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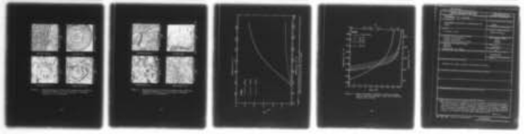

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FINAL REPORT

ANISOTHERMAL OXIDATION OF TITANIUM AND ITS ALLOYS

1. OBJECTIVE

The objective of this research has been to provide from laboratory experiments and analyses a capability for the prediction of oxidation-associated ignition of reactive metals; especially titanium and its alloys. Emphasis was placed upon the generation of basic information for subsequent application to technical problem areas where high rates of heating prevail or are suspect, as in engine fires and laser-assisted ignition.

2. METHOD OF ATTACK

The research performed has been expressly intended to exploratory and experimental in nature, involving continuously alternating emphases upon experimental observation and the mathematical modeling of those observations. Much of the conceptual basis for this research has been derived from our prior research now publised as AFML-TR-74-265 under the title, "Exploratory Development on Oxidation Behavior of Titanium Alloys under High Heating Rates" which is here incorporated by reference.[1] The additional concepts of computer data acquisition, modeling and analyses coupled with the generation of specialized testing techniques have been primary missions of this research term and are described below.

3. FIRST YEAR ACTIVITY

The major thrust of this grant research conducted between 01 October 1975 and 30 September 1976 was summarized in the paper entitled: "Anisothermal Oxidation of Titanium - Initial Reactivity and Ignition" which was presented at the 150th meeting of the Electrochemical Society in Las Vegas, Nevada on 19 October 1976. That presentation has subsequently been published in "Proceedings of the Symposium on Properties of High-Temperature Alloys" and is thus incorporated by reference.[2]

In that work involving the reaction of unalloyed titanium with 200 torr oxygen, we showed that the anisothermal oxidation was describable by parabolic reaction kinetics at low heating rates (~0.5°C/s) so that oxygen fixation could be expressed as:

$$N^2 = N_o^2 + K_p t. \qquad (1)$$

At intermediate heating rates (~10°C/s) it was found that the kinetics were initially asymptotic and describable as:

$$N = N_o + K_a\,[1-\exp\,(ct)] \qquad (2)$$

which behavior was superceded by parabolic reaction kinetics for exposure time in excess of the temperature-dependent transfer time:

$$t_{xf} = 1.47 \text{ X } 10^{8} \exp(-0.0101)\ T \tag{3}$$

Still higher heating rates ($\gtrsim$ 20°C) led to an effective reaction area multiplication which we had described by the dimensionless parameter (γ) and the deposition of the chemical heat of reaction for which we had constructed the dimensionless partition function (β). As these higher heating rates often led to ignition, a heat delivery parameter was develo[illegible] in the form:

$$\overset{\circ}{q}_{v} = \overset{\circ}{N}\ \Delta H\ S_{v}\ \beta\ \gamma \tag{4}$$

which proved to be a semiquantititative predictor for the oxidation-associated ignition of unalloyed titanium. This parameter takes into account effects arising from variations in chemical reactivity and heating rate (through the $\overset{\circ}{N}$ - term), chemical heat and its coupling to the substrate (through the ΔH - and β-terms), specimen geometry (S_V) and effective areal dilitation (γ).

Application of Eq. 4 to tests involving CP titanium specimens of various thickness and subjected to a variety of thermal regimes indicated that ignition was induced when $\overset{\circ}{q}_V$ exceeded a value on the range between 0.1 and 1.0 cal/cm^3-s. Based upon this, we concluded that localized rather than general heating of the substrate is a probable precursor step in the ignition process.

4. SECOND YEAR ACTIVITY

4.1 - Equipment

The basic volumetric apparatus consists of a Vycor reaction tube surrounded by a 12KW infrared furnace with ancillary gas handling, power control and recording devices described previously.[1] During the course of this research, that equipment was modified to provide analog signals for temperature, pressure, furnace voltage and current and was subsequently interfaced with an analog/hybrid computer for the purpose of data acquisition at rates up to 120/second.[2]

As a result of questions posed by others concerning the quality of measurements produced by our apparatus, special modifications to and tests of the apparatus were instituted during the current report period. These operations specifically involved the pressure and temperature sensing channels.

The characteristic time of the pressure transducer was determined in response to questions which were raised during the Las Vegas presentation. A 40 ml sealed glass cylinder containing air at one atmosphere was placed in the reaction tube and the system was subsequently evacuated to a pressure of 100 torr. The glass cylinder was broken by dropping a metal plunger and the resulting pressure increase was measured using the graphic results from the recorder. The characteristic time (τ) was determined to be 0.10 ± 0.02 sec. by fitting the graphic results to the equation:

$$P = P_f\,[1-\exp(-^{t}/\tau)]. \tag{5}$$

Using this information, the maximum specific reactivity ($\mathring{N}$) which the transducer could measure would be 1.1×10^{-2} mole/s-cm^2. Similar results were obtained after the system was evacuated to 50 torr; the maximum measurable specific reactivity being 2.9×10^{-2} mole/s-cm^2. These specific reactivity values are at least one order of magnitude larger than any ($\mathring{N}$) value heretofore measured during ignition. It was concluded that the characteristic time of the pressure transducer is sufficiently short to allow accurate determinations of ($\mathring{N}$) both prior to and during ignition.

Having verified an adequate response in the pressure-sensing channel, a technique for the semiautomatic analysis of oxidation kinetics was developed. In all prior reported work, the oxidation kinetics were derived from graphic pressure-time traces which involved the manual comparative analysis of "blank" and "test" pressure data.[1,2] In order to obviate this task and the attendant requirement for dual tests to provide a single set of kinetic data, average "blank" run data were modeled and stored in the computer. Thus, for example, the pressure data for a "blank" run of 8°C/s to 1100°C with a 15 minute "hold" at 1100°C were modeled using the fifth order polynomial:

$$P = P_o - 8.38 + 0.286t - 5.91 \times 10^{-4}t^2 + 4.13 \times 10^{-7}t^3 + 6.22 \times 10^{-10}t^4 - 1.20 \times 10^{-12}t^5; \quad (6)$$

where (P_o) is the initial pressure in torr and (t) is the time in seconds. This polynomial was primarily chosen so the model curve would closely fit (maximum error 0.5%) the sigmoidal shape of the pressure curve during heating. The polynomial also fits the graphic (recorder) curve within an error of 3% of the pressure at the end of the 15 minute "hold." These errors are considered acceptable for the purpose of analyzing the anisothermal oxidation kinetics of titanium under the "closed-loop" heating mode where heating rates do not exceed ~10°C/s.

Storage of data from ignition experiments has also been accomplished and one result of these experiments was the computer-assisted measurement of a heating rate of approximately 2,000°C/s. This value is an order of magnitude above our previous rates measured graphically and indicates the limit of the rates which can be recorded using computer-assisted acquisition of data. Also, this value is an indication of the relatively low thermal inertia of the thermocouples located at the base of the test specimen.[1]

This result notwithstanding, questions have been posed concerning the validity of our temperature measurement technique. The doubts raised here were emphasized by other experimenters who had indicated that they observed the onset of ignition at or near the melting point of titanium (~1810°C); whereas, our observations indicated the onset of ignition at temperatures as low as 400°C. In view of these factors, the equipment was modified to provide a second temperature monitor.

