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ZIRCONIUM AS A STRUCTURAL MATERIAL FOR NAVAL SYSTEMS

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RESEARCH AND TECHNOLOGY DEPARTMENT

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The important basic physical properties and steps in the manufacture of elemental zirconium and several of its important alloys are discussed. Once considered prohibitively expensive for structural uses, its current cost is becoming competitive with other special alloys for various industrial applications. Its actual life cycle cost in many cases has been considerably lower than that experienced with alternative materials.

Some of the physical properties of zirconium which make it particularly

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attractive for naval use include: high strength (particularly when alloyed), outstanding resistance to all forms of corrosion in seawater (and most other) environments, superior fatigue resistance, and good metallurgical workability. Its oxide compound zirconia has recently become a base material for a new generation of tough ceramics of potential structural use. These ceramics are also candidates for fiber reinforcement. Several modern ceramic fabrication techniques are discussed.

Although its moderately high density probably will preclude widespread aerospace usage, zirconium and zirconium-based materials could find extensive application in naval surface systems. Finally, there is a ready availability of the raw ore from friendly nations and a very abundant domestic supply, should other sources fail. This assurance certainly increases the attractiveness of these materials for future Navy needs.

FOREWORD

This report is a compilation of data and information from various sources concerning the physical properties, manufacture, and availability of zirconium and zirconium-based materials. Particular emphasis is given to the potential expansion of zirconium alloys and materials usage in naval systems.

This report is not an exhaustive analysis of the subject. Rather, it should serve as a convenient introduction and practical guide for those interested in alternative structural materials for naval system applications.

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INTRODUCTION

Many factors drive the search for substitute materials in our era. In some cases, the demands of high technology require that new materials be found to fill a need for higher performance where others fail. In other cases the life cycle cost of operation is the primary factor. The natural cycle of growth of use and subsequent resource depletion often provides a long-term incentive. In strategically important areas, the uninterrupted availability and security of supply sources may be an overriding consideration. This is certainly becoming the case with the technologically critical chemical elements chromium and cobalt, for example, from a military perspective. The case, therefore, for continuing research efforts directed toward the identification and development of substitute materials can be made on numerous grounds. These are basic investments in our technological future.

The intent of this report is to examine the potential of the element zirconium as a structural material for present and future Navy requirements. In pursuit of this goal, the desirable physical properties and drawbacks of this material are documented. This includes discussion of its properties in alloy, oxide, and composite form. A review of present uses of zirconium indicates the extent to which these properties have been exploited. Finally, some recommendations concerning the types of applications and direction of research efforts on zirconium-based materials likely to meet future Navy needs are discussed.

CHAPTER 2

BACKGROUND

Zirconium was discovered in 1789. It is found primarily in zircon ($Zr SiO_4$) bearing sands which are plentiful along coastal waters of the United States and in many other areas of the world. A discussion of the ore supply situation and relative cost comparison with other metals of similar properties is presented in Chapter 4. Zirconium is a steel-gray, strong, ductile, high-melting point, chiefly tetravalent metallic element of the second row in the periodic table. It is separated from the sand borne zircon by heating with carbon and chlorine and passing the volatile zirconium tetrachloride formed into hot molten magnesium or sodium to yield a spongy form of the free metal containing up to three percent hafnium. It resembles titanium and hafnium chemically (being vertically positioned between these in the periodic table). In its massive form (low surface area) zirconium exhibits good corrosion resistance in diverse environments at ordinary or moderately elevated temperatures. This important property of zirconium will merit expanded discussion as it impacts upon many current uses of the material.

CHAPTER 3

PHYSICAL PROPERTIES OF ZIRCONIUM

Some appreciation of the system/structural potential of zirconium will be gained by a review of its physical properties. Table 1 lists the important ones for the pure element, including some comparisons with other common structural metals. From the table we learn that the density of zirconium is intermediate between titanium and aluminum and nickel and steel. Its melting point is relatively high compared with the more common structural metals, but not inconveniently so. Its coefficient of thermal expansion is relatively low compared with those of stainless steel or aluminum. This property tends to minimize warping on welding or dimensional changes in zirconium equipment components used at elevated temperatures. The thermal conductivity of zirconium approximately equals that of stainless steel which is rather poor. However, its strength in thin walled construction and other properties allow wide use in heat transfer applications.

The elastic modulus of zirconium is close to that of aluminum. Its unalloyed ductility and workability are such that it readily may be hot forged, hot rolled, cold milled, and rolled and extruded. Some aspects of production and processing will be treated below. The electrical resistivity of zirconium is some 20 X that of copper but about half that of stainless steel. This conductivity is sufficient for applications requiring components to be good electrical conductors.

CORROSION

Corrosion properties of a material are perhaps most important after other material criteria such as strength and thermal properties have been met. This is particularly true in environments likely to be encountered in naval systems.

Chemical Corrosion

Zirconium has found relatively wide use in industrial and chemical processing applications due to its excellent resistance to corrosion in many chemical environments, even at elevated temperatures and pressures. These include most organic and mineral acids, strong alkalis, and specific molten salts. Because of this rather broad spectrum of chemical corrosion resistance, zirconium is an excellent material for use in processes which require alternate contact with strong acids and alkalis.

TABLE 1. TYPICAL PHYSICAL AND MECHANICAL PROPERTIES OF UNALLOYED ZIRCONIUM

PHYSICAL PROPERTIES		COMPARISON
ATOMIC NUMBER	40	
ATOMIC WEIGHT	91.22	
ATOMIC RADIUS		
A°(Zero Charge)	1.60-1.62	- Aluminum: A° - 1.43
A° (+4 Charge)	0.80-0.90	- Aluminum: A° (+3 Charge) -0.45
DENSITY		
(g/cc at 20°C)	6.490	- Titanium: 4.51
(lbs./cubic inch)	0.234	- Titanium: 0.169
CRYSTAL STRUCTURE		
Alpha Phase (below 865°C)	Hexagonal Close-Packed	
Beta Phase (above 865°C)	Body-Centered Cubic	
TRANSFORMATION TEMPERATURE		
Alpha Beta	865°C(1590°F)	
MELTING POINT	1845°C(3350°F)	- Iron: 1536 °C
BOILING POINT	3577°C(6480°F)	- Iron: 3000 °C
COEFFICIENT OF THERMAL EXPANSION per °C 25°C(73°F)	5.89 x 10^{-6}	- Stainless 304: 17.3 x 10^{-6} - Aluminum: 25 x 10^{-6}
THERMAL CONDUCTIVITY (300-800°K)		
Watts/m-°K	22	- Stainless 304: 16.9 - Copper: 380.8
SPECIFIC HEAT [BTU/lb/°F (32°-212°F)]	0.068	Aluminum: .215
VAPOR PRESSURE (mm Hg)		
2000°C(3632°F)	0.01	
3600°C(6512°F)	900.0	
ELECTRICAL RESISTIVITY [Michrohm-cm at 20°C,(68°F)]	39.7	- Copper: 1.7 - Stainless 304: 72

TABLE 1. (Cont.)

PHYSICAL PROPERTIES		COMPARISON
TEMPERATURE COEFFICIENT OF RESISTIVITY PER °C 20°C(68°F)	0.0044	
LATENT HEAT OF FUSION (Cal/gm)	60.4	- Iron: 65.7
LATENT HEAT OF VAPORIZATION (Cal/gm)	1550	- Iron: 1515
Mechanical Properties		
MODULUS OF ELASTICITY (psi)	14.4×10^6	- Stainless 304: 28×10^6 - Aluminum: 10×10^6
SHEAR MODULUS (psi)	5.25×10^6	
POISSON'S RATIO (Ambient Temperature)	0.35	

Zirconium and its special alloys are not readily attacked by oxidizing media unless halides (Fl^-, Cl^-) are present. It has excellent oxidation resistance to 400°C in air, steam, carbon dioxide, nitrogen, and oxygen. These alloys have little need for anodic protection systems. Zirconium's corrosion resistance is due to rapid formation of a dense, stable oxide film on the metal surface upon exposure to such media. This adherent film is self-healing and protects the base metal from chemical and even mechanical attack such as abrasion and functional wear at temperatures to 300°C. Table 2[1] lists a sample of chemical corrosion data on pure zirconium and several alloys. The corrosion rate is given in mils (.001 inch) per year for general surface attack, except where noted otherwise.

An examination of this corrosion data gives appreciation of the versatility of zirconium in resisting corrosive attack in very harsh acid and caustic environments even at elevated temperature. While the very broad range of corrosion resistance is evident, some halogen compounds containing fluorine and chlorine, such as $FeCl_3$ and NH_3F, must be avoided. Fortunately, the corrosion mechanism depends strongly on the chemical bond strength of the halide compound. Thus, compounds such as CaF, $AlCl_3$ and, most importantly, an Na Cl environment produce virtually no corrosive attack on zirconium even at quite elevated temperatures. The data of Table 3 illustrate this point. Corrosion rates in various salt solutions are given. They are uniformly low with the exception of $FeCl_3$ and $CuCl_2$. The selectivity of the corrosion mechanism is indicated by comparison of these entries with that of $NiCl_2$ which shows a very low corrosion rate.

Other Corrosion Mechanisms

In determining the utility of a material for specific applications, especially those involving structural usage, various corrosion processes must be considered. These include galvanic, crevice, pitting fretting, and stress corrosion. It will be valuable for a complete picture of the capabilities of zirconium to discuss each type briefly, stressing any observed vulnerabilities of the metal.

Galvanic Corrosion. Galvanic or electrolytic corrosion occurs when two dissimilar metals are placed in electrical contact in an electrolyte solution. In this case, the most anodic (or active) material will corrode. This is essentially what occurs in a primary battery when the circuit is closed. Table 4 indicates some entries of the galvanic series in seawater.

