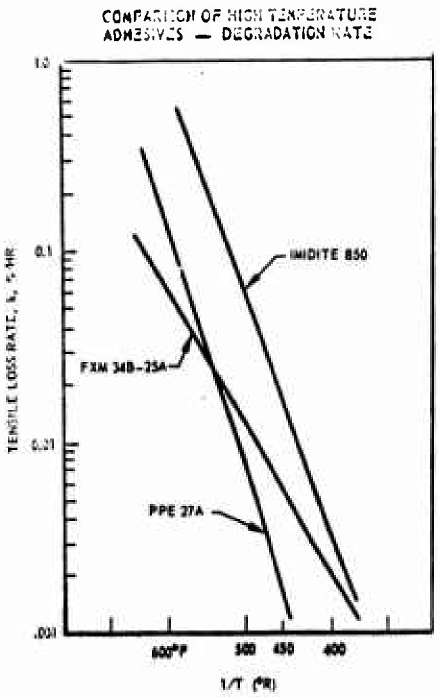

FIGURE 7

The polyimide types have the best thermal stability, the modified polyphenyl ethers are slightly less stable, whereas the polybenzimidazoles are considerably less stable. The polyimides and modified polyphenyl ethers are expected to meet SST requirements for life while the polybenzimidazoles will not.

The polyimides and polybenzimidazoles cure by condensation; the polyimides condense out water to form the cyclic imide ring, while the polybenzimidazoles condense out either ammonia and water or phenol and water to extend the chain length to high molecular weight. In both cases, the volatiles exceed 10 percent by weight. These quantities of gases evolved in cure prevent bonding of completely sealed honeycomb-sandwich panel structures and generally leave a foamed bond area. The modified polyphenyl ethers emit about 2 to 4 percent by weight of volatiles in cure and present no problem in bonding of sealed honeycomb-sandwich panels.

Adhesive Application and Bonding

Adhesive

Normally, adhesives are supported on a glass scrim cloth or other similar weave of glass cloth. The glass cloth generally is recognized as being sufficiently inert and of no value to the adhesive except as a carrier. The carrier does act as a shim during the application cycle, and provides a fairly direct means of maintaining consistent bond thickness.

The multi-strand-filament structure of glass cloth may afford a means for moisture and oxygen to diffuse into the adhesive along the axes of the glass fibers by capillary action and may aid in degradation of the adhesive. In addition, the large differences in thermal expansion coefficient between glass and organic polymers generate high stresses in the glass/polymer interface during temperature cycling. This could cause microcracks to form in the glass/adhesive interface, thus weakening the adhesives.

For these reasons, monofilament cloth made from metal, preferably aluminum or boron, or from a heat-resistant polymeric fiber, is suggested as a replacement for glass cloth as the carrier. The monofilament metallic cloth would be free of the wicking tendency and of large differences in thermal expansion between adhesive and carrier. Another possible means to eliminate the wicking tendency is via complete removal of a carrier cloth. The adhesive formulation could be applied directly to the metal skins and core by spray, painting, or roller coating. These techniques would reduce the weight of the adhesive, allow for easy and rapid application, and would provide a protective coating to the metal bonding surfaces after they have been cleaned and treated.

Bonding

Bonding with high-temperature adhesives may require the use of hot bonding presses or metallic air bag pressure chambers if cure temperatures higher than about 375 F are required. Preliminary evaluations of the three adhesive types indicate that the polyimide and modified polyphenyl ether types can be cured sufficiently at 375 F to maintain bond integrity during post-cure handling and during post-cure cycles. Normally, these two adhesive types will require post-cure at 500 F for a few (8 to 12) hours to obtain maximum strength. The polybenzimidazoles require cure temperatures up to 600 F, and therefore, will require the special high-temperature bonding fixtures.

Types of Bonds

The types of bonds and materials expected to be bonded in supersonic aircraft are titanium metal and titanium alloys, high-temperature resistant glass-reinforced plastics, and perhaps, stainless steel. Combinations of these materials include (1) metal-to-metal, (2) metal-to-metal core, (3) metal-to-glass plastic core, (4) glass plastic laminate-to-glass plastic core, and (5) glass plastic laminate-to-glass plastic laminate. Types of bonds will include (1) Tee, (2) honeycomb sandwich, (3) interlocking, (4) butt, (5) hat section, (6) core splice, and (7) lap shear.