As the ignition of titanium occurs in our apparatus only under relatively rapid "open-loop" heating, the "feedback" thermocouple is redundant and was altered in function to become a second temperature-sensing element. It was located at the upper tip of the 1 by 5 cm test specimen as illustrated in Figure 1. In this position, the thermal inertia of the specimen is minimal and if general (vs. localized) melting or burning were to initiate it should do so there. The output of this thermocouple element was in turn "conditioned" and fed to the data acquisition section of the computer system. In this manner, both upper and lower thermocouple outputs were sampled and recorded at rates of up to 120/s. It was found that this upper thermocouple did record both higher temperatures and heating rates than did the lower thermocouple; however, these differences were of a relatively minor nature.

4.2 Materials

Both CP titanium and several titanium-base alloys were examined during the second year of grant operations. Approximately 20 pounds of sheet stock was supplied to us through the courtesy of Dr. S.R. Lyon of the AFML. Materials of that shipment included CP titanium and the 3 structural alloys: Ti-6Al-4V, Ti-8Mn and Ti-11.5Mn-6Zr-4.5Zn (β-III alloy).

Additionally, late in the second year of operation, we received small quantities of "ignition-resistant" alloys in the form of slabs, sheets and castings through the courtesy of Mr. Brian Manty of the Pratt & Whitney Aircraft Corp. The materials of that shipment included: the intermetallic TiAl, the intermetallic Ti_3Al, and the following structural alloys: Ti-8Al-1Mo-IV (8Al super alpha), Ti-6Al-2Sn-4Zn-6Mo (6-2-4-6) and Ti-13Cu (a developmental alloy of the Garrett Corp.).

Specimens for oxidation/ignition tests were fabricated from these materials by diamond slab-sawing to plan dimensions of 1 by 5 cm. Secondary sawing and/or wet grinding operations were employed to set final gage thicknesses in the range 0.01 to 0.03 cm; the terminal finish of all specimens being a 600-grit SiC metallographic finish.

4.3 Experimental

During the second year of grant research, experimental efforts were directed toward several facets of the problems involved with oxidation-associated ignition. These efforts evolved several distinct but related experiments in the following major areas: 1) Studies of oxide scale morphology, 2) an investigation of the effect of oxygen pressure upon ignition behavior, 3) an attempt to evolve a screening test for alloy ignitibility, 4) an investigation of the effect of prior oxygen saturation upon ignition behavior and 5) applications of computer modeling to areas of technical importance. These items will be described below in sequence.

4.3.1 - Scale Morphology Studies

There are two primary driving forces in this research for an investigation of the structural evolution of oxide scales upon titanium: a) one dealing with its influence upon the parameters (β) and (γ) which govern the partition of the chemical heat of reaction and describe the areal expansion, respectively and b) one dealing with a potential structural factor in the pressure sensitivity of oxidation-associated ignition. The latter concept will be directly addressed in the following section of this report.

Recall that the geometric dependence of (β) was expressed as:

$$\beta_g = \frac{X - X_D}{X X_D} , \qquad (7)$$

Where (χ) is the total scale thickness and (χ_D) is the characteristic thermal diffusion distance.[2] The central question now becomes whether or not it is reasonable to presume that the oxide structure can attain the rapid "degree of advancement" predicted by equation (7) as fit to observation; i.e., for example, a near-total recrystallization during the nominal 15 s heating period from 25° to 564°C (ignition at 40°C/s.[2]). The development of faceted oxide grains upon the external surface of the scale would indicate that a high degree of advancement had been attained.[3] The development of the porosity in the depth of the scale layer or other "short-circuit" paths could provide a similarly effective mechanism operating on (β_g) and would also strongly suggest the existence of an oxygen-pressure dependence upon reactivity.

Both short - and long-term oxidation tests were undertaken to investigate the scale structure. The short-term tests involved heating 0.01 cm. thick CP titanium specimens at the rate of 10° or 20°C/s to 600°, 700° and 800°C, holding the specimens isothermal at each of these temperatures for various fractions of the asymptotic-to-parabolic transfer time (t_{xf}; Eq. 3) and subsequently cooling them at an initial rate of 8°C/s. The SEM photomicrographs of Figures 2, 3 and 4 illustrate the oxide surface microtopography generated after heating at 10°C/s. Calculations based on this and similar information indicated that at the transfer time (t_{xf}), the oxide thickness was of the order of the oxide grain dimension upon the gas-oxide interface. From these photographs, several other significant observations may be made:

1) That there is no major indication of oxide cracking despite the mild thermal shock imposed.

2) That clear evidence of oxide faceting occurs for isothermal exposure times less than 12 percent of (t_{xf}) in all cases and at the immediate end of the heating period for the higher temperatures.

3) That there is little evidence of oxide exudation in any of the photographs indicating that the oxide has limited plasticity as compared to ductile oxides such as NiO,[4] and,

4) That as isothermal exposure times approach a major fraction of (t_{xf}), void space between oxide crystals develops into the depth of scale.

The SEM photomicrographs of Figure 5 illustrate the oxide surface microtopography generated after heating CP titanium at ~20°C/s to the same maximum temperatures as above and immediately quenching. The scale topographies illustrated there indicate that a marked "degree of advancement" in the microstructural features has been induced by doubling the heating rate.* As with the structures developed at the heating rate of 10°C/s, there is no major evidence of either oxide cracking or oxide exudation, however; in contrast to them:

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*Compare the upper left photographs of Figures 2, 3 and 4 with the corresponding Figures 5a, 5b and 5c, respectively.

1) The oxide grain dimension upon the gas-oxide interfaces is very much larger.

2) Faceting has occurred at the immediate end of the heating period (t_i = 0% t_{xf}) for all maximum exposure temperatures, and

3) Void space has developed between the oxide crystals and into the depth of the scale by the immediate end of the heating period.

The reason that heating rate so profoundly affects the microstructure of oxide grown upon titanium is not known. It is hypothesized that the interfacial stains resulting from differential thermal expansion may have induced a rapid recrystallization and grain growth in the oxide.

The long-term scale morphology tests involved the total oxidation of CP titanium wires in air using a conventional laboratory furnace where relatively lower heating rates obtained. It was found that complete oxidation of 0.079 cm. diameter wire had occurred after 89 hours at 1000°C, 336 hours at 900°C, and 2760 hours at 800°C. Oxidized specimens were cooled, mechanically fractured and examined in the hope that the oxide structures so developed might provide some further understanding of oxidation-associated ignition.

The SEM photomicrographs of Figures 6 and 7, for 800° and 1000°C oxidations respectively, illustrate that porosity, layer formation and interconnected void space are probably present throughout the bulk of these complete scales. There is some evidence of "healing," but not complete closure, of the void space at the higher temperature as would be expected to result from sintering or allied processes.