Due to the protective oxide film which normally forms on zirconium in air, the highly reactive zirconium surface assumes a noble potential similar to silver or passivated stainless steel. If this passive film is removed, as it is when in contact with the more noble metals of Table 4, zirconium will become activated and corrode. Other less noble metals will corrode when in contact with zirconium with its oxide protective layer in place. For example, in seawater (or acid solutions), carbon steel, aluminum, and zinc will corrode rapidly in electrical contact with zirconium. Therefore, care should be taken

TABLE 2. ZIRCONIUM CORROSION DATA

CORROSIVE MEDIA	CONCENTRATION %	TEMPERATURE °C	CORROSION RATE, mpy			REMARKS
			Zr	Zr 704	Zr 705	
Ammonia (wet)	+ water	38	<5	-	-	
Aluminum Chloride	5,10,25	35-100	<1	-	-	
Calcium Fluoride	Saturated	28	nil	-	-	pH = 5
Chlorine (water saturated)	-	Room	>50	-	-	
Ferric Chloride	0-50	Room-100	>50	>50	>50	
Hydrazine	Mixture	109	<1	-	-	2% Hydrazine + saturated NaCl + 6% NaOH
Hydrochloric Acid	2	225	<1	-	<1	
	32	82	<1	-	-	
20% HCl + Cl_2 gas	-	58	5-10	-	-	*Pitting
37% HCl + 100 ppm $FeCl_3$	-	53	<5	-	-	SCC Observed

TABLE 2. (Cont.)

CORROSIVE MEDIA	CONCENTRATION %	TEMPERATURE °C	CORROSION RATE, mpy			REMARKS
			Zr	Zr 704	Zr 705	
Nitric Acid	10-70	Room-260	<1	-	-	
	70-98	Room-Boiling	<1*	-	-	*SCC Observed
Nitric Acid + 1% $FeCl_3$	70	120	nil	-	-	
Hydrogen Peroxide	50	100	<2	-	-	
Phosphoric Acid	50	Boiling	<5	5-10	10-15	B.P. = 108°C
Silver Nitrate	50	Room	<5	-	-	
Sodium Chloride + Saturated SO_2	25	80	nil	-	-	
	Saturated	80	nil	-	-	
Sodium Hydroxide	73	110-129	<2	-	-	
Sulfuric Acid	0-75	20	<1	<1	1	
	70	100	<2	-	5	
+10,000 ppm $FeCl_3$	65	Boiling	<5	<5	20	
+1000 ppm NO_3^-	60	Boiling	<5	-	-	Added as HNO_3

TABLE 2. (Cont.)

CORROSIVE MEDIA	CONCENTRATION %	TEMPERATURE °C	CORROSION RATE, mpy			REMARKS
			Zr	Zr 704	Zr 705	
Sulfuric Acid						
+200 ppm Cu^{2+}	60	Boiling	<5	-	-	Added as $CuSO_4$
+1000-10,000 ppm Cu^{2+}	60	Boiling	<1	-	-	
Ammonium Fluoride	20	28	50	-	-	pH = 8
Water - Sea (Pacific)	-	Boiling	nil	-	nil	
		200	nil	-	-	pH = 7.6

(From Reference 1)

TABLE 3. CORROSION RATES OF ZIRCONIUM IN SALT SOLUTIONS

ENVIRONMENT	CONCENTRATIONS, WEIGHT %	TEMPERATURE, °C	CORROSION RATE, MPY
$AlCl_3$	5,10,25	35-100	≤ 0.2
NH_4Cl	1,10,Sat.	35-100	<0.2
$BaCl_2$	5,20	35-100	<0.07
$CaCl_2$	5,10,25	35-100	<0.03
$CuCl_2$	5,10,20	35-100	>50
$FeCl_3$	5,10,20	35-100	>50
$MgCl_2$	5,20,42	35-Boiling	<0.1
$MnCl_2$	5,20	35-100	<0.09
$HgCl_2$	1,5,10,Sat.	35-100	<0.07
$NiCl_2$	5,20	35-100	<0.1
KCl	Sat.	60	0.009
KF	0.5 Molar	Boiling	<0.2
NaCl	3,Sat.	35-Boiling	<0.03
$SnCl_4$	5,24	35-100	<0.1
$ZnCl_2$	5,20	35-Boiling	<0.08

(From Reference 2)

TABLE 4. GALVANIC SERIES IN SEAWATER

Cathodic	
(Most Noble)	Platinum
	Gold
	Graphite
	Titanium
	Silver
	Zirconium
	Type 316, 317 Stainless Steel (passive)
	Type 304 Stainless Steel (passive)
	Type 410 Stainless Steel (passive)
	Nickel (passive)
	Silver Solder
	Cupro Nickels (70-30)
	Bronzes
	Copper
	Brasses
	Nickel (active)
	Naval Brass
	Tin
	Lead
	Type 316, 317 Stainless Steels (active)
	Type 304 Stainless Steel (active)
	Cast Iron
	Steel or Iron
	Aluminum 2024
	Cadmium
	Aluminum (commercially pure)
Anodic	Zinc
(Active)	Magnesium and Magnesium Alloys

(Taken from Reference 1)

to keep them electrically insulated. A good understanding of service condition details is required for avoiding galvanic corrosion. Its effects are encountered in many more subtle ways than are indicated here.

Crevice Corrosion. Crevice corrosion is a form of localized corrosion usually associated with small volumes of stagnant solutions caused by lap joints, surfaces around gaskets, bolt holes, or crevices under fastener heads. For example, in chlorine service, many metals are subject to crevice attack due to dehydrated chlorine trapped in the crevice. Crevice corrosion in Zirconium has not been reported.[3] Of all the corrosion resistant metals, zirconium and tantalum are the most resistant to crevice corrosion.

Pitting Corrosion. Pitting corrosion occurs when the potential developed at the surface of a metal immersed in a solution locally exceeds its pitting potential. Halide and hydrogen ions aggregate in elevated concentration due to a surface imperfection or random variation in solution composition. If these ions are not swept away, they create conditions necessary for high rate localized dissolution of the metal characterized by pit formation. Zirconium is quite resistant to pitting corrosion in chloride and other halide environments. Electrochemical measurements, however, can determine zirconium's proclivity to pitting in specific solutions. The presence of oxidizing ion impurities (such as Fe^{3+} or Cu^{2+}) in halide solutions will increase the corrosion potential and when this becomes greater than the pitting potential pits will be initiated. The data of Table 1 shows an entry documenting the pitting of zirconium in the very harsh hydrochloric acid-chlorine gas environment.

Fretting Corrosion. This type of corrosion occurs when vibrational contact is made at the interface of tight-fitting, highly-loaded surfaces. The leaves of a spring or parts of sleeves or roller bearings are examples of these conditions. If it cannot be eliminated mechanically, the best way to overcome this type of corrosion is to allow a heavy oxide coating to grow on the exposed zirconium or zirconium alloy surfaces. This heavy oxide coating greatly reduces the frictional resistance and prevents the removal of the natural thin passive protective oxide film. The value of zirconium oxide and zirconia ceramic coatings will be discussed below under applications of zirconium.

Stress Corrosion Cracking. Stress corrosion cracking (SCC) characteristically occurs at the grain boundaries within a metal or alloy under conditions of sustained high stress in a specific corrosive medium. The detailed mechanism is still a matter of discussion. A plausible explanation suggests that solution ions microscopically infiltrate along the boundaries by electrochemical action under the stressed condition, causing weakening and eventual cracking of the structure. Zirconium and its alloys are resistant to stress corrosion cracking in many environments (such as NaCl, H Cl, MgCl, Na OH, H_2S), which will induce SCC in other alloys. The high SCC resistance of zirconium probably can be attributed to its high repassivation rate. Any break in the surface film will be healed quickly provided there is sufficient oxygen content. Even in dehydrated systems, there is generally sufficient oxygen present for repassivation. Passivation in this case is a surface condition in which the presence of an oxide film blocks further chemical action by oxygen or salts in contact with the surface.

Two entries of Table 2 indicate observed SCC of zirconium in the presence of $FeCl_3$ and very concentrated nitric acid. A few other environments not likely to be encountered in applications of interest are known to cause SCC in zirconium. In the case of exposure to a seawater environment, the quantity of $FeCl_3$ or $CuCl_2$ in solution is insignificant. Table 2 indicates no detectible corrosion of zirconium in seawater even at elevated temperature. This property should have important significance for its scope of potential use in naval shipboard systems.

Other Physical Properties

Gas Embrittlement. This is observed in many metals due to diffusion of oxygen or hydrogen into interstitial positions within the lattice. There, the gas atoms act as pinning sites to decrease ductility. Zirconium may be annealed in air at temperatures up to 500°C with no detriment. Above 540°C it begins to react, producing a white zirconium oxide film which is very refractory, brittle, and porous. At temperatures above 700°C it absorbs oxygen and becomes embrittled with long exposure. The oxide film provides an effective barrier to the absorption of hydrogen, although in a pure hydrogen atmosphere, absorption begins at 310°C, and the metal ultimately becomes embrittled. Absorbed hydrogen, however, can be removed by vacuum annealing above 750°C.

High Temperature Fatigue Failure. This failure occurs when a material is subject to cyclic stress in high temperature applications. These stresses can lead to fatigue damage and the possibility of ultimate fatigue failure. At high temperatures there is a greater tendency for polycrystalline materials to fail along grain boundaries by the formation and growth of either cavities or cracks. Figure 1[4] compares the temperature dependence of fatigue life of zirconium with that of copper and the cobalt-based superalloy L-605 (Haynes 25). The fatigue life of single crystal copper is essentially independent of temperature to 400°C, due to its lack of grain boundaries. Zirconium, however, shows a larger temperature range of resistance to fatigue than either polycrystalline Cu or the superalloy. Zirconium, therefore, can be used in applications where cyclic stresses are encountered at elevated temperatures.

Suitability for Nuclear Applications

A discussion of the important physical properties of zirconium would be incomplete without treating the subject of its suitability for nuclear applications. This use category of zirconium is without a doubt its most important to date.