Testing of Adhesives and Bonded Structures

Before an adhesive can be qualified for use in supersonic aircraft, its strength properties under various conditions and aging life under these conditions must be known. Testing of simple lap-shear in thermal environments and after exposure to thermal aging will give a fairly reliable measure of the adhesive strength and life under pure thermal environments. The effects of moisture, salt corrosion, jet fuels, and lubricating oils on adhesive properties can likewise be determined by lap-shear tests.

The most critical tests for high-temperature adhesives will be their ability to maintain strength and integrity while stressed at elevated temperatures, and perhaps, while subjected to some of the environmental conditions listed before. Additionally, the adhesive will have to withstand fatigue under cyclic thermal exposure. Tests suggested to evaluate these conditions are creep-rupture tests at elevated temperature and under environmental exposure, and fatigue tests after thermal aging. The thermal aging may reduce strength properties and increase adhesive brittleness, so that fatigue failure occurs prematurely.

Other tests required to qualify an adhesive are strength properties of honeycomb sandwich panels under tensile, shear, peel, compressive, and acoustic stresses before and after thermal and environmental exposures. Adhesives passing these tests will then be used to fabricate prototype structures for specialized tests and to generate design data for supersonic aircraft applications.

SPECIFIC ACTIVITY IN THE ADHESIVE BONDING OF TITANIUM

Titanium Surface Treatments

Treatment of titanium surfaces for bonding has been evaluated by comparison of lap-shear tensile strengths before and after thermal aging and exposure to salt spray and water atmospheres. The best surface treatments representing each of three types of treatment are listed in order of preference:

(1) Chemical oxidation - proprietary treatment resulting in black oxide

(2) Chemical conversion coating - phosphate-fluoride

(3) Anodic oxidation - proprietary treatment.

Adhesive Development

Research and development of a high-temperature resistant adhesive system suitable for application in supersonic aircraft has been actively pursued over the past 4 years. The research and development work at Northrop Norair has resulted in a modified polyphenyl ether adhesive (PPE 27A) with the properties listed in Table 6. This adhesive has no storage problems, that is, it has been stored at ambient conditions between brown kraft paper for over a year and still has strength properties identical to those obtained initially (Table 7).

The adhesive is characterized further by (1) low amount of volatiles (2 to 4 percent) emitted during cure, (2) low fusion or flow point, 220 to 250 F, which permits good wetting and filleting during cure, (3) moderate cure temperatures, 375 F, for 6 hours plus post-cure at 500 F for 8 to 16 hours, and (4) the adhesive has adequate strength and thermal stability to meet supersonic aircraft applications (see Table 6).

Bonding of Honeycomb Panels

Large prototype panels have been fabricated from (1) titanium skins and titanium core, and (2) from titanium skin, glass-reinforced core, and glass-reinforced laminate. Additional panels will be fabricated as above and tested for various strength properties before and after aging and for acoustic fatigue before and after aging. The panels are to be fabricated so that they are completely sealed. Only by using an adhesive which emits low volatile content in cure is this possible. Panels so fabricated will be tested nondestructively for integrity of bond before mechanical property testing.

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TITANIUM FASTENERS

L. H. Stone*

The majority of the fasteners employed in the aerospace industry today consist of nuts and bolts, screws, pins, rivets, blind bolts, and blind rivets. Mechanical fastening provides a means for joining dissimilar metals, heavy sections, and components not amenable to the high temperatures required for diffusion bonding, brazing, and welding. These joints are produced with relatively simple tools, little or no jigging, and can be disassembled if need be.

Titanium fasteners offer several advantages over steel and aluminum fasteners currently being used in the aerospace industry. The obvious weight savings of titanium over steel fasteners is readily apparent. Titanium fasteners possess higher strengths than aluminum fasteners. In addition, titanium fasteners exhibit excellent corrosion resistance, far greater fatigue life, and can be used at higher elevated temperatures than aluminum fasteners.

The attributes of titanium fasteners were realized as early as 1953 when the B-52 SAC bomber was fabricated with thousands of titanium fasteners. In later years, the B-58, satellites, and missiles employed titanium fasteners mainly for the weight-savings advantage afforded.