In overviewing the structural features of the oxide as presented in Figures 2 through 7, the following inferences are drawn:

1) With regard to elements of the heat delivery parameter ($\overset{\circ}{q}_v$), it appears that the areal expansion term (γ) must be retained in that context as neither oxide cracking, spalling nor exudation has been proven. Whether effective areal expansion occurs at the metal-oxide interface or at a gas-oxide interface within the bulk of the scale is unknown as either circumstance would provide a qualitative enhancement of reactivity as has been observed. Similarly, it appears that our prior description of the heat partition parameter (β) has been qualitatively correct.[2] For example, the high "degree of advancement" of the oxide scales illustrated in Figure 5 make plausible the idea that the effective site of gas-metal reaction may exist deep within the scale at higher heating rates after relatively short exposure times. As stated above, such phenomenology is required to semiquantitatively describe the ignition of titanium at 564°C when subjected to a heating rate of ~40°C/s.

2) Both the early intrusion of void space into the scale, Figure 5, and the porosity generated within scale structures, Figures 6 and 7, indicate that sufficient "short-circuit" transport paths may be available to provide a sensible effect of external oxygen pressure upon the reaction kinetics and/or ignition of titanium. Such effect will, of course, only obtain provided that the controlling reaction rate involves transport of gaseous oxygen.

3) It appears that there may be a regular progression or evolution of scale structure with heating rate which may be used in part to rationalize the sensitivity of both the oxidation kinetics and the ignition of titanium to heating rate. The following hypothesis is offered. At low heating rates (~1°C/s), the scale is initially columnar and closed at the gas-oxide interface such that principally diffusive transport obtains and parabolic oxidation kinetics ensue with the primary reaction occurring at the gas-oxide interface. At intermediate heating rates (~20°C/s), interfacial strains produce a recrystallization of the oxide which results in both the penetration of oxygen into the bulk of the scale and a shift of the primary reaction interface into the depth of the scale. The irregularity of this reaction interface provides an effective areal expansion and permits an initially rapid reaction as is characteristic of the observed asymptotic oxidation kinetics.[2] Subsequent to heating, this structure "heals" by oxide grain growth in a manner which produces an areal contraction of the primary reaction interface and leads to the diminution of reactivity (asymptotic behaviour). At high heating rates (~100°C/s), the oxide recrystallization, oxygen penetration and areal expansion all become more pronounced than in the previous case resulting in the deposition of the chemical heat of reaction in a very narrow near-surface region of the metal. This, in turn, provides the energy required to produce a localized "hot spot" which may involve melting and/or vaporization of the metal and which does lead to the onset of ignition.

4.3.2 Effect of Oxygen Pressure on Ignition

In view of both the scale porosity cited above and the experience of those in the field involved with jet engine dynamics, it was decided to mount a limited investigation into the effect of pressure upon the ignition of 0.01 cm. thick CP titanium. This series of ignition tests invloved the use of a stagnant environment at pressures of 100, 200 and 400 torr oxygen. For each pressure, there were conducted 4 tests at the nominal heating rates of 25°, 50°, 75° and 100°C/s. The furnace power, oxygen pressure and specimen temperature were measured during each test. The temperature was measured both near the bottom of the specimen and about 1 mm from the top of the specimen; see Figure 1. These four signals were fed to the computer and were measured at a rate of 15/s; subsequently, a "calcomp" plot was obtained for each test using the computer-acquired data.

Upon heating these titanium specimens from room temperature at the rates noted, ignition was observed at all pressures and occurred in the temperature range from approximately 300° to 800°C. In general, the bottom thermocouple bead was lost during ignition while the top thermocouple bead was seldom destroyed. One leg of the top thermocouple was often cut during the "shower" stage of ignition. The ignition temperature was determined as the last thermocouple measurement before any discontinuity occurred in either thermocouple output. Thus the "ignition temperature" was determined for both thermocouples at the same time whether or not both thermocouple beads were lost at the same time. These ignition temperature data are summarized in Table I.

Inspection of the data in this table indicate the following:

1) That there is no strong or systematic dependence of ignition temperature upon ambient oxygen pressure in the range from 100 to 400 torr oxygen. Thus, if scale porosity were present its effect could be only to "bury" the reaction site deep in the scale; but not to directly affect the degree of the oxidation-associated ignition reaction. This suggests oxidation rate control by either the existence of a compact layer within the scale or alternatively, a phase boundary control of that reaction. Based upon this observed lack of pressure dependence, we terminated any further studies concerning the effect of pressure levels or pressure pulses upon oxidation kinetics.

2) That the ignition temperature is quite sensitive to heating rate, decreasing with increasing heating rate. This behavior is expected on the basis of the form of the heat delivery parameter (Eq. 4) and has been noted earlier.[2]

3) That from both the table and from ancillary data plots of temperature-time histories, the upper thermocouple registers both higher temperatures and higher heating rates than the lower thermocouple.* This effect is most probably associated with the thermal inertia afforded to the lower thermocouple by the presence of the alumina insulators; see Figure 1. Bulk melting was neither proven nor strongly indicated.

Because the upper thermocouple does respond somewhat more rapidly than the lower, it was presumed to represent more nearly correct values of heating rate than those which we have previously published. Based upon this, two concepts contained in reference 2 have been modified in degree as follows:

1) Various data for clean specimens heated from room temperature to ignition at constant rates indicate that there is an inverse relationship between heating rate and sensible ignition temperatures which,

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*An unexplained exception is the data of Table I for the nominal heating rate of 75°C/s.

for the case of 0.010 cm. thick unreacted specimens ($S_V = 200\ cm^{-1}$), may be expressed as;

$$Tig = 338° + 4.97 \times 10^5/r^2 °C, \tag{8}$$

where (r) is the constant rate of heating expressed in °C/s. This relation extrapolates to the minimum bulk ignition temperature of titanium (1580°C) as cited by Reynolds at the modest heating rate of 20°C/s for which our asymptotic model of titanium oxidation should apply,[5] and,

2) that the dimensionless term (γ) describing areal expansion of the specimen surface is proportional to the square of the heating rate (r) such that it takes the form:

$$\gamma = \gamma_o\ (r/r_o)^2, \tag{9}$$

where (r_o) is the heating rate just subcritical to ignition (~30°C/s) and (γ_o) takes on the value of approximately 2.26 which has been estimated previously.

4.3.3 - Alloy Screening test for Ignition

A testing scheme was developed which purpose was to rank the relative ignitibility of titanium, selected structural alloys of titanium and titanium-aluminum intermetallic compounds. In these tests, the specimen thicknesses were standardized to 0.023 cm. and all were provided a 600-grit SiC finish.

The prepared specimens were emplaced in the reaction chamber which was backfilled with 200 torr oxygen. Subsequently, each specimen was subjected to the following heating regime: heat at ~10°C/s to 600°C, hold for 3600 s ($>>t_{xf}$) at 600°C, and heat at ~75°C/s to either ~1000°C or ignition. As the quantity of specimen stock available for the intermetallic compounds TiAl and Ti_3Al was limited, they alone were subjected to a heating regime more conducive to ignition*; i.e.: heat at ~75°C directly from room temperature to either 100°C or ignition. For all tests, the ignition temperature was monitored and the maximum value of the heat delivery parameter ($\mathring{q}_v$) was calculated from the acquired temperature-time information by the use of the asymptotic model. This calculation was made with the full knowledge that the alloy oxidation kinetics might differ significantly from those for CP-titanium, upon which this model was based.