In water cooled thermal nuclear reactors, the uranium dioxide fuel is inserted into canning tubes which separate the fuel from the water used as primary thermal transfer medium. Prime requirements on these canning materials

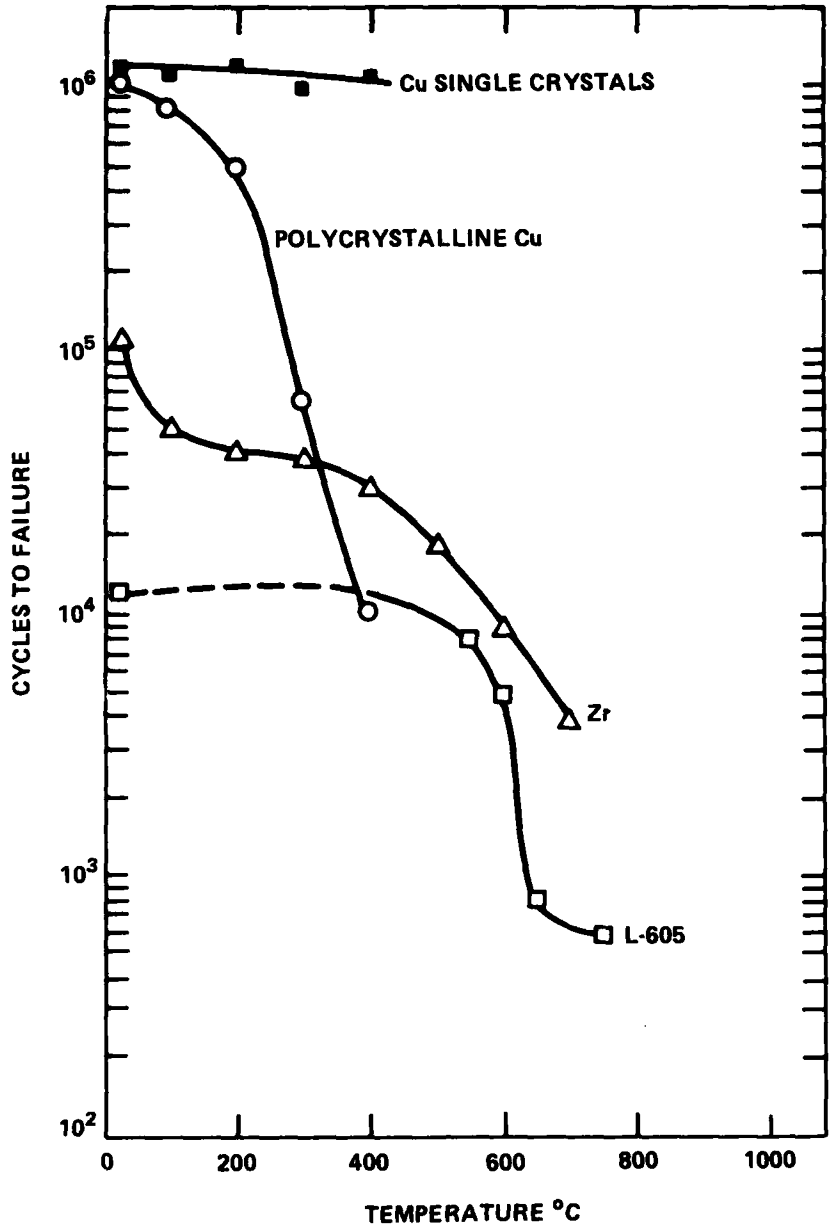


FIGURE 1. TEMPERATURE DEPENDENCE OF FATIGUE LIFE OF Zr, ALLOY L-605 AND SINGLE CRYSTAL AND POLYCRYSTALLINE Cu (TAKEN FROM REFERENCE 4)

include: low cross section for thermal neutron absorption, adequate strength and ductility, compatibility with the nuclear fuel, corrosion resistance to the water, and adequate heat conductivity. Low thermal neutron cross section is a critical prerequisite for nuclear fuel rod application. This cross section varies from metal to metal. The sequence for the important metals in increasing order is:[5]

Be Mg Zr Al Nb Fe Mo Cr Ni

Only those up to Al are possible with respect to neutron absorption, but of these, only zirconium and aluminum resist corrosion adequately. Aluminum has too low a melting point (660°C) and, therefore, too low strength at reactor service temperatures (300°C to 400°C). There remains zirconium.

When vacuum melted zirconium was first tested for hot water and steam corrosion resistance at 240°C to 400°C erratic results were obtained. Trace impurities in the zirconium were found to be responsible for these. By adding small amounts of tin, iron, nickel, and chromium, the impurities were effectively bound or coalesced within the metal and the corrosion resistance improved. To increase the strength, a small amount of oxygen was added. The strength increase arises from the pinning role of oxygen as it is distributed along the metallic lattice planes. Thus the alloy Zircaloy 2 was developed. In further studies, it was found that the presence of nickel increased the pick up of hydrogen and consequent tube embrittlement. Zircaloy 4, therefore, was developed in which nickel is replaced by an increased amount of iron. For nuclear cladding use, the zirconium starting material must be specially refined to remove the 2 to 4 percent hafnium which is normally present in the zirconium sponge. Hafnium has a high cross section for thermal neutron capture. Zirconium and its special alloys represent a mainstay in the nuclear industry. The nuclear industry application of zirconium alloys is an example of an almost ideal meshing of material properties with specific requirements.

CHAPTER 4

METAL FORMING OF ZIRCONIUM AND ITS ALLOYS

PRODUCTION OF ZIRCONIUM METAL STOCK

The crude (zircon) ores are refined and reduced to base metal sponge. This is chopped, crushed, and graded. The process of consolidation involves compaction at high pressure in a press to form large cylindrical briquettes. These briquettes are stacked end to end and electron beam welded to form a consumable electrode for melting. This consumable electrode is placed in a vacuum arc furnace and melted into large diameter ingots. These ingots, weighing up to 18000 pounds, are machined for sizing and removal of surface contaminants. Fabrication is initiated by heating the ingot and processing it into either flat or round stock using a forge press.

METAL WORKING AND FINISHING

A variety of mill equipment, including press and rotary forges, hot and cold rolling and milling, extrusion presses and swages, is used to produce finished stock. Flat product can be produced from thick plate (≥1 inch) down to foil (.0008 inch). Tubing, round products, and wire are produced by extrusion, swaging machining, drawing, and annealing. Most common metallurgical processes can be applied to the production of zirconium and its alloys with good results. Zirconium is ductile and workable and can be fabricated using standard shop equipment. The metal can be machined, ground, sawn, gas cut, punched drawn and spun. Tubing can be bent with both inside and outside tube surfaces in tension to prevent buckling. Small radius bends are produced by hot forming or special techniques. Dies of a non-galling material with clearances and tolerances comparable to those used for austenitic stainless steels should be employed with zirconium. Heat treatment from full annealing to stress relief after deep drawing or severe forming is easily performed according to well documented procedures.[6]

Joining

Zirconium is readily fabricated by welding. Its weldability under proper conditions is superior to that of some more common construction materials such as certain alloy steels and aluminum alloys. The small coefficient of thermal expansion and modulus of elasticity (see Table 1) of zirconium contribute to a low distortion during welding and low residual stresses in the finished weld. The hot or cold metal does not normally crack in welded joints of unalloyed zirconium unless the weld is grossly contaminated. Inclusions usually are not a problem in zirconium welds because the metal has a high solubility for its own oxide and since no fluxes are used, flux entrapment is eliminated.

Welding of zirconium must be carried out with proper inert gas shielding because of its reactivity to gases at welding temperatures. Welding without proper shielding (argon or helium) will cause absorption of oxygen, hydrogen, and nitrogen from the atmosphere, embrittling the weld. The techniques used for zirconium welding are gas tungsten arc welding (GTAW), tungsten inert gas (TIG) welding, gas metal arc welding (GMAW) with zirconium welding rod, plasma arc welding, electron beam welding, and resistance welding. The first two methods are by far the most common because of relative cost and flexibility. Figure 2 shows the design of welding heads for inert gas welding of zirconium (l) and a sample of welded zirconium plate (r) indicating the weld quality achievable.

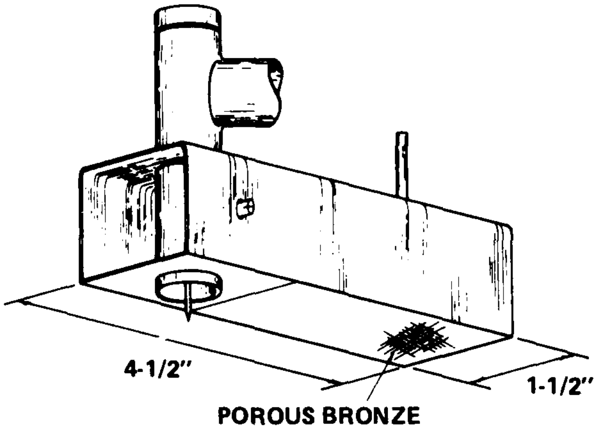
Zirconium cannot be welded directly to other structural metals with the exception of titanium, vandium, and niobium. Fabrication of all zirconium structures or the lining of other metals with zirconium is necessary. In the latter case, special butt welding techniques are used.

Special Fabrication Techniques

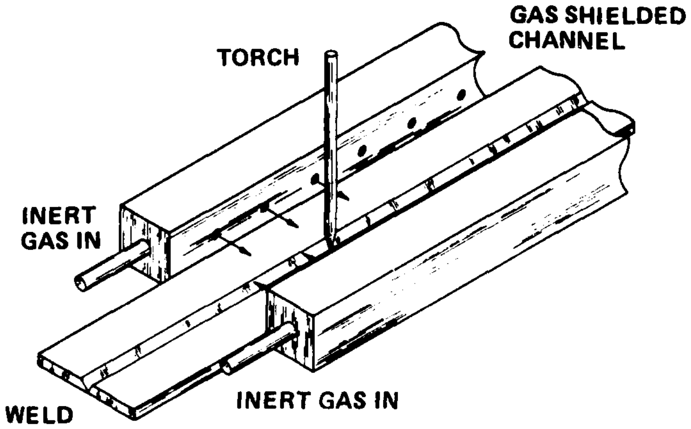
There are a number of methods used in preparing zirconium, zirconium alloys, and oxides for specific applications. This discussion begins with well established techniques and moves toward more recent experimental methods. The intent here is to describe the method mechanics, important material properties and limitations, and hopefully to provide food for thought regarding future applications.