Titanium fasteners are available in several alloys as shown in Table 1. Fasteners made from the off-the-shelf alloys are available on short notice since the majority of fasteners have been fabricated with these alloys. Fasteners made from the alloys in the middle category are available on a semi-production basis. IMI-679 alloy is being experimentally evaluated for fastener applications. Even though some of the alloys in the middle classification exhibit higher strength and better creep properties than Ti-6Al-4V, the Ti-6Al-4V alloy is being considered for the new generation of aircraft because of user confidence on present-day flying hardware.

TABLE 1. TITANIUM FASTENER AVAILABILITY

Off the Shelf	Semi-Production	Experimental
Pure titanium	Ti-8Al-1Mo-1V	IMI 679 (Ti-2.25Al-11Sn-5Zr-1Mo-0.2Si)
Ti-6Al-4V	Ti-6Al-6V-2Sn	
Ti-4Al-4Mn	Ti-7Al-12Zr	
Ti-7Al-4Mo	Ti-1Al-8V-5Fe	
	Ti-13V-11Cr-3Al	

The advantages that titanium fasteners offer over other materials are only realized when sound quality control measures are observed during the manufacturing processing sequence, Table 2. Incoming material must be qualified with respect to chemistry, roundness, surface condition, metallurgical soundness, and hot headability. The first step in the fabrication of a titanium fastener, the hot heading operation, is the most critical from a reliability standpoint. The heading temperature and strain rate must be closely controlled to achieve the proper microstructure and grain flow in the head. Since hot heading is done in air, a machining operation is necessary to remove oxygen contamination. After hot heading and machining, heat-treatable alloys are heat treated in an argon atmosphere to eliminate contamination. The final operation in the case of threaded fasteners is the thread rolling operation.

TABLE 2. PROCESSING SEQUENCE FOR THE MANUFACTURE OF TITANIUM FASTENERS

Material Qualification
Fabrication
Hot Heading
Machining
Heat Treating
Roll Threads
Fastener Qualification
Metallurgical
Mechanical

Finished fasteners are futher qualified by metallurgical and mechanical analyses. Metallurgical analysis consists of a microstructural evaluation of the head and shank regions. In addition, threaded fasteners are examined for evidence of cracks, laps, and seams in the threaded area. Hydrogen content of the bead is determined by vacuum extraction techniques.

Mechanical testing qualifies the fastener from a design standpoint. Fatigue life, shear strength, and ultimate tensile strength is established as a final quality-control measure.

Titanium fasteners, once qualified, have many end uses. Pure titanium rivets are bucked or squeezed at room temperature much the same as their aluminum counterparts. However, titanium alloy rivets may crack and split under the deformation of squeezing or bucking, thus swaged collars of aluminum or steel are sometimes employed to facilitate using titanium alloy rivets to make joints. On the other hand, titanium alloy rivets can be driven hot. However, this technique is still in the experimental stage. For threaded fasteners, the galling problem can be severe. To alleviate galling, thread lubricants or stainless steel nuts can be employed. Thread anodizing has proved to be an effective way to alleviate galling also.

Titanium fasteners offer several advantages over competitive joining techniques for titanium. There is no distortion, oxygen contamination, or loss of heat-treated mechanical properties due to the extra heat input required for metallurgical joining. Joining with titanium fasteners offers a simple, reliable, and relatively inexpensive technique for joining titanium configurations. The fastener industry has experience to offer to the aerospace industry due to the reliability of titanium fasteners as typified by a decade - plus of service on the B-52.

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DESIGNING WITH TITANIUM

R. E. Pearson*

INTRODUCTION

This paper presents a very brief discussion on the design application of titanium and its alloys to aircraft and aerospace structures. Unfortunately, hard and fast rules or simple antidotes cannot be legislated or substituted for good old common sense and ingenuity in titanium design. However, some guides and rules must be established to suggest the practical aspect of titanium design. These design suggestions and guides will be combined with their actual application on typical aircraft hardware to show what potentially can be accomplished if certain factors are recognized. Essentially a 20 percent reduction in structural weight may be achieved using titanium in lieu of steel and/or aluminum. This significant reduction in weight which represents an improvement in aircraft performance may be obtained with competitive economics.