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*See Section 4.3.4 below for a discussion of the effect of oxygen solution upon ignition.

The results of these screening tests are presented in Table II. As indicated there, the intermetallic phases TiAl and Ti_3Al alone survived the test without igniting.* All structural alloys ignited on the range 738° to 911°C with attendant maximum values of ($\overset{\circ}{q}_v$) ranging approximately from 0.3 to 3.0 cal/cm^3-s.

Of the ignitible structural alloys, both Ti-6Al-4V and Ti-8Mn exhibited ignition at temperatures within the range observed for CP titanium. Two of the structural alloys, Ti-13Cu and β-III ignited at notably higher temperatures and with attendant larger than average values of the heat delivery parameter. There is a minor trend indicating that higher values of ignition temperature may be associated with lower temperatures of initial metal liquation - a concept which earlier had been transmitted orally to us by Mr. Manty of Pratt & Whitney Aircraft.

The results presented in Table II indicate that the definitiveness of our screening test was somewhat lacking. It does, however, allow a coarse ranking of materials in order of increasing resistance to ignition; e.g.: 1) least resistant were CP titanium, Ti-6Al-4V and Ti-8Mn, 2) intermediate resistance was exhibited by Ti-13Cu and the β-III alloy, and 3) most resistant were the Ti-Al and Ti_3Al intermetallics. Further investigation will be required to either substantiate or modify this ranking with regard to ignition resistance.

4.3.4 - Effect of Oxygen Saturation

We have known for some time that the high-temperature exposure of CP thin titanium specimens to oxygen prior to their subsequent rapid heating in oxygen suppresses or makes more difficult the initiation of ignition[2]. However, it was not until late in the experimental program that some clarity was achieved with regard to the root source of ignition suppression. As a result of recent critical experiments, we are now of the opinion that the solution of oxygen in titanium inhibits ignition and that the role of the external scale, if any, in this inhibition is secondary. The considerations leading to this conclusion are outlined below.

It has previously been shown that "virgin" 0.10 cm thick CP titanium specimens may readily be ignited in 200 torr oxygen at heating rates** of 40°C/s or greater.[2] When similar specimens were slowly heated to 800°C, held isothermally for a preoxidation time of (t_p) seconds and subsequently heated to ignition at ~75°C/s; it was found that the ignition temperature was then dependent upon (t_p) as:

$$T_{ig} = 900° + 2.58\, t_p^{1/2}\ .°C \qquad (10)$$

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*Some sparking did occur at the tips of these specimens as if ignition were initiated and immediately quenched.

**All heating rates discussed here have been referenced to the upper thermocouple pursuant to Section 4.3.2 above.

This result indicates the inhibition of ignition by prior exposure to oxygen under conditions where the solution of oxygen in the substrate can occur.

In a second series of experiments, 0.010 cm thick CP titanium specimens were slowly heated (8°C/s) in 200 torr oxygen at 25°, 600°, 800° and 1000°C, held isothermally for 240 s, cooled to room temperature and immediately reheated at the rate of 40°C/s. The specimens exposed at 25° and 600° ignited at 475° and 560°C, respectively; whereas, the specimens exposed at the higher temperatures did not ignite. These results also indicate that those specimens exposed under conditions promoting oxygen solution (800° and 1000°C) did not ignite; while those exposed under conditions limiting oxygen solution (25° and 600°C) did ignite.

Finally an attempt was made to perform a "critical" experiment in this investigation which purpose was to separate the effects of (a) scale formation and (b) oxygen solution on the inhibition of ignition. In part at the suggestion of Dr. R.A. Rapp of Ohio State University, we attempted the ignition of 0.025 cm thick CP titanium specimens which had been subjected to prior oxidation and vacuum annealing such that oxygen solution occurred in the absence of any external scale. Specimens were prepared by oxidation in 200 torr oxygen at 1000°C for a period of 3 minutes followed by "vacuum" (~1 torr O_2) annealing at 1200°C for a period of 15 minutes. Microhardness measurements of these prepared specimens indicated an average hardness of 825 KHN with no sensible oxygen gradient detectable. This observation, coupled with the brittle nature of the specimen, indicated the desired oxygen solution had been obtained. On five occasions, such oxygen-rich specimens when heated from either room temperature or 600°C/s exhibited no tendency to ignite; whereas, their "virgin" counterparts consistently ignited under similar conditions. We have therefore concluded that oxygen solution rather than scale layer formation per se is responsible for the inhibition of ignition.

Unfortunately, while a causal agent for ignition inhibition has been identified, the mechanism of its action is not known. While some might argue that the heat of solution of oxygen in titanium is principally responsible for the observed inhibition*, this suggestion is not tenable as the ignition of "virgin" CP titanium when heated at ~100°C/s obtains at ~375°C; i.e., oxygen solution would have to take place in 3.5 seconds at temperatures of less than 400°C. Rather, it appears more likely to the writer that the effect of oxygen solution delimits the areal expansion term (γ) of the heat delivery parameter as expressed in equation 4; thus, for the case of oxygen saturation prior to ingition, the titanium lattice has both undergone dilitation and has been hardened making areal expansion during any

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*Such presumption would involve modification of the ΔH-term of equation 4.

subsequent heating much less likely. The limiting impact of this mechanism may be estimated from equation 9 using the specific conditions of 0.010 cm thick CP titanium heated at the rate of 100°C/s as follows: a) for "virgin" titanium $\gamma = 25.1$; while, b) for oxygen-saturated titanium $\gamma = 1$ (in the limit). Thus, the value of the heat delivery parameter, which is our semiquantitative ignition index, may be attenuated by a factor of up to 25 as a result of oxygen solution. This is an adequate effect to suppress the value of $\overset{\circ}{q}_V$ below the threshold value for ignition (0.1 to 1.0 cal/cm^3-s) and is in qualitative agreement with the foregoing experimental evidence.

4.3.5 - Model Applications

In our earlier work on the oxidation of titanium, we had found that the maximum value of the specific linear reaction rate was directly related to the rate of specimen heating.[1] Later it was found that, for a given specimen geometry, the ignition temperature was inversely related to the heating rate.[2] It is now believed that both of these phenomena arise as a direct result of the initial asymptotic oxidation kinetics of titanium coupled with the concepts expressed in the heat delivery parameter of equation 4.

The sensitivity of the calculated value of the heat delivery parameter to heating rate is illustrated in Figure 8. Here, calculated values of ($\overset{\circ}{q}_V$) are presented for the case of a 0.010 cm thick CP titanium specimen heated at the rates of 25°, 50° and 100°C/s. At the lowest heating rate, no ignition is observed; whereas, ignition temperatures of 475° and 388°C have been observed for the heating rates of 50° and 100°C/s, respectively.[2] It thus appears that values of ($\overset{\circ}{q}_V$) in excess of 0.1 cal/cm^3-s, as calculated from the asymptotic model, are adequate to permit ignition while those of lesser magnitude are not. Curves similar to those illustrated in Figure 8 may therefore apparently be used in a predictive sense.