Zirconium Cladding

Often, a structure is to be subject to high temperature and/or high internal pressures such as a boiler or to a corrosive environment in a situation requiring a 1-inch or greater thickness. Since the cost of pure zirconium is rather high, it may be advantageous to explosively bond thin zirconium plates to a strong low-cost base metal such as carbon steel. The cladding will be metallurgically bonded to the base metal due to atomic diffusion produced by the local heating/compression. The corrosion resistance and excellent heat transfer characteristics of zirconium with the steel contribute to the desired mechanical strength. There is also a resistance welding method process available for very thin zirconium sheet over a variety of base metals. A variant of the cladding process is used to produce bi-metallic zirconium lined tubing. In this case, an annular zirconium cylindrical billet is inserted into a larger annular base metal billet. The combination is co-extruded to form the tube. In applications where zirconium clad material will be used in a corrosive environment (for example seawater), the realities imposed by the data of Table 4 must be considered, and galvannic couples avoided.



TYPICAL TRAILING SHIELD DESIGN FOR TIG WELDS



SIDE-SHIELDED WELDING SETUP. A BACKUP SHIELD BELOW THE WELD BEAD IS ALSO NECESSARY

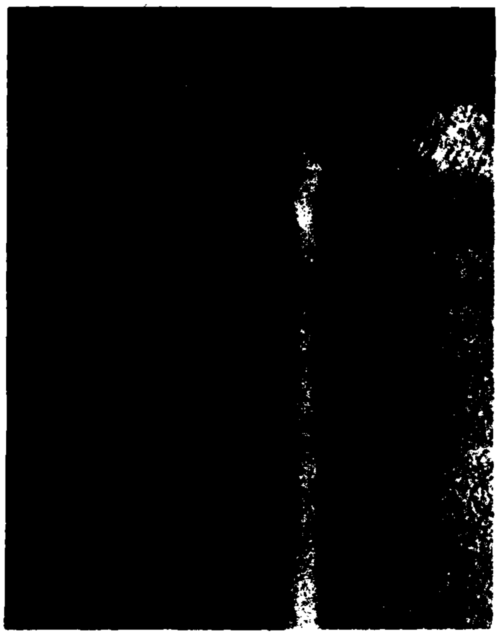


FIGURE 2. INERT GAS WELDING HEAD DESIGNS AND TYPICAL ZIRCONIUM PRODUCT WELD

ALLOYS

Alloying is a standard means of tailoring properties of metals to particular needs. As increasing amounts of alloying elements are added to zirconium, strength and corrosion resistance are often increased. This is true up to the solubility limit of the alloy element in zirconium. The alloying element atoms act as pinning points in the zirconium lattice increasing its strength (hardness) at the expense of ductility. Corrosion resistance is increased when the alloying element inhibits intergranular corrosion by reducing impurity segregation at zirconium grain boundaries. Once the solubility limit is exceeded, intermetallic compounds or second phases are formed which tend to lower ductility and degrade the alloy corrosion resistance. One element whch has a pronounced effect on zirconium mechanical properties and which can be considered an alloying element for some purposes is oxygen. Oxygen is soluble in alpha zirconium (see Table 1) to approximately 30 percent. As the amount of oxygen is increased, the strength at room temperature of zirconium also increases while its ductility decreases. At elevated temperatures, however, oxygen content has little effect on its strength. Oxygen content has no effect on the corrosion resistance of zirconium in chemical applications.

As indicated in Table 1, zirconium has a hexagonal close-packed crystal structure (alpha) below 865°C (1590°F) which transforms to a body-centered cubic structure (beta) above this temperature. Small amounts of impurities including oxygen affect this altotropic transformation temperature. The zirconium beta phase structure cannot be retained even by rapid quench. Typical wrought and annealed alpha zirconium displays a uniform equiaxed grain structure. The presence of this structural transformation in zirconium and the relatively low solubility of many alloying elements leads to three general alloy categories: alpha stabilizers, beta stabilizers, and low solubility intermetallic compound formers. The alpha stabilizers raise the alpha to beta transformation temperature and usually exhibit a peritectic reaction with the liquid portion of a zirconium melt. Among these elements are Al, Su, Pb, N, O, and Cd. The beta stabilizers lower the alpha-beta transition temperature and usually exhibit eutectic behavior resulting in a lower overall melting temperature of the alloy than for either constituent. Some of the typical beta stabilizers are Fe, Cr, Ni, Mo, Cu, Ti, Mn, Co, and Ag. The low solubility materials which readily form stable intermetallic compounds include principally carbon, silicon, and phosphorous. The compounds formed are relatively insensitive to heat treatment.

One important reason for discussing the alpha and beta stabilizing alloys at this point is to indicate the presence of a strong anisotropy in many physical properties in wrought or drawn zirconium product. At normal operating temperatures (alpha phase) zirconium deforms by slip mainly in the close packed direction. The material also deforms by crystal twinning under tensile stress.[7] This anisotropy in the micromechanisms of deformation is observed in the macroproperties of zirconium (alloys). Such physical properties as thermal expansion, yield strength, ultimate tensile strength, elongation, and bend ductility vary with direction in the material. Much effort, therefore, was devoted to the prediction of the yield locus zirconium alloy tubes under multi-axial states of stress as required in nuclear industry applications. Mechanical anisotropy in zirconium alloy tubing is apparent on comparing the directionality of results of burst and tensile tests. Transverse strength of the tubing can vary significantly with radial direction. Clearly, such anisotropy must be considered when designing structures using zirconium alloys.

Alloys containing zirconium can be divided basically into two categories: small percentage additions of zirconium to other alloys and major constituent zirconium alloys for special purposes. Zirconium has been used for many years as a grain refiner in various alloy systems to produce higher strength and better corrosion resistance. These properties usually are achieved with zirconium additions of the order of 1 percent. The second category includes alloys for special purposes such as the zircalloys which take advantage of the corrosion resistance of zirconium and desirable properties of alloys, metals such as toughness, weight, cost, etc. Several examples of each alloy type are presented below.

Minor Constituent Zirconium Alloys

Cu-Zr and Cu-Zr-Cr (containing 0.1 to 0.8 percent Zr) series alloys offer not only an example of the first type discussed above, but also of one of several novel processing techniques applied to Zr alloys. These systems have potential commercial interest. The aim of this research was to produce high strength, high electrical conductivity copper alloys having excellent hot and cold working capability, while exhibiting much improved structural stability in the temperature range 500°C to 750°C compared with previous commercial alloys.[8] The production of alloys by means of ingot technology often leads to micro- and macro-segregation and separation of phases and impurities. Large, brittle particles and coarse grain size results. Alloy development is sometimes restricted because of coarseness of structure resulting in limitations on hot and cold plasticity. The slower the solidification process, the greater the degree of this segregation, structural coarseness, etc. One means of avoiding these problems is to produce the alloy in fine powder or pellet form and hot process aggregates of this material. In practice, the research referenced above used nitrogen atomized alloy powders produced at the relatively high-cooling rate 10^3 to 10^4 °C/sec. The powders were canned and hot extruded to produce bar stock.

This method of Cu-Zr and Cu-Zr-Cr alloy production resulted in superior ductility to ingot-type material and in excellent hot and cold plasticity. The high-temperature stability of the alloys, as measured by stress-rupture data at 400°C to 650°C and by the retention of room temperature properties after exposure to temperatures of 400°C to 800°C was excellent. Thus in this case a superior copper alloy was produced by the combination of small zirconium additions and special matallurgical processing.

Another example of the first category is the use of zirconium to stabilize the substructure of aluminum alloys. In particular, strip-cast zirconium bearing Al-Mn-Zr (about 0.25 percent Zr) have been developed.[9] These can be tailored to be ultra-fine grained superplastic Zr-bearing aluminum alloy or half-hard as used in low-alloy sheet material. Strip casting is another fabrication method for achieving the higher cooling rate necessary for obtaining a high supersaturation of Zr. This property is necessary in combination with cold rolling and heat treating to achieve an excellent balance of strength and ductility.

Major Constituent Zirconium Alloys

There are numerous examples of major constituent zirconium alloys. One class of this type is intended to replace the zircaloys. The requirements for such alloys are very high strength with sufficient ductility, for drawing into tube product for nuclear industry applications. Work on a Zr-Mo-Nb-V-Sn alloy showed that high strength levels (170K p.s.i.) can be achieved with ductility (3 percent) somewhat higher than previous high strength zirconium alloys.[10] The alloying elements in this material function as follows: Sn (3 wt%) acts as an alpha (h.c.p.) stabilizer that provides solid solution strengthening of the alpha zirconium phase; V (2 wt%), Mo (0.75 wt%), and Nb (2 wt%) serve as beta phase (b.c.c.) stabilizers. Strengthening is primarily by the formation of a second phase, either the beta or an intermetallic compound such as $ZrMo_2$ or ZrV_2.

Finally, a relatively young member of the alloy family is the metallic glass. The glass is an amorphous alloy usually made by rapidly solidifying the molten material before a lattice structure has an opportunity to form. Zirconium is known to form glasses with other metals. In practice, the high cooling rates require production as thin ribbons. Outstanding tensile and corrosion properties are measured on some glasses due to the absence of grain boundaries and crystalline defects. A typical zirconium glass is $Cu_{46}Zr_{54}$, which can be annealled below its glass transition (devitrification) temperature (Tg) to vary micro-hardness and sheer stiffness depending upon the properties sought.[11] Table 5 shows the high values of hardness, fracture stress, and other properties obtained on a $Cu_{57}Zr_{43}$ amorphous ribbon alloy compared with a beryllium bronze alloy. Unfortunately, the geometrical and production cost constraints have generally restricted structural uses of metallic glasses, although special applications of certain glasses in transformer cores, transducers, and sensors have been made.