GENERAL DESIGN CONSIDERATIONS

The preceding papers have pretty well established the desirability of titanium alloys for aircraft structures. From an engineering viewpoint comparisons of strength-weight ratios, fatigue efficiency, fracture toughness, corrosion resistance, and thermal behavior have made this readily apparent. However, to understand the application of titanium to component or system design, the designer must appreciate the basic reasons for selection of the structural material. Generally, more than one structural material will perform a specific task. Therefore the designer must select a material which will provide best performance for least end-item cost. This economic factor may be in the form of a lower initial cost, but usually initial cost plus operational costs must be considered. Economic advantages may be realized in using titanium alloys for aircraft structures because of their better strength-weight ratio when compared to steel or aluminum structural alloys. For example, Figure 1 shows a significant reduction in the structural weight of a typical supersonic transport (SST) through use of titanium alloys. The regenerative effect of structural weight reduction is apparent in the much larger reduction in the aircraft gross weight. The smaller engines required, which use less fuel, still further reduce the structural weight. In the example considered, a gross weight reduction in excess of 100,000 pounds has been realized over a comparable aluminum or steel aircraft which has the same payload range. This weight reduction and the improved fuel mileage combined with better fatigue performance, corrosion resistance and reduced maintenance will result in a lower total system cost over the projected life of the aircraft. However, the initial investment cost may be slightly higher than a comparable steel or aluminum airplane.

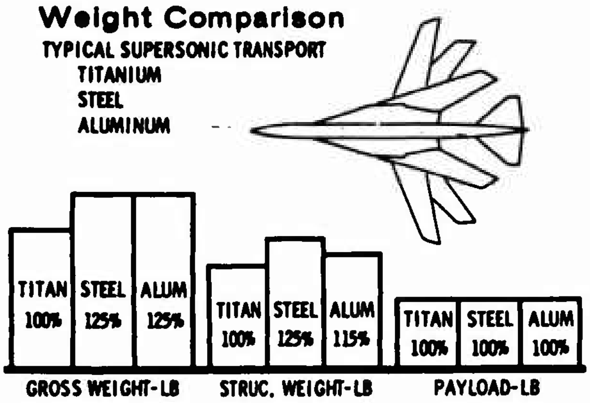

FIGURE 1

BASIC DESIGN REQUISITES

The first step that a designer must take before attempting to use titanium for a specific application is an analysis of what job or function the part must perform. After the function has been defined, material alternates must be assessed for compatibility with the task.

Titanium and its alloys are more sensitive to proper design applications than most structural alloys because of the relatively high cost of the raw material and related processing. However, if used properly, titanium can be structurally and economically superior to the best aluminum and steel alloys in many applications. The designer specifying titanium must recognize the overall effect of this material in the conceptual design state to successfully obtain the desired design and cost effectiveness. One sure way to invite high costs without realizing improvements in structural efficiency is to substitute titanium into a design calling for aluminum or steel. The result is a higher end-item cost with little or no weight saving or product improvement to offset the higher raw material and processing costs on a total system cost basis.

If the analysis of component function and design requisites suggest titanium to be a desirable material, the items listed in Table 1 should be carefully considered in the design application to ensure a high degree of structural efficiency and competitive economics.

(1) The proper titanium or titanium alloy in its optimum raw material form for a specific job should be used for the part. The part should not be made of titanium when lower cost materials would do an equal or better job.

(2) Part design should maintain extensive raw material utilization. A large percentage of the purchased raw material should be found in the end item, not in a scrap barrel as chips or excess trimmings.

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TABLE 1

Basic Requisities Of Titanium Design

1. SELECT OPTIMUM RAW MATERIAL TYPE AND FORM
2. MAINTAIN EXTENSIVE RAW MATERIAL UTILIZATION
3. USE MATERIAL STRENGTH EFFICIENTLY
4. USE SIMPLIFIED CONCEPTS - COMPATIBLE WITH MATERIAL LIMITS AND PROCESSING CAPABILITIES
5. OBTAIN GOOD COST EFFECTIVENESS

(3) Strength of the material should be used efficiently.

(4) Detail parts and complete design must be compatible with processing requirements and manufacturing capabilities. The designer must avoid complex forming and machining operations and marginal manufacturing operations by following simplified design concepts well within the physical limits of the material and its processing methods.

(5) Minimum reduction in weight of 20 percent compared to aluminum or steel structure must be achieved in weight sensitive applications. The finished part must be producible at a practical dollar/pound of finished weight to be economically competitive with alternate materials.