Following this general mode of analysis, we were asked to construct a predictive model for the instance of a turbine compressor operating at 482°C (900°F) for protracted isothermal periods after which a temperature pulse (surge) is applied. The problem was simulated by heating at the relatively slow rate of 10°C/s under asymptotic oxidation kinetics, holding isothermally up to 100 hours including the transfer time (t_{xf}) here equal to 19.9 hours and, finally, simulated heating at 50°C/s to 1300°C. Under this regime, oxygen solution in the base metal was neglected due to the relatively low isothermal holding temperature.

The results of the above model calculations are shown graphically in Figure 9 which illustrates that the threshold value for ignition ($\overset{\circ}{q}_V = 0.1$ cal/cm^3-s) may be reached at temperatures as low as 825°C (or in 6.9 s) relatively early in compressor life. At compressor lives in excess of 20 hours, the transfer time has been exceeded and the oxidation is governed by parabolic kinetics. For the same threshold value of ($\overset{\circ}{q}_V$), ignition is now not predicted until temperatures approach the range of 950°C (or in 9.4 s of surge). Stronger surges involving higher heating rates than that modeled will, of course, reduce both the temperature for and time of ignition in a manner qualitatively described by Figure 8.

4.3.6 - Collection of Oxidation Data

An additional goal of this research has been to devise a method for the automated collection of oxidation data in a manner which would also permit iterative corrections to oxidation models. Unfortunately, the time necessary to properly execute this specific task was not available; however, results of cursory work in this area indicate that the general concepts involved are feasible.

Central to this task is the idea that the degree of a gas-metal reaction at any specific time during the course of reaction may be monitored and/or estimated by three independent methods: 1) by ex post facto gravimetric analysis, 2) from the pressure-time data as corrected for "blank" system response; the latter exemplified by equation 6; and 3) from the temperature-time data through the use of the asymptotic oxidation model established previously.[2]

Proper automated data collection may be certified by demanding data "closure" on methods (1) and (2). This has been accomplished to within ±5 percent on a weight basis which we consider to be acceptable. The mathematical oxidation model may be certified by demanding data "closure" on either/both methods (1) or (2) with method (3). To date, this has not been accomplished because of what we feel may be relatively minor programming errors.

5. EXTERNAL INTERACTIONS

During this grant term, several exchanges of both scientific and technical information took place with persons external to either the AFOSR or Clemson University.

On 09 and 10 March 1976, the informal "Titanium Fire Working Group" met at the Pratt & Whitney Aircraft Corporation facilities at West Palm Beach, Florida. Both technical and scientific aspects of titanium oxidation/ignition were discussed by all members of this group which then included:

Name	Affiliation
Dr. W. F. Laverty	P & W (Hartford)
Mr. C. Mayer	P & W (Hartford)
Mr. B. A. Manty	P & W (West Palm Beach)
Dr. M. Glickstein	P & W (West Palm Beach)
Mr. J. Zuk	NASA (Lewis)
Dr. A. Clark	NBS (Boulder)
Dr. S. R. Lyon (Chmn.)	AFML (WPAFB)
Dr. C. Elrod	AFAPL (WPAFB)
Dr. J. S. Wolf	Clemson

The second major disclosure of grant-associated information occurred on 19 October 1976 during the 150th Meeting of the Electrochemical Society at Las Vegas, Nevada. At that time, the material represented in reference 2 of this report was presented to an international audience of approximately 50 persons by the principal investigator. That material has subsequently been discussed in some detail with and has been distributed to several individuals who have shown interest in the scientific or technical aspects of this research. To date that distribution has included:

Name	Affiliation
Dr. S. R. Lyon	AFML (WPAFB)
Dr. B. A. Manty	P & W(West Palm Beach)
Dr. M. Glickstein	P & W(West Palm Beach)
Dr. R. G. Connell	University of Florida
Dr. F. N. Rhines	University of Florida
Mr. T. Redden	G.E (Evandale)
Dr. J. V. Cathcart	ORNL (Oak Ridge)
Maj. W. C. Simmons	AFOSR - Program Mgr.
Dr. D. B. Butrymowicz	NBS (Washington, D.C.)
Mr. Hal Kessler	Reactive Metals, Inc. (Niles, Ohio)
Mr. John Moulder	NBS (Boulder, Colo.)
Dr. Robert Altman	NASA (Ames Lab.)

The third grant-associated information exchange occurred on 10 and 11 March 1977 at the second meeting of the "Titanium Fire Working Group", hosted by the AFML at Wright-Patterson AFB, Ohio. During that meeting Dr. Wolf presented a review of reference 2 as well as an outline of scale morphology studies and computer modeling applications then available. Both the technical and the scientific aspects of the oxidation and ignition were discussed by several members of this group which included:

Name	Affiliation
H. W. Bates	G. E. (Dayton)
D. H. Bergevin	Naval Weapons Center (Calif.)
R. Burton	Northwestern Univ.
A. F. Clark	NBS (Boulder)
C. Elrod	AFAPL/TBC
M. B. Glickstein	P & W (West Palm Beach)
R. W. Harrison	G. E. (Evandale)
W. F. Laverty	P & W (East Hartford)
P. J. Linko	G. E. (Evandale)
L. P. Ludwig	NASA (Lewis Lab)
S. R. Lyon	AFML/LPJ
R. Mahorter	NAVAIRDEVCEN
B. Manty	P & W (West Palm Beach
J. V. Melink	G. E. (Evandale)
A. L. Meyer	G. E. (Evandale)
J. C. Moulder	NBS (Boulder)
L. O. Pary	AFAPL/TBD
W. R. Patterson	G. E. (Evandale)
A. B. Pruitt	Clemson Univ.
J. D. Schell	AFML/LPH
J. M. Short	AFML/LPB
W. C. Simmons	AFOSR/NE
J. S. Wolf	Clemson University
J. Zuk	NASA (Washington, D.C.)

Finally, remnants of the specimen stock supplied to us by Mr. B. Manty and Dr. S. R. Lyon were shipped to Dr. John Moulder at the NBS Boulder facility for testing in his AFOSR-sponsored research project.

6. SECOND YEAR SUMMARY

The summary of technical activity for the first year of grant operation is contained both in Reference 2 and in Section 3 of this report. Major results of the technical activity for the second year indicate:

1) That the volumetric apparatus was sufficiently sophisticated to permit the proper automated computer acquisition of both the anisothermal oxidation and ignition data for titanium.

2) That the oxide scales developed upon titanium at high temperatures are porous and readily tend to exhibit faceting.

3) That the oxide scale morphology is strongly dependent upon heating rate; becoming structurally more advanced as the heating rate increased.

4) That the ignition of titanium is essentially independent of external oxygen pressure over the range from 100 to 400 torr oxygen and may regularly be made to ignite at sensible bulk temperature as low as 300° to 400° if heated at rates near 100°C/s.

5) That of the materials tested: a) those most resistant to ignition were TiAl and Ti_3Al, b) those of intermediate resistance were Ti-13 Cu and βIII alloys and, c) those least resistant to ignition were CP titanium, Ti-8Mn and Ti-6Al-4V alloys.