Recent Developments in Amorphous Zirconium Alloys

As noted above, rapid solidification methods normally produce only thin ribbons, flakes, or particles. A new diffusion process in the developmental stage has produced several compositions,[12] however, this low temperature (100°C to 300°C) method holds promise for a wide variety of useful alloys currently made by rapid solification. A major advantage of the new method lies in its ability to make bulk amorphous (glassy) alloys. In addition to applications mentioned above, high strength and exceptional corrosion resistance has been found in ferrous versions of amorphous materials. Instead of heating metals 1500°C to 2000°C before impinging them upon cooling surfaces, the diffusion process utilizes mixtures of metals which react exothermically. The heat of reaction allows the diffusion to take place at lower than crystallization temperatures. Amorphous "hybrids" of zirconium and rhodium were the first produced. Since then other mixtures including nickel-zirconium have exhibited amorphous structures in bulk form.

TABLE 5. MECHANICAL PROPERTIES OF $Cu_{57}Zr_{43}$ AMORPHOUS ALLOY AT ROOM TEMPERATURE

ALLOY	HARDNESS (DPN)	FRACTURE STRESS (kg/mm^2)	PROPORTIONAL LIMIT (kg/mm^2)	YOUNG'S MODULUS (kg/mm^2)	ELONGATION (%)
Amorphous $Cu_{57}Zr_{43}$	540	200	138	7.6×10^3	0.1
Beryllium bronze 25 alloy	380 445	130 140	112 120	--	1 2

Strain rate: 6.6×10^{-5} sec^{-1}

(From: S. Tomizawa, T. Masumoto, "Mechanical Properties of Amorphous Cu-Zr Alloy, Science Reports of Research Institutes, Vol. 26 #4-5 (1977) Sendai, Japan)

ZIRCONIUM COMPOSITES AND CERAMICS

Current research and development in the ceramics and composites areas can be described as quite vigorous. Ceramic substitutes having superior physical properties are being sought for replacement of metals used in certain structural applications. Ceramic substitutes will be welcome especially in components (engine hot parts, thermal surfaces, etc.) subject to high temperatures and harsh environments. They are expected to extend the service life and operating temperature range significantly over current practice. Fabrication methods are being developed for producing bulk ceramics, coatings, and composites of better more reliable physical properties. Stabilized zirconia ($Zr\ O_2$) and ZrN are materials for consideration in this context. Fabrication methods and potential applications will be discussed in the following sections.

Zirconia ($Zr\ O_2$), the principal ceramic forming compound of zirconium, normally forms a monoclinic structure below 1200°C. Above this temperature a phase transition occurs with some volume change to a tetragonal structure which is stable to its melting point 2672°C. The volume change brought about by this transition will cause very high internal stresses in zirconia fiber metal matrix composites subject to high temperatures (>1200°C) with detrimental effects on fracture toughness and crack propagation.[13] It has been found that the addition of about 6 wt% $Y_2\ O_3$ (YTTRIA) during fiber production can stabilize the tegragonal structure at room temperature to yield fibers of 1.2 GN/m^2 ultimate tensile strength and 150 GN/m^2 modulus.[14] The above discussion indicates the possibility at least of practical ZrO_2 fiber-metal matrix composites for service in high temperature environments.

Zirconia Fiber--Metal Matrix Composites

Based upon the above discussion and taking the work of References 13 and 14 as a basis, a few remarks concerning zirconia fiber--metal composites are appropriate. Graphite and alumina fibers, used in most metal matrix composites, have moduli of 3.5 to 15 GN/m^2 and tensile strengths in the range 28 to 45 GN/m^2. Therefore any advantage of a zirconium fiber composite will not be based primarily upon the fiber tensile strength, but rather upon the fiber-matrix compatibility (surface bonding) and favorable high temperature properties.

In the work of Reference 14, stabilized zirconia fibers were added to a nickel alloy matrix. Although the study dealt with high temperature oxidation behavior of these composites in aggressive environments such as those found in jet engine components, there is much room for development of such composites for other less demanding applications. The factors underlying the choice of ZrO_2-nickel included: the ready availability of the relatively inexpensive, stable fibers; the use of nickel as basis for many existing superalloys and existence of several nickel coating techniques for the fibers; molybdenum, present in solid solution as a strengthening agent in the nickel matrix, also aids in improving fiber wettability.

Electroless nickel was chosen for fiber precoating. The uniformly nickel coated fiber bundles were laid up in cloth form and hot pressed into the matrix material in the range 900°C to 1300°C. This produced homogenous, fully dense composite material from which samples were taken for oxidation testing. It was noted that relatively good bonding was obtained for this composite system, and that thermal mismatch was minimized since the coefficient of thermal expansions (CTE) of Ni and ZrO_2 are respectively $10\text{-}13 \times 10^{-6}$ and $10\text{-}11 \times 10^{-6}$.

The oxidation tests included exposing sheets of this material to a flow of dry air in the temperature range 900°C to 1100°C. Results of these tests indicated rapid oxidation of the structure. This was surprising and raised the question of how the strong inert zirconia fibers change the oxidation behavior of the normally resistant nickel alloy matrix. Since the nickel alloy matrix material did not melt until about 1300°C, catastrophic-like oxidation was not expected at 900°C. In addition, no evidence for local oxide melting nor any fiber-matrix interaction could be found to account for the presence of a non-protective oxidation system. Upon consideration, the mechanism was believed to arise through oxygen ingression by anionic conduction of O^{2-} through the zirconia fibers to the alloy matrix. The high aspect ratio of the fibers and their high volume fraction (up to 33 percent) increases the effective surface area of the metallic phase which is exposed to the oxidant, rapidly increasing the rate of reaction. The fibers, acting as an oxygen pump, provide a continuous source of oxygen, oxidizing the matrix immediately adjacent to the fiber. This area mechanically separates from the fiber and gross ingress of oxygen can then occur.

Thus the interesting mechanical properties of the composite are undermined at high temperatures by inadequate oxidation properties. A more resistant matrix alloy must be developed or a cladding applied, which would prevent oxygen from reaching the fibers. A major problem with coatings, however, is the maintenance of integrity throughout the composite lifetime, since any local failure would lead rapidly to general failure by oxidative attack. This effect will be accelerated in harsher environments such as those containing fuel or water vapor. Should it prove the case that this corrosion mechanism (O^{2-} pumping) is a general phenomenon in fiber metal-matrix composites, then those who seek high temperature applications for them ignore it to their detriment. The study, however, did show that ceramic fiber-metallic matrix composites be made by practicable routes using techniques of pressure sintering. Fiber bonding requirements were satisfied such that adequate stress transfer occurred. The favorable fiber properties were exploited in a mechanically sound composite. The future of such composites, however, appears to be in applications operating at moderate temperatures where density is not an important factor.

The work of Reference 12 was a more theoretical study on internal stress and fracture behavior of pure zirconia fiber ZrO_2 in a zirconium metal matrix. In this case, the composite was observed to acquire high internal stress due to the volume change of the fiber as it cooled through its transition temperature from the high (>1200°C) formation temperature of the composite. Since for the fiber $V_{monoclinic(X)} > V_{tetragonal(B)}$, $\Delta V\alpha\beta > 0$ and it is known that the enthalpy of the monoclinic tetragonal transition is positive (endothermic). Therefore, a negative temperature change (ΔT) leads to a positive pressure (P), meaning that the fiber is under compressive stress. This implies a tensile stress in the surrounding matrix metal (in the case studied, zirconium). This condition sets up a periodic stress field. In general, the presence of such a periodic stress field energy will be released by a crack travelling along the interface separating the compressive and tensile regions. The zirconium-zirconia composites, crack propagation was observed to be transgranular. When an external load was applied to extend a crack in this material, a higher fracture load was needed to extend the crack. Two reasons for this were: (1) the wavy path of the crack increases its line energy and (2) the crack must enter compressive regions which tend to retard its growth. On the basis of this work it was concluded that the internal stresses do not impair fracture performance of the composite. Also, physical charcteristics of the composite such as elastic modulus, density, and fracture strength remain substantially unaffected by thermal treatments intended to alter the internal stresses.

In this work, no corrosion studies were carried out. Properties such as stress corrosion cracking resistance and the presence of oxygen infiltration mechanisms (as noted above) to the fiber-zironcium metal interfaces in oxygen bearing environments at elevated temperature need to be investigated. Therefore, although further physical performance studies are necessary, the indications of this work are encouraging for the development of zirconia fiber-metal matrix composites.

Zirconium (Alloys) Reinforced with Other Fibers

Other non-ceramic fibers, notably graphite, might be considered for reinforcement of zirconium and zirconium alloys. No applicable research efforts were documented on this subject. However, several observations may be made from previous experience with graphite-metal matrix composites. Most applications of graphite fiber composites have as goal a light-weight, high modulus material which is easily fabricable and low in cost. The physical properties of zirconium which relate directly to these from Table 1 are its density 6.49 g/cc and melting temperature 1845°C. Compared with the densities of aluminum and magnesium (2.7 and 1.74 g/cc and melting temperatures 660°C, 650°C, respectively), zirconium is not a lightweight material. Its high melting temperature poses two problems with its use as a matrix material. First, infiltration of the fibers must take place at this temperature, at which a very large amount of radiant thermal energy will emanate. This condition would virtually preclude hand operations in the infiltration process. More importantly, contact with the liquid zirconium would likely produce zirconium carbide at the fiber metal interface (the stable -ZrC phase is apparent in Figure 3). This will embrittle the fiber, probably destroying it, and at least prevent formation of a satisfactory bond at the interface. Physical properties of such a degraded composite may be expected to be quite poor. Therefore, zirconium does not appear to be a promising candidate for such metal-matrix composites.