These items constitute the major factors that a designer must comprehend to successfully apply titanium to structure design. He must be aware of the influence of these factors on structural efficiency and end-item cost. Compatibility of the basic structural concepts with the mill product shapes, the processing methods, and the manufacturing technology is of paramount importance.

SELECTION OF RAW MATERIAL TYPE AND FORM

The designer must acquire enough basic knowledge of mill production methods, mill processing limitations, current and future product availability, and mill product cost factors to intelligently design parts from titanium using the best mill product shapes available at the lowest cost. He must become familiar with available material forms, projected technology improvement, and the influence of material shape and size on cost. For example, Figure 2 shows the current price structure for titanium alloy sheet with respect to additional costs incurred by increasing width for various gages. The cost of 48-inch wide material is 15 to 50 percent greater than the cost of 36-inch wide material, depending on gage. A severe cost penalty is also incurred, particularly in thinner gages. Merely changing from 0.012 to 0.010 gage will add 50 percent to raw material cost. Similar comparisons can be made for other extra features such as length. Thus, it can be seen that these factors can significantly affect end-item cost.

Effect Of Sheet Width And Gage On Material Cost - Titanium Alloys

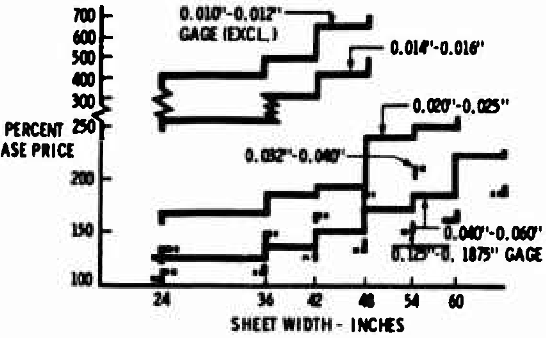


FIGURE 2

Products such as extrusions should also be evaluated from the cost standpoint. If machining is required for weight control or for stress distribution, precision or warm drawn extrusions should not be used because the additional processing costs cannot be justified. As a rule the simplest mill product form that will produce the part will show a product improvement through lower rejection rates and lower procurement and processing costs.

Another important factor in design is alloy selection. In choosing an alloy, the designer should consider strength, ductility, ease of processing, weldability, and cost. For instance, high cost alloy grades should not be used where minimum gage or part stiffness rather than strength are controlling factors in design. Instead, commercially pure unalloyed grades should be considered. This would hold true for parts of honeycomb construction (such as the control surface tab shown in Figure 3), control brackets, and pump housings.

Outboard Aileron Tab

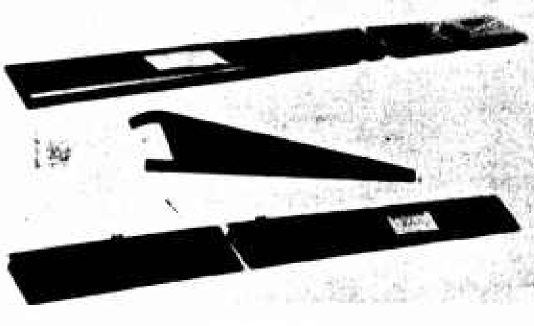
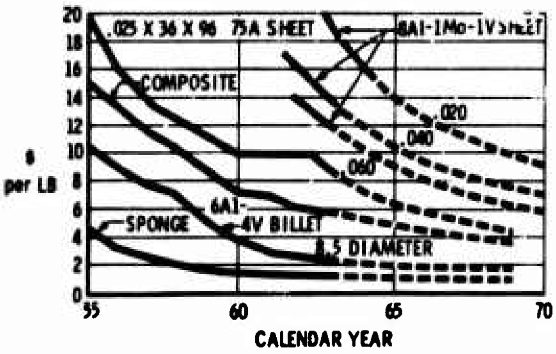


FIGURE 3

The cost of titanium raw material has dropped appreciably in the last decade as indicated by the data shown in Figure 4. This price decline has stemmed from improved melting technology and mill processing methods and increasing volume. Although additional price reductions are anticipated as usage increases and strip conversion of alloy sheets becomes a reality, raw material costs of titanium will always be an important consideration because of the exacting process necessary for raw material production.