6) That the ignition of titanium may be inhibited under conditions which provide prior oxygen solution.

7. ACKNOWLEDGMENT

The authors wish to acknowledge that the work described in this report was supported by the Air Force Office of Scientific Research via Grant No. AFOSR-76-2919 and continuations thereof with Major Wilbur C. Simmons acting in the capacity of Project Manager. We also wish to acknowledge with thanks the technical support of Dr. David D. Moyle and Mr. Jay Smith of our project staff without whose efforts the development of the above material would not have been possible.

8. REFERENCES

1. J. S. Wolf: "Exploratory Development on Oxidation Behavior of Titanium Alloys under High Heating Rates," AFML TR-74-265, April 1975, 356 pp.

2. J. S. Wolf, D. D. Moyle, A. B. Pruitt and J. H. Bader: "Anisothermal Oxidation of Titanium: Initial Reactivity and Ignition," in *Proceedings of the Symposium on Properties of High-Temperature Alloys,* Ed. ty Z. A. Foroulis and F. S. Pettit, Electrochemical Society, Inc., 1976, pp. 363-385.

3. F. N. Rhines and J. S. Wolf: "The Role of Oxide Microstructure in the High-Temperature Scaling of Nickel," Met. Trans. *1*, 1970. pp. 1701-1710.

4. J. S. Wolf and J.M.Grochowski: "Nature of Gas-Metal Reactions Under Conditions of Anisothermal Oxidation," in *Stress Effects and the Oxidation of Metals*, Ed. by J. V. Cathcart, TMS-AIME, 1975, pp. 274-297.

5. W. C. Reynolds: "Investigation of Ignition Temperatures of Solid Metals," NASA TN D-182, October 1959, 71 pp.

6. P. Kofstad: *High Temperature Oxidation of Metals*, pub. by J. Wiley & Sons, Inc., New York, 1966.

9. BIBLIOGRAPHY

A single published document has been generated during the total term of this grant operation. That document is represented by Reference 2, above.

TABLE I

SUMMARY OF OBSERVED IGNITION TEMPERATURES FOR CP-TITANIUM AT VARIOUS OXYGEN PRESSURES AND HEATING RATES

Heating* Rate, °C/s	Thermocouple Position	Ignition Temperature, °C		
		100 torr O_2	200 torr O_2	400 torr O_2
25	Upper	800	774	726
	Lower	531	528	503
50	Upper	589	690	594
	Lower	297	519	370
75	Upper	438	303	383
	Lower	464	485	428
100	Upper	401	364	442
	Lower	294	309	304

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* Nominal heating rate based on lower thermocouple response to "open loop" heating programs.

TABLE II

SUMMARY OF RESULTS OF THE ALLOY SCREENING TEST FOR IGNITION

Titanium Alloy Type	Qualitative Test Result	Ignition Temperature, °C	Maximum Heat Delivery cal/cm^3-s
CP	Ignition	738	0.84
CP	Ignition	754	1.42
CP	Ignition	791	0.81
CP	Ignition	796	1.40
Ti-6Al-4V	Ignition	759	0.31
Ti-8Mn	Ignition	796	1.19
Ti-13Cu	Ignition	906	1.56
β-III	Ignition	911	3.68
TiAl*	No Ignition	>927	--
Ti_3Al*	No Ignition	>927	--

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*Heated directly from room temperature; see text.

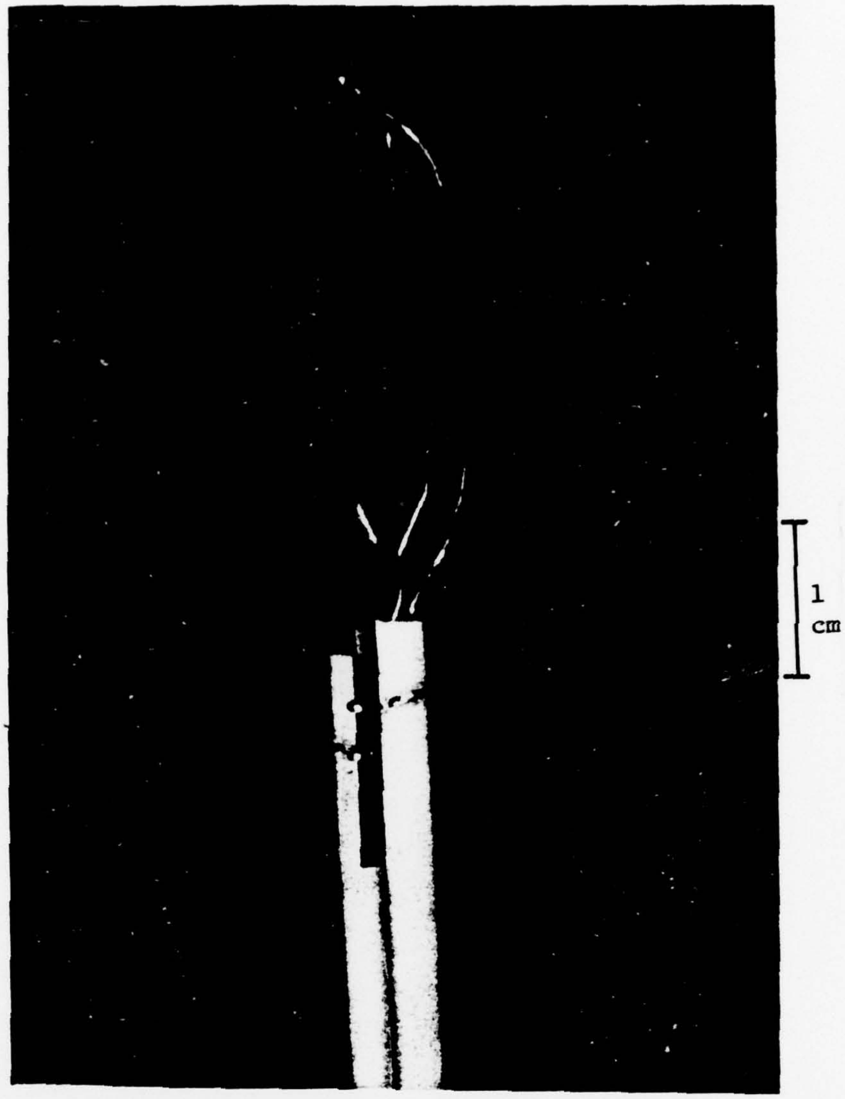
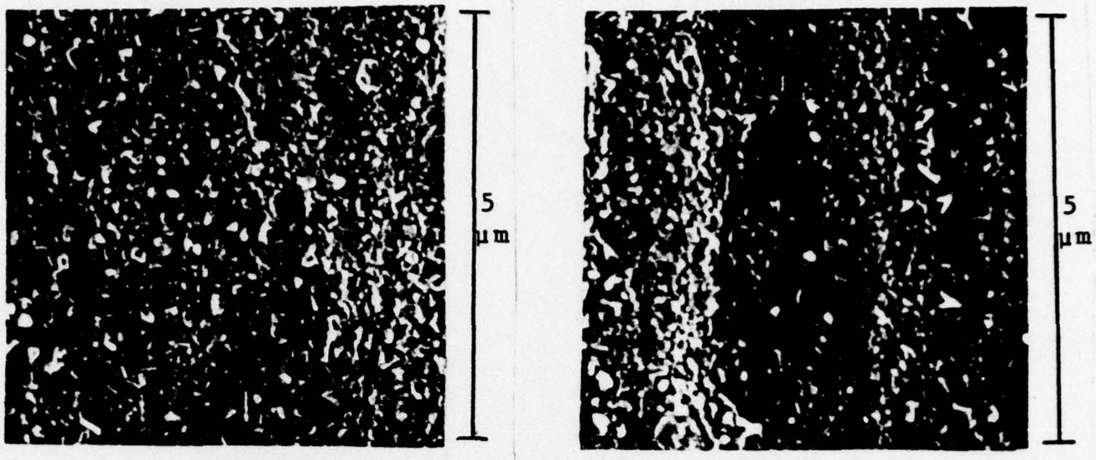
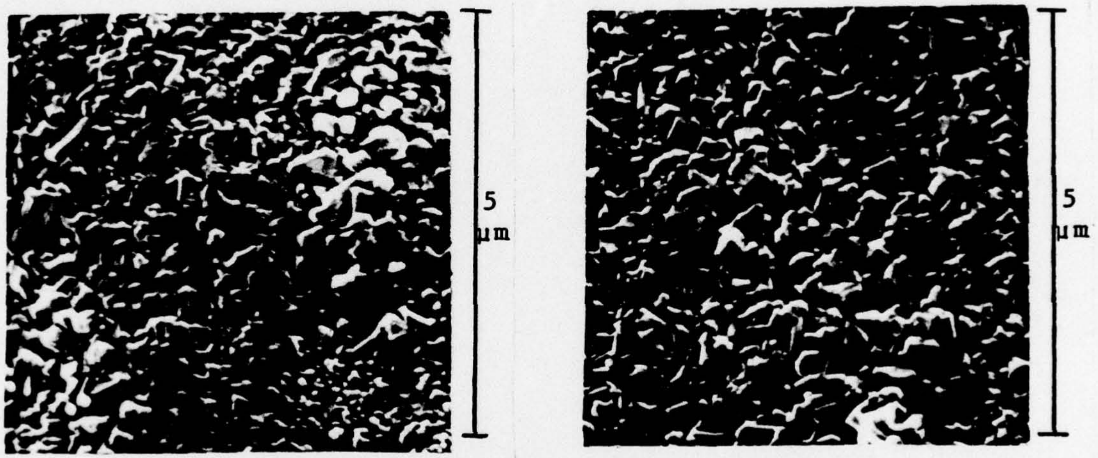