Recent Fiber Development Research

Recent efforts at improvement of ceramic fibers for composite applications have centered on polymeric precursors for ceramic fibers. One process puts an organometallic polymer containing titanium through a pyrolizing step to produce a fiber combining silicon carbide and titanium carbide.[15] Fibers are melt

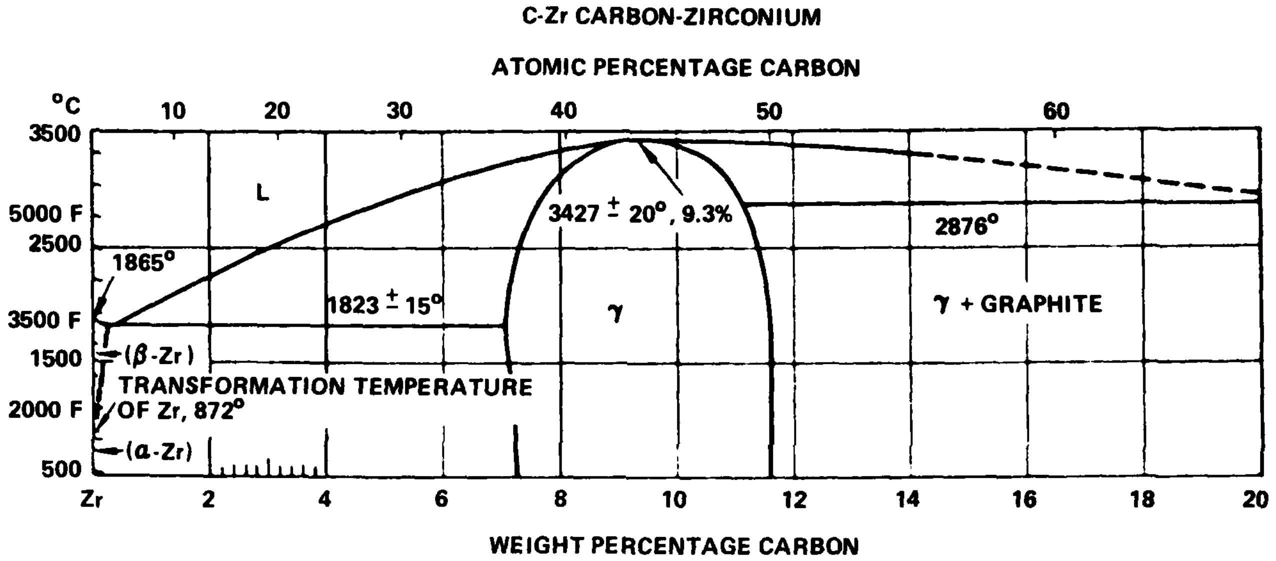


FIGURE 3. THE CARBON-ZIRCONIUM PHASE DIAGRAM (TAKEN FROM REFERENCE 18)

spun, then heat treated at temperatures to 1300°C. Fibers produced by this process may have good high temperature properties and wettability in metal matrices. The chemical similarity of titanium and zirconium make this process a good possibility for a zirconium carbide based fiber with favorable thermal and surface bonding properties. Figure 3 is the binary alloy diagram for zirconium-carbon mixtures which shows the clean zirconium carbide phase. The metal-organic precursor route is being followed in several domestic developmental programs.[16] These efforts should have considerable future impact on ceramic composite development, high modulus fiber synthesis, and ultimately in metal component replacement, especially of alloys requiring strategically important elements.

ZIRCONIA PROPERTIES, METHODS, AND APPLICATIONS

A discussion of zirconia, the ZrO_2 ceramic forming compound, focusing initially on its properties very quickly proceeds to production method and application since in most cases all are closely related. Physically, use categories of ceramic materials may generally be divided into those of surface and bulk. Surface applications include primarily corrosion protective ceramic coatings, tribological coatings, and thermal barrier coatings. Bulk uses consist largely in substitute materials for metal alloy structural members and in special components subject to high thermal stress such as rocket nozzles or certain hot engine components.

Corrosion Resistant Ceramic Coatings

As was discussed in the Corrosion Section, the finely divided metallic zirconium surface is highly reactive in an oxygen environment, however, the bulk metallic surface rapidly acquires an oxide film which protects against further oxidation. Such oxide films may be grown directly on zirconium and its alloys. Yttria stabilized zirconia may be plasma sprayed, sputtered, or hot dipped onto other alloy substrates. These coatings do protect the substrate alloys with the superior corrosion resistance of the zirconia. However, if the coating is breached mechanically, corrosion products will tend to build up in the exposed region. Plasma or flame-sprayed, stabilized zirconia over a thin Ni-Cr-Al-Y alloy intermediate bonded to the base superalloy has been the most successful ceramic coating for use on high temperaure gas turbine blades. However, even with this coating, in the temperature range 700°C to 1000°C severe cracking and spalling was noted in the presence of impurities, particularly Vanadium, in the fuel.[17] Thus, additional research on the corrosion resistance of zirconia at high temperatures in the presence of aggressive impurities is necessary.

Thermal Barrier Coatings

Perhaps the primary use of zirconia coatings is for thermal protection of metal alloys exposed to high service temperatures. Problems encountered in using ceramics for this purpose include: (1) poor thermal shock resistance of low thermal conductivity ceramic materials applied directly to metal substrate, (2) difficulties in obtaining a good ceramic material-substrate bond, and (3) large differences in CTE between ceramics and high temperature alloys.

Stabilized zirconia is a favorable thermal barrier material because of its low thermal conductivity and its high CTE making it compatible with superalloys. In the case discussed above, approximately a 200°C temperature gradient is maintained across the barrier oxide layer at blade operating temperature. This allows the possibility of operating the turbine at higher temperature, increasing its thermal efficiency. However, the benefits of applying any ceramic barrier coating depend critically upon its integrity and its ability to remain adherent to metallic substrates. For example while plasma spraying has achieved success in some hot components, a fully viable zirconia coating for critical applications, such as the case of turbine blades and vanes, has been elusive due to loss of adhesion and molten salt penetration.

A more recently developed method for producing the zirconia coatings is by hot dipping. This method shows promise of mitigating the shortcomings of plasma spraying. The ceramic barrier is achieved by dipping an alloy substrate into a relatively low melting point eutectic then selectively oxidizing the more active component. The Zr-Ni system was used in this effort.[18] Its binary phase diagram (see Figure 4) shows the low temperature eutectic at about 1000°C, 73% Zr-27% Ni (arrow in Figure 4). By dipping a Co-10% Cr-3% Y alloy at 1027°C, a highly adherent, uniform, low porosity coating, which could withstand repeated thermal cycling to 1000°C in air, was produced. Apparently the formation of a ceramic/metallic composite layer between the outer ceramic layer and the inner metallic substrate is highly advantageous. This composite layer reduces the stresses generated from the mismatch in coefficients of thermal expansion of the outer coating and substrate. The dipping technique has the further advantages of relative simplicity and of being applicable to any substrate shape. It is a quite recent development which appears to deserve further study for suitability over a variety of alloy substrates.

Tribological Coatings

There is a need for reproducible surface treatments to improve the tribological or frictional response of mating precision mechanical parts, especially in service where only limited lubrication can be made available. Sputtered layers of refractory metal compounds (ZrN, TiN) have been suggested and tested for their ability to reduce friction and extend the lifetime of rotating parts. Where a hard refractory metal compound layer is required, most sputtering methods are likely to thermally overstress the component being coated in order to obtain an adequately adherent and homogeneous coating. Such components normally require maintenance of exact tolerances which are easily destroyed by thermally caused distortions. A hot rod target sputtering system eliminates this problem since, despite high sputtering rate of the target, the total power dissipation is modest and the components being coated remain relatively cool.[19] This method ensures adherence of stable compound layers by its ability to deposit a reactive elemental layer of high purity metal before synthesis of the compound is initiated. For preparation of the nitride ZrN, the argon sputtering atmosphere contains nitrogen gas which forms the nitride from the sputtered coating. Complex shapes can be so coated. In the reference study a very high quality film was deposited over various superalloys with excellent results. The zirconium nitride target sputtered coatings applied to valves and rotating parts prevented erratic running and local welding that occurs in such