Titanium Mill Product Cost



COMPOSITE PRICE BASED ON BASE QUANTITY OF .030 X 36 X 96 75A

STRIP .016 X 20" COIL 1" DIA ALLOY BAR ALLOY BILLET "8.5 DIAMETER"

FIGURE 4

MATERIAL UTILIZATION

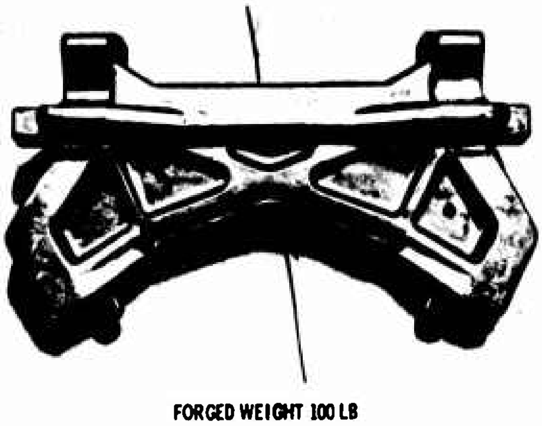
Material utilization constitutes another significant item in titanium design. The total concept of design tooling, material procurement, planning, and processing must be aimed at raw material conservation to be economically competitive with other structural materials. This facet starts with ensuring material procurement compatibility with the design. For example: providing stock coils of varying gages and widths will reduce excessive waste in length and width trimming. This compatibility, combined with stringent material issuance control can significantly improve material utilization.

Next, the designer should carefully consider the effect of processing methods on material utilization. For example: excessive machining will result in high end-item cost due to high labor costs involved in removing excess material and to the increased raw material cost for the unused weight. The direct impact of processing methods is illustrated in the following simplified cost study.

Figure 5 shows a forging weighing approximately 100 pounds. The finished part shown in Figure 6 weighs 20 pounds. The raw material cost of this forging at $8.00 per pound will equal $800. Processing cost at $15 per pound removed will be $1200 [15 x (100 - 20)]. When a 10 percent nonrecurring tooling factor is added to these costs the end-item cost is $2200 ($800 + 1200 = $2000; + 10 percent = $2200) for a 20 pound part or $110 per pound. If the material utilization were improved through proper design to 50 percent the forging would weigh only 40 pounds for the same 20 pound part. The forging cost would now be $400 (assuming $10.00/lb for improved definition) and the machining cost would be only $300 ($15 x 20). Tooling costs will be $70 [10 percent x ($400 + $300)]. Total part cost would then be $770, or $38.50 per pound. This simplified example illustrates the point. Similar examples can be cited for nonjudicious use of material in forming and skin stiffener sculpturing.

Several processes are available to a designer to improve material utilization; such as fusion welding, resistance welding, adhesive bonding, and diffusion bonding. Awareness of the material utilization factor combined with ingenuity are the most effective tools at the designer's disposal. However, he must be careful to avoid loss of practical perspective in this area. Sometimes, increased material costs are a better choice than additional processing costs with less structural efficiency.

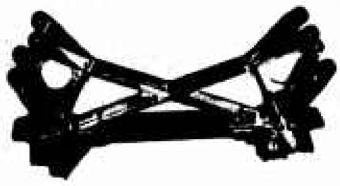
727 Center Engine Mounting Forging



FORGED WEIGHT 100 LB

FIGURE 5

Machined Center Engine Mounting Fitting



FINISHED WEIGHT 20 LB

COST COMPARISON

DESIGN PRACTICE	Forging Cost		Machining Cost		Tooling Cost Non-recurring - $	Total Part Cost - $	Net Part Cost - $/lb
	$/lbs.	Total $	$/lb	Total $			
STANDARD	8.00	800.00	15.00	1200.00	200.00	2200.00	110.00
PROPER	10.00	400.00	15.00	300.00	70	770.00	38.50

FIGURE 6

UTILIZATION OF MATERIAL STRENGTH

Utilization of material strength is primarily a design-oriented function. Early attempts to design titanium components resulted in little or no weight saving compared to aluminum structure, particularly in applications designed by minimum gage considerations, compression loading, or sonic fatigue resistance. The higher strength of the material resulted in thinner sections for a given load and thus, column and panel stability became a very important aspect of the design. However, as titanium design technology was developed, a consistent weight advantage existed for any given part over comparable aluminum designs, when full utilization of the material strength was made. One method makes use of thin honeycomb structure incorporating titanium face plies combined with aluminum or plastic cores to provide sheet stabilization. Figure 7 shows a flap rib embodying this type of design - the face skins are 0.005 gage titanium bonded to a 3/16-inch-thick aluminum core. This part is 30 percent lighter than the