Figure 1. - Photograph illustrating the dual thermocouple configuration used in various ignition tests. Entire assembly shown fits within Vycor reaction chamber during test operation.

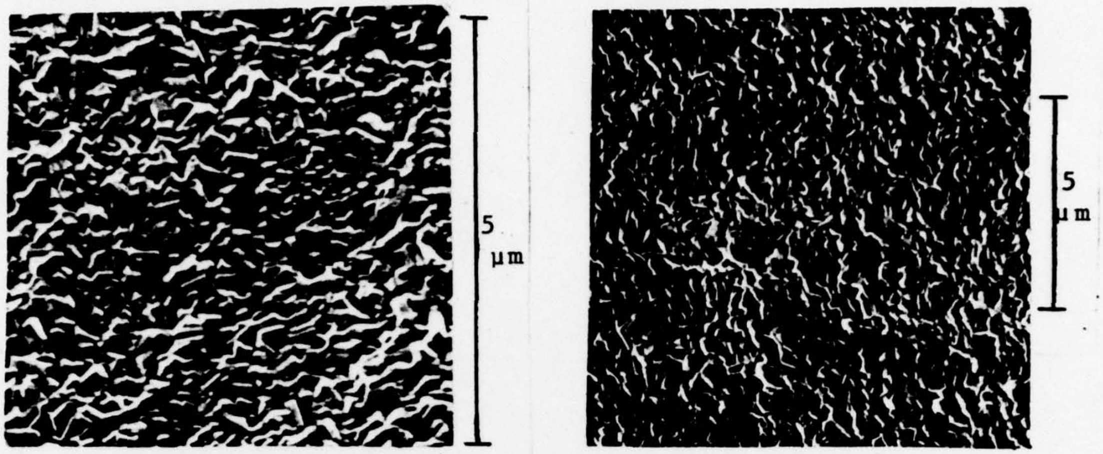


t_i = 0 min.= 0% t_{xf} t_i = 22.7 min.= 6% t_{xf}

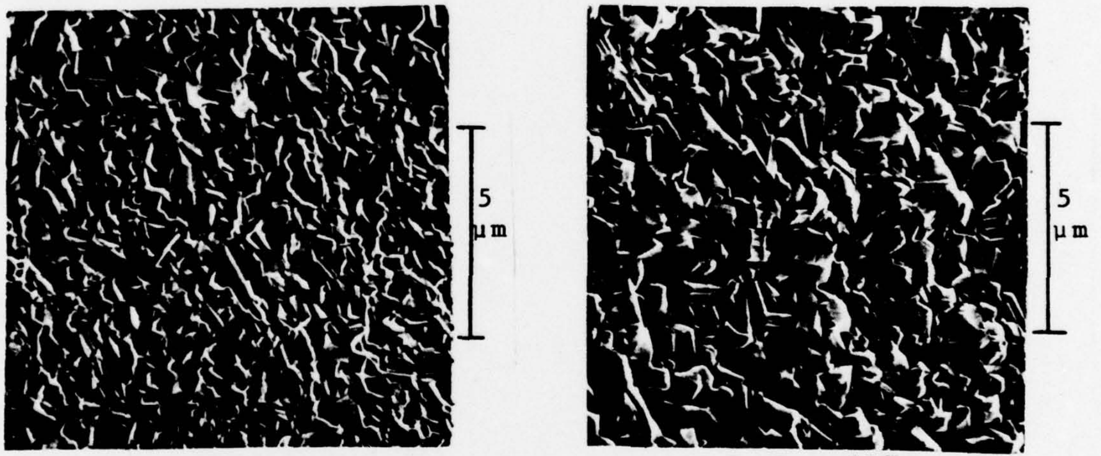


t_i = 45.4 min.= 12% t_{xf} t_i = 90.7 min.= 25% t_{xf}

Figure 2. - SEM photographs of oxide surfaces developed on CP titanium heated at 10°C/s to 600°C in 200 torr O_2 and held isothermally for various times (t_i).