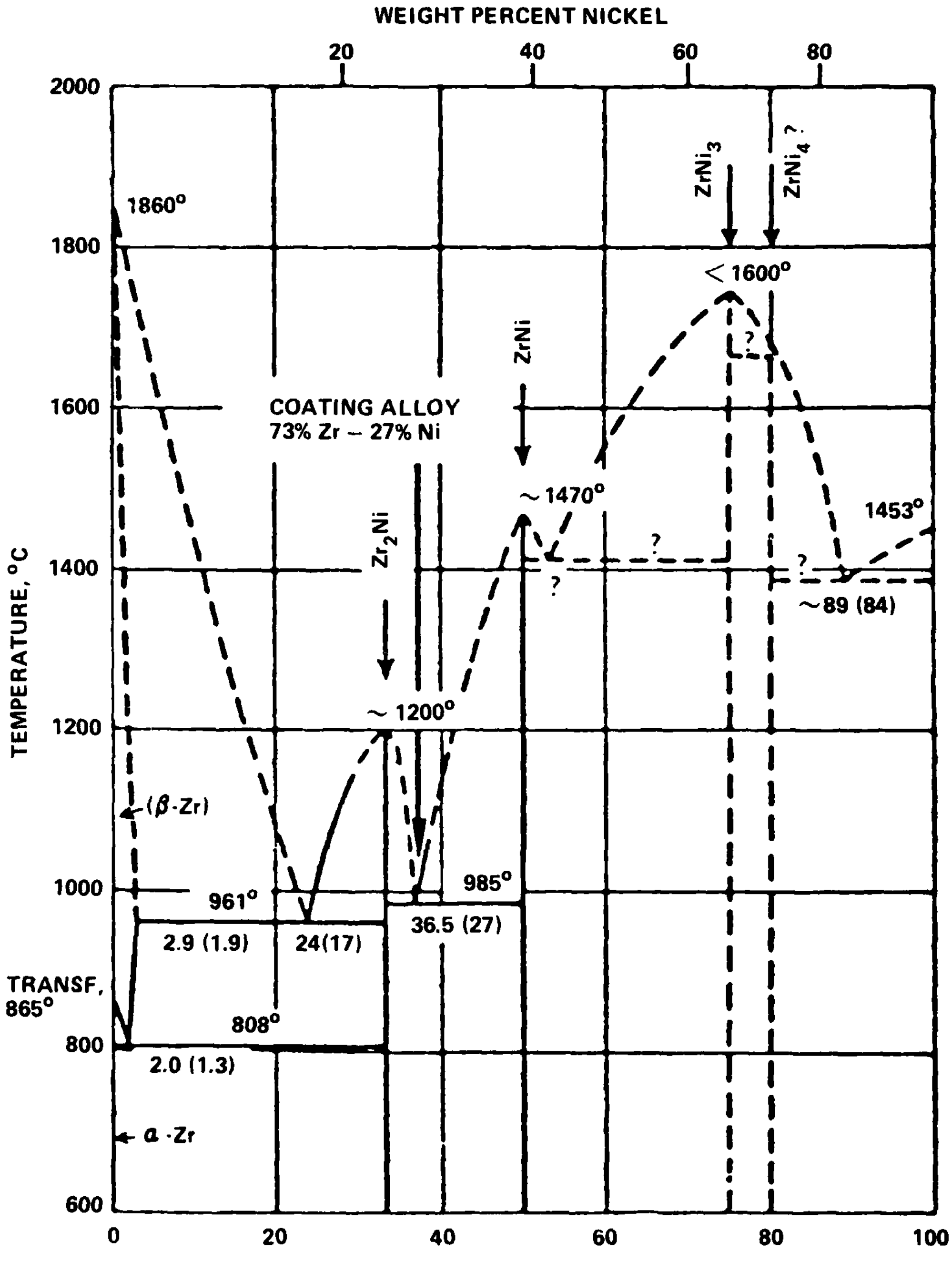


FIGURE 4. THE ZIRCONIUM-NICKEL PHASE DIAGRAM (TAKEN FROM REFERENCE 18)

applications under as ground conditions. Even at highest applied driving and side load forces smooth running was obtained even at very high operating speed. This demonstrates the adherence, toughness, and smoothness attainable in a zirconium based coating for surfaces subject to severe mechanical service requirements.

BULK ZIRCONIA CERAMIC FABRICATION METHODS FOR STRUCTURAL APPLICATIONS

Ceramics for most bulk component and structural applications have been hampered by the virtual lack of fracture toughness and sensitivity to micro-voids and cracks. However, recent developments in fabrication methods, which have resulted in improved physical properties, hold the promise of far wider use of ceramics as structural materials. Zirconia may be expected to take an important role mostly as a ceramic matrix material.

Ceramic Composites

Methods of ceramic formation are discussed below and research has been proposed[20] to demonstrate how the reliability of structural ceramics can be increased by using high performance refractory fibers, whiskers, or platelets as reinforcements. The proposed research will consider specific shaping techniques. Organometallic binders will be examined for their ability to control the quality of the matrix-reinforcement interface. This interface is of prime importance in controlling crack propagation through the ceramic matrix. In a conventional ceramic, a crack starting at any point in a stressed cross section, will be quickly transferred throughout the cross section as cleavage occurs. If reinforcement fibers are added to reduce this tendency to fracture, they must be loosely coupled to the ceramic matrix. If the interface bonding is too strong, the energy of a crack impinging from one direction in the cross section will be transmitted directly around the fiber through the remainder of the cross section. If the fiber-matrix coupling is weak, a crack will tend to dissipate its energy by pulling out the fiber. Recently, special coating of ceramic fibers has provided this weak coupling and demonstrated increased toughness as well as tensile strength.[21] It was shown that for matrices which normally give strong bonding and hence brittle fracture, low strength, and toughness, the use of coated fibers gave up to a hundred fold increase in toughness and four fold increase in strength. These techniques of composite ceramic fabrication are expected to significantly impact the scope of structural ceramic applications.

Ceramic Sintering with Additives

Sintering has been a standard ceramic fabrication method. Recent developments have shown that the sintering temperature of zirconia can be reduced substantially. Sintering of monoclinic zirconia powders were carried out at temperatures below 1150°C using a vanadate (V_2O_5) flux additive. Greater than 92 percent theoretical density has been obtained indicating densification by reactive liquid phase sintering, aided perhaps by defect migration. The optimum combination of density, strength, and expansion coefficient was found to occur for a V_2O_5 content of 1.5 wt%.[22] The careful use of additives, therefore, can result in significantly improved ceramic properties.

Dynamic Compaction of Ceramic (and Metal) Powders

Dynamic powder compaction is a materials fabrication process which utilizes a combination of extremely high velocity and pressure to densify powders very rapidly. Although development of this process began in the 1940's, little domestic effort has been devoted to the process, principally because other powder fabrication processes have been more attractive economically. Recently, however, the advent of amorphous and metastable micro-crystalline, rapidly solidified materials and the need for very high strength ceramics have called for fabrication requirements which probably cannot be met by the more common powder fabrication techniques. Dynamic powder compaction can potentially meet some of these requirements.

In this context, dynamic compaction is identified as a process in which powder densification is achieved by a high-pressure shock wave (generated by gas gun, explosive, dynamic ram, etc.) which exceeds the yield strength of the powder mass. The velocity and pressure required are dictated by the properties of the powder being compacted. Figure 5 shows one method of producing the compressive shock wave. Some unique advantages of this method are expressed as follows:

> "Theoretical densities approachable in wide variety of metals and ceramics, compaction often achievable at ambient temperature without subsequent thermal treatment, unique micro-structure achievable while maintaining powder properties, high process pressures can be used to synthesize unique and difficult to produce materials phases and combinations of materials can be compacted without direct interaction between the constituent phases."[23]

Shock conditioned ceramic powders have been found to be unusually responsive to sintering operations. This high activity is believed to be related to the introduction of large numbers of (strain-induced) defects into the crystal lattice by the shock treatment. Use of such shock-conditioned ceramic powders in various fabrication processes may provide a unique way to produce materials with improved microstructure and properties. The experimental evidence suggests that shock treatment of ceramic powders corresponds to cold-working in metals. This degree of freedom in controlling microstructure is not normally available in ceramic fabrication. This is one of numerous interesting phenomena observed with this largely unexploited technique. Among many other metals and ceramics, Zircaloy-2, ZrB_2, ZrC, and ZrO_2, alone and in combination with other materials have been successfully compacted by this method.

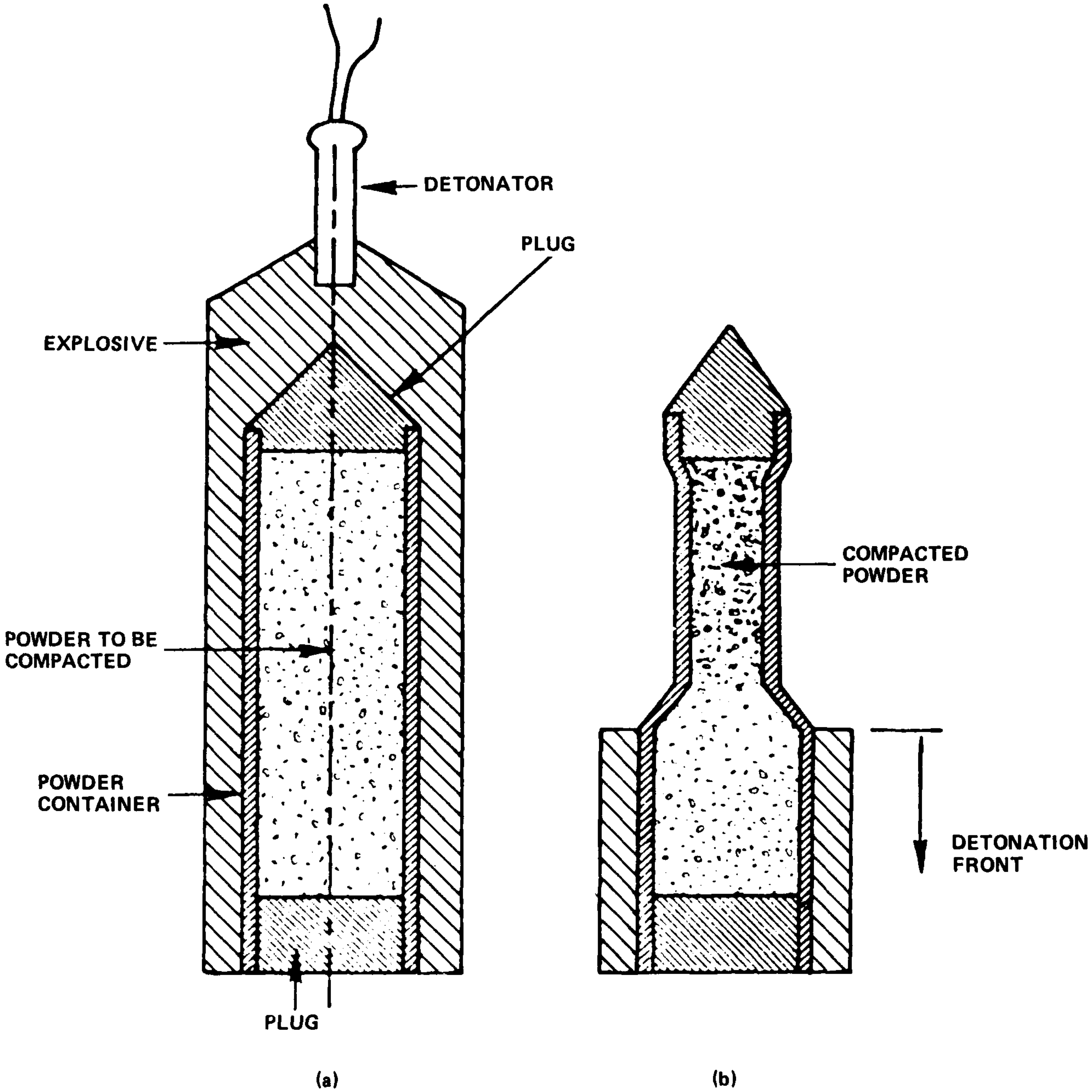


FIGURE 5. ASSEMBLY FOR EXPLOSIVE COMPACTION OF POWDERS: (a) PRIOR TO COMPACTION AND (b) DURING COMPACTION (TAKEN FROM REFERENCE 23)