Titanium Flap Rib

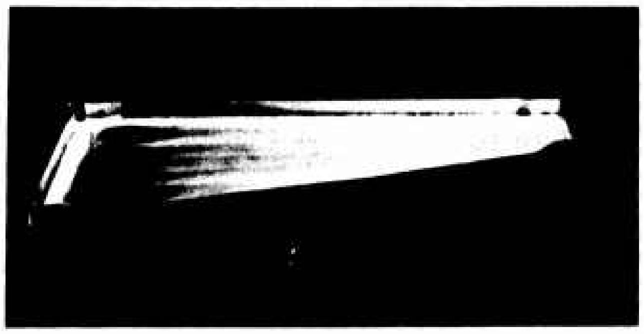


FIGURE 7

production aluminum part. Use of weldtrusions,* plastic filler, and aluminum core has also resulted in a less expensive part because of full material utilization and simplified processing. Construction details of the part are shown in Figure 8.

Section Detail Flap Rib

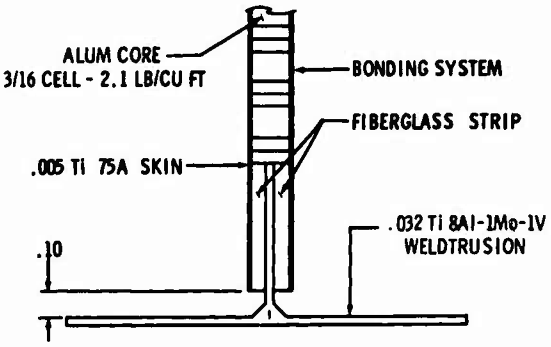


FIGURE 8

PROCESSING COMPATIBILITY

By far the most important factor in titanium applications and one which defines the success or failure of the part is the design ingenuity which ensures that the part is compatible with each processing and manufacturing requirement.

Titanium, more so than most structural alloys, is particularly sensitive in this area. The designer must have an acute awareness of processing methods and their effect on manufacturing. Alloy selection, thermal heat-treat requirements, stress relief, flatness requirements, and cleaning can have a profound effect on processing costs and design practicality. The designer should avoid difficult machining practices such as small diameter pocket end milling, indiscriminate tolerance control, and small corner and fillet radii. Machining preference should favor peripheral milling or face milling to allow fast stock removal rates for low cost machining. Fillet radii should be as large as practical with a generous negative tolerance to allow full cutter utilization when regrinding.

Forming practice in design should avoid complex die-formed parts and multiplicity of small details in favor of simple brake or Yoder-formed parts in combination with stretch and creep forming. Although titanium has excellent ductility, parts requiring full utilization of this property for processing should be avoided to ensure a low part rejection ratio. Figure 9 illustrates an effectively formed leading edge honeycomb access panel. The inner pan is normally an aluminum hydropressed part; the comparable titanium part is merely brake-formed using fiberglass reinforcing at the corners to avoid hot-forming and hot-sizing requirements.

Titanium L.E. Access Panel

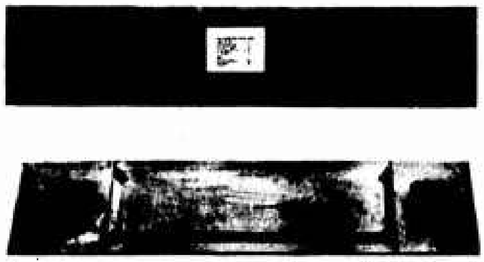


FIGURE 9

Thermal processing requirements for various heat-treat conditions must be understood to maintain compatibility with manufacturing processing capability. Thermal treatment should be used with the broadest processing tolerance which will produce an acceptable part. For example: formed ribs, clips, and stiffeners are rarely designed to fracture toughness considerations or stringent strength requirements. If these parts are to be made of Ti-8Al-1Mo-1V material, a heat-treat option of mill anneal, duplex anneal or any variation between should be provided. This permits use of a broad thermal band between 1100 and 1500 F with no critical control rate cooling. A similar situation exists with other titanium alloys. By contrast, specific heat treatments such as duplex annealing require very stringent temperature and cooling rate control which imposes severe manufacturing limitations on equipment, tooling, and processing flexibility. Generally, the base raw material should be the same heat treat as the finished part to reduce thermal treatment time for simple forming stress relief.