Transformation Toughening of ZrO_2 Ceramics

Recent research has resulted in a process to manufacture structural ceramics far stronger and more adaptable for component applications than are most conventional high-grade ceramics.[24] The key has been the adaptation of the technique of transformation toughening to slip casting, the most common method of ceramic forming. In this adaptation, a mixture of aluminum oxide and zirconium dioxide powders is pressed together at very high temperature. Prerequisite, however, are the prior reduction of the powder particle size to less than 1 micron and the use of a dispersant to facilitate flow of the powder/water mixture into the casting mold. Materials produced using this hybrid process show a fracture strength of 125,000 psi compared with that of high-grade porcelain of 5,000 to 10,000 psi. It is interesting and rather exciting that relatively simple modifications of existing techniques can yield such an improvement in properties. This appears to be a particularly auspicious development for the future of zirconia-based structural ceramics.

STRUCTURAL CERAMICS LIMITATIONS/QUALITY ASSURANCE

Despite the favorable supply picture and new ceramic fabrication methods, basic limitations of ceramics as structural components cannot be overlooked. Mechanical reliability has always been a problem. Even the toughest ceramics lack the ductility of metals. They are conspicuous for their sensitivity to tiny flaws. The newer particle- and fiber-toughened ceramics, while they bring important benefits, unfortunately often exhibit reduced flex strengths and moduli. Environmental effects and fatigue enters the picture for some of these toughened ceramics. This brittle behavior imposes a challenge on designers to develop unique approaches for assuring product reliability. There are important issues to be faced if structural ceramics are to achieve mass-production status. Statistical distribution analysis of flaws has been applied to failure probability prediction, a technique which shows promise in this area. Measuring only in tial properties has its limitations, however, as slow crack growth and service environments play a role in performance. Proof testing to levels of maximum anticipated service stress has been done, but also is limited. Duplicating thermal stress conditions in tests on turbine engine components, for example, is all but impossible. Non-destructive evaluation (NDE) also holds promise, but an adequate data base will have to be accumulated before reliable correlations between flaw characteristics and long term performance can become useful. One of the basic problems is that test methods and quality control systems do not allow for changes in material properties of components in service. As emphasis on ceramic substitute and new applications increases, efforts at developing reliable comprehensive testing methods under in-service conditions should keep pace.

CHAPTER 5

ZIRCONIUM: SOME FACTORS IN COST AND PRODUCTION

From the viewpoint of raw material availability and product output capacity, the prospect of increased use of zirconium and its compounds is good. Some 80 percent of the free world zirconium supply is U.S. produced with most of the balance French produced. According to a senior production engineer, sufficient plant capacity is readily available for foreseeable increased demand for the metal. Large quantities of zirconium (alloy) sheet, tube, and special stock could be produced. The present domestic production of finished zirconium is about 10 x 10^6 lbs/year.

Although zirconium bearing sands are plentiful in coastal regions of the continental U.S., there are rather serious environmental barriers to the major exploitation of this resource. In addition, the concentration of zirconium in domestic ores is only about 50 percent that of the material presently processed. The latter is obtained at very low rates on long term contract from Australia. There is a virtually unlimited supply of this raw material. The present price of refined pure zirconium metal of $20 to $35 a pound (depending upon the final form, viz., tubing, sheet, etc.) would necessarily rise significantly if domestic ores were used. Not only would twice as much raw material have to be processed, but also the necessity of environmental protection would generate additional costs. As a structural material, zirconium has been considered expensive. However, zirconium production has largely been untouched by the economic, political, and environmental problems which have caused substantial price increases in other critical metals. This, of course, has been due to the very favorable ore supply situation coupled with an expanding industrial market. Table 6 compares recent specific costs of zirconium with several industrially important similar metals (alloys). The entries indicate the relative cost competitiveness of zirconium.

Processing costs for zirconia (ZrO_2) for bulk ceramic structural applications can be expected to be significantly lower than for the pure metal. To produce ZrO_2 from the $ZrSiO_4$ bearing sands, thermal processes are available to extract ZrO_2 without first reducing to the metallic state. This offers the possibility, at least, of wide future use of ceramic structural materials.

TABLE 6. COST OF SOME ALLOYS COMPARED TO ZIRCONIUM

ALLOY	RELATIVE PRICE PER UNIT WEIGHT	RELATIVE PRICE PER UNIT VOLUME
Zirconium	1.0	1.0
Titanium, Grade 2	0.7	0.5
Hastelloy Alloy B-2	1.1	1.4
Hastelloy Alloy C-276	1.0	1.2
Tantalum	20.0	50.0

(Taken from Reference 3)

CHAPTER 6

RECOMMENDATIONS FOR ZIRCONIUM APPLICATIONS AND RESEARCH EFFORTS

Based upon the foregoing information, various recommendations can be made depending upon assumed viewpoint. Also several categories of application are discernible. Perhaps the most meaningful division might be in terms of more conventional component substitute applications versus substitute and new applications requiring special high-performance properties. The latter category will most likely entail research and development effort using one of the innovative fabrication methods discussed above.

ZIRCONIUM ALLOYS/COMPONENT SUBSTITUTION

It is quite apparent from the foregoing discussion that zirconium is, and will no doubt always remain, a specialty metal. Thus recommendations for its indiscriminate use as a structural material would be quite unjustifiable. Indeed, many of the industrial processes involving handling of acid or alkali liquids at high temperatures, distillation of corrosives, and the like have no direct counterpart in marine systems. However, the Navy's need for long-lived, durable systems in intimate contact with salt environment should provide numerous opportunities for zirconium-based substitutes for vulnerable conventional metals.

An example of such a substitution might be a heat exchanger continually exposed to seawater. Since heat exchanger applications in harsh industrial environments are ideally suited to zirconium, there is little question as to adequacy of performance. The important question becomes whether the higher initial cost is justified by the prospect of virtually maintenance free (no painting, no corrosion, etc.) operation over the entire life of the ship system. Again one can envision the use of a relatively thin zirconium or zirconium alloy cladding bonded over a lightweight metal or metal composite hull structure. In this case, the cladding provides maintenance-free corrosion resistance while the base metal (or composite) provides a lightweight strong substructure. The question again is one of life cycle cost of the component. Special factors must be included in the analysis such as in this case the prevention of possible galvanic couples in seawater which will corrode the less noble base metal (see Table 4) or the special welding techniques required for damage repair. In any event, cost-benefit analyses must be performed to determine the feasibility of zirconium metal substitutes in basic marine systems.

Special uses of zirconium include ordnance casings and liners where its incindiary properties are exploited. Other structural uses include those in which strength, toughness, and workability in fabrication coupled with relatively high melting point and excellent corrosion resistance. Examples of such might be antenna arrays, high temperature engine components, replacement for superalloys, special parts for weapons systems, and the like. Candidates for substitute or modification could be identified from operational experience on systems with durability, reliability, or maintainability problems. In each case, a cost-benefit analysis should be made to determine whether the substitute with inevitably higher component cost would be justified for life-cycle cost savings. In the case of planned future systems, consideration should be given to substitution with zirconium based alloys of components such as pumps, valves, or other parts subject to thermal and mechanical stress in the marine environment. Substitutions of this type take advantage of the great resistance to subtle corrosion mechanisms of zirconium alloys noted above.

Deliberately omitted has been mention of zirconium alloys and compounds in space structures. Generally speaking the density of zirconium (6.42 g/cc) and zirconia (5.6 g/cc) are not compatible with the requirements of very lightweight structures. In addition, the very high corrosion resistance of zirconium is of little value in such applications. Thus, except perhaps for some specialized parts, zirconium and zirconia probably will not find widespread use in these structures.

ZIRCONIA CERAMIC/COMPOSITES RESEARCH

Possibilities for research and development efforts in the areas of zirconia ceramics, composites, and coatings have been implied in the foregoing discussion on zirconia ceramics, composites, and refractory coating technology. These probably constitute the most fertile areas for increased use of zirconium as a structural material. The new developments in producing high strength bulk ceramics by dynamic compaction and transformation toughening seem to be quite exciting for the future, as are the prospects of structural ceramic composites employing zirconia or other materials as matrices reinforced with high-performance refractory fibers. Structures such as sonar domes or other components requiring nonconducting materials could be built from these materials. Engine components, heat shields, and the like could be manufactured from high-performance ceramics. Substitutes for critical elements cobalt, chromium, tantalum, and niobium used in nickel-based superalloys might best be achieved in some cases by outright replacement with ceramic components.

With regard to research commitment to improved ceramics and ceramic composites, Japan has taken major steps in this direction over the past several years. There is no reason, given the materials expertise present in our country, that a highly successful domestic program could not be mounted in these areas. There are still basic materials problems to be addressed such as the development of ceramics having fracture toughness and ductility as well as strength and consistent batch-to-batch properties. Solving these should lead to a burgeoning of applications for structural ceramics. If recent prototype work by many manufacturers on ceramic (largly zirconia based) engine components (and indeed complete engines in some cases) is any indication, new applications are just around the corner. With a directed effort at development and integration of these materials within the Navy toward its future needs, many new applications could be found and perhaps an entire new generation of structural materials.

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