When processes such as fusion or resistance welding are used, care must be exercised in the design and planning phase to ensure that the composite assemblies are compatible with stress relief and subsequent cleaning requirements. In some cases this may require use of mechanical fasteners in lieu of welding to allow assembly.

SUMMARY AND CONCLUSIONS

In summarizing the thoughts discussed, the following facts are apparent as requisites of good titanium design. The designer must:

---

* Weldtrusion is a term used to describe a shape manufactured by fusion welding strips of material together to form the required configuration.

(1) Strive for good material utilization.

(2) Strive for manufacturing simplicity through understanding and appreciation of manufacturing methods, limitations, and problems.

(3) Utilize the material strength efficiently.

(4) Continuously and effectively apply value engineering using and integrating all disciplines available. For example; the cost analyst is an excellent aid in achieving competitive economics. He can point out areas of high cost which may be eliminated or substantially reduced through good design.

Basically, designing of titanium components requires practical and continuous application of value engineering by the designer to achieve favorable cost effectiveness. A dollar per pound value must be assigned to structural components, and the designer must evaluate the proposed designs before proceeding to ensure compatibility with the total end-item.

An evaluation of a good prospective titanium design should show a 20-percent weight improvement over comparable aluminum or steel design. If it does not, the material strength is not being utilized effectively, and other design concepts should be considered.

Primary structure such as fuselage sections, wing panels, and beams having relatively high end loading will not vary greatly from aluminum construction used in today's aircraft (possible exceptions include some replacement of mechanical fasteners with resistance welding and/or diffusion bonding). A typical example of this type of structure is shown in the photograph of the wing torque box (Figure 10). However, as end load decreases, titanium's greater strength compared to aluminum results in skin gages which are less stable. This then requires more extensive use of honeycomb and bonded construction for sheet stabilization to realize the inherent weight saving in the materials. The engine cowl shown in Figure 11 is a typical example of this type of construction.

Titanium Wing Box

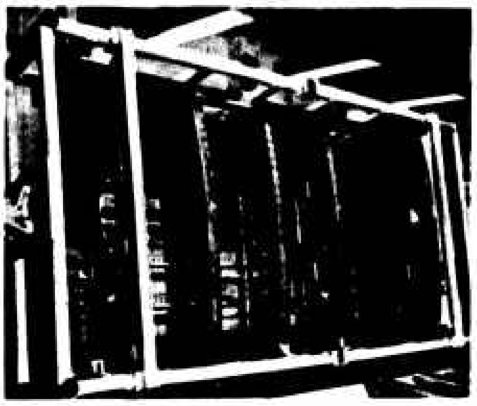


FIGURE 10

Ducted Engine Cowling

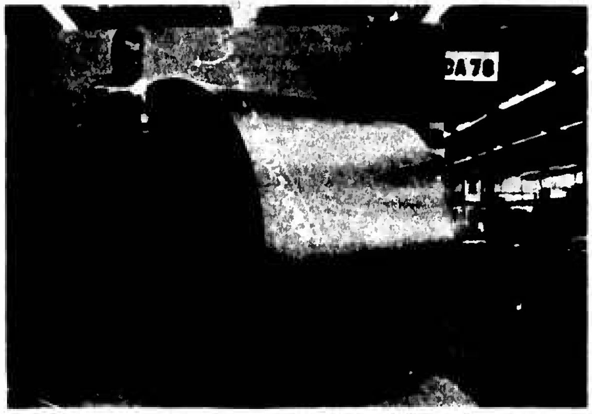


FIGURE 11

In the final analysis the use of any new structural material must be substantiated by a product improvement. The design using titanium must improve the engineering function or economics of the product to justify its use. The goal must be - the best part for the least total cost.

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13. ABSTRACT

This memorandum reproduces thirteen lectures delivered at a Titanium Symposium held on March 28-29, 1966, at Hawthorne, California, under the auspices of the Norair Division of the Northrop Corporation. These lectures follow a logical sequence of topics including production aspects, metallurgy, manufacturing technology, and the design of titanium parts for aircraft and aerospace applications.

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