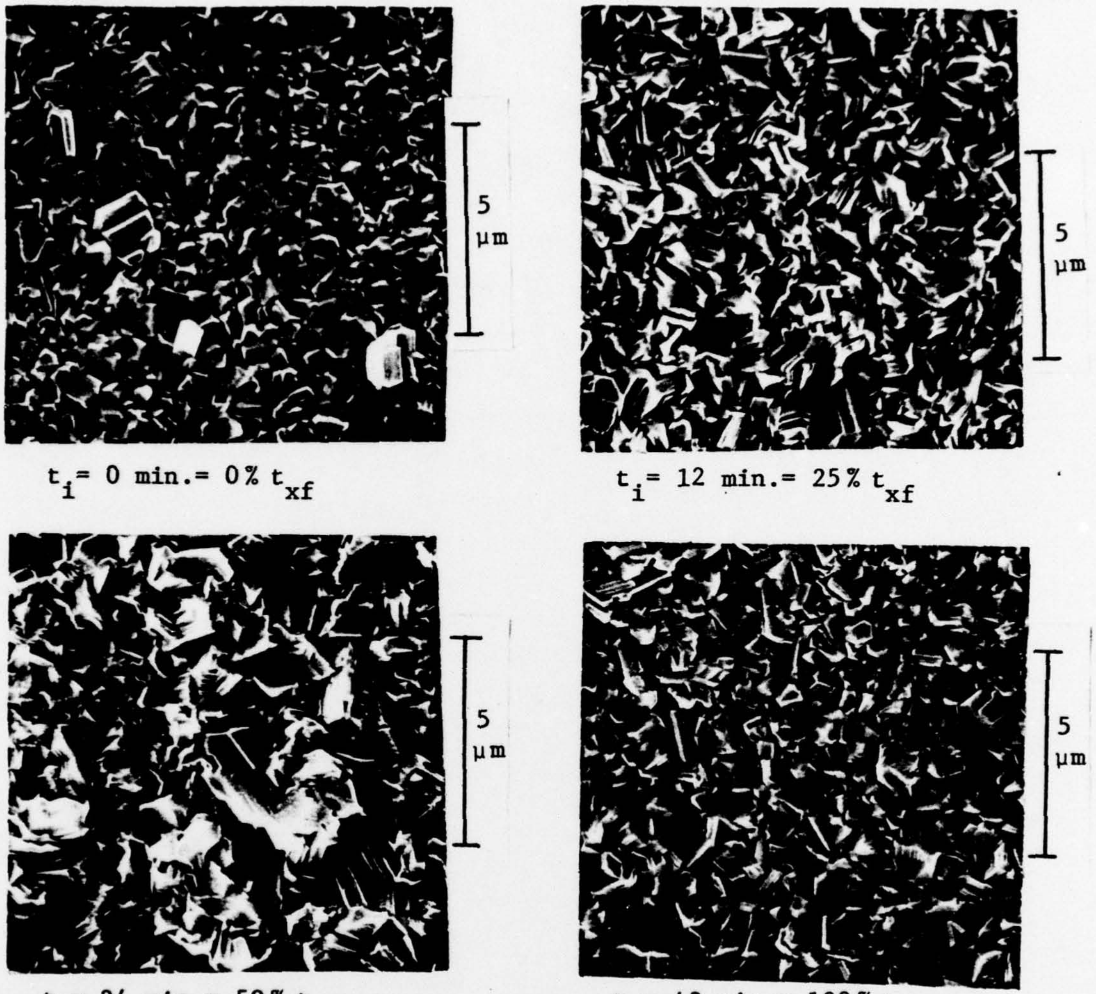


t_i = 0 min.= 0% t_{xf} t_i = 4.1 min.= 3% t_{xf}



t_i = 16.5 min.= 12% t_{xf} t_i = 61.1 min.= 46% t_{xf}

Figure 3. - SEM photographs of oxide surfaces developed on CP titanium heated at 10°C/s to 700°C in 200 torr O_2 and held isothermally for various times (t_i).



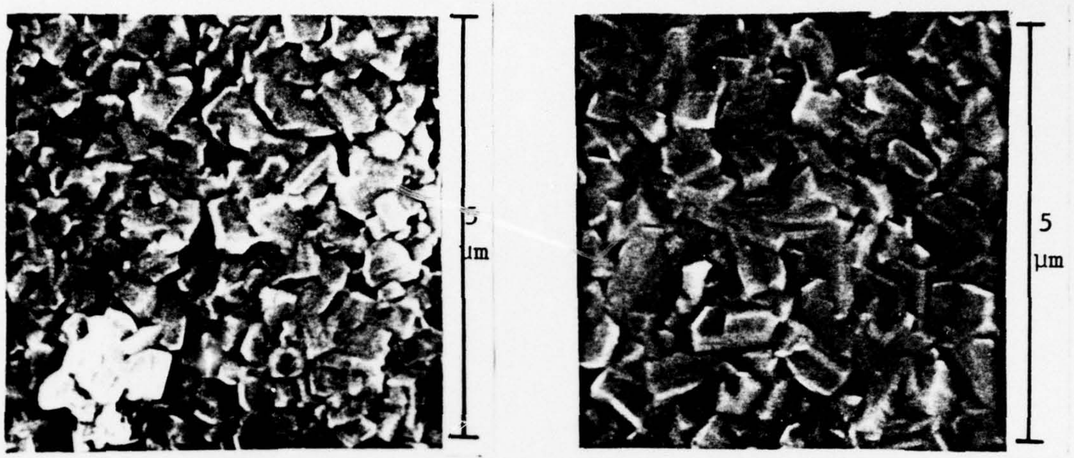
$t_i = 0$ min. $= 0\%\ t_{xf}$

$t_i = 12$ min. $= 25\%\ t_{xf}$

$t_i = 24$ min. $= 50\%\ t_{xf}$

$t_i = 48$ min. $= 100\%\ t_{xf}$

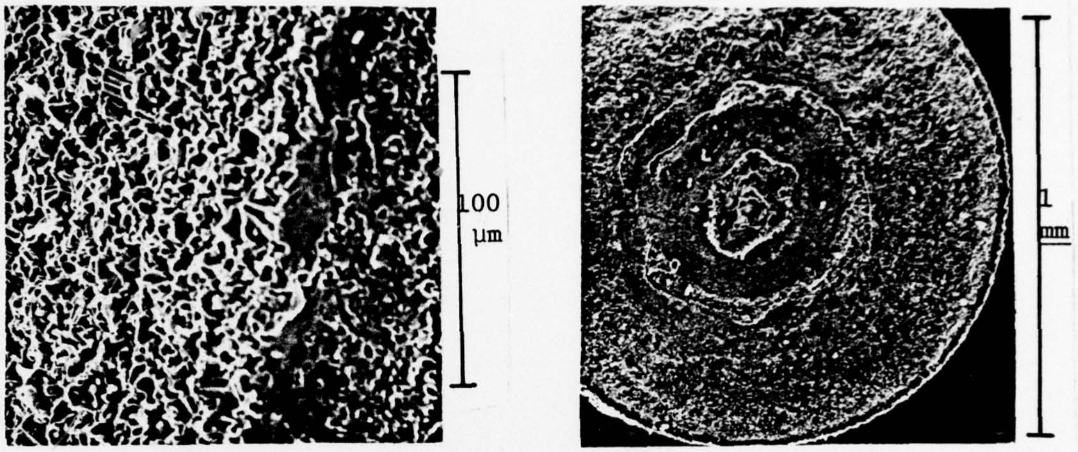
Figure 4. - SEM photographs of oxide surfaces developed on CP titanium heated at 10°C/s to 800°C in 200 torr O_2 and held isothermally for various times (t_i).



(a) 600°C (b) 700°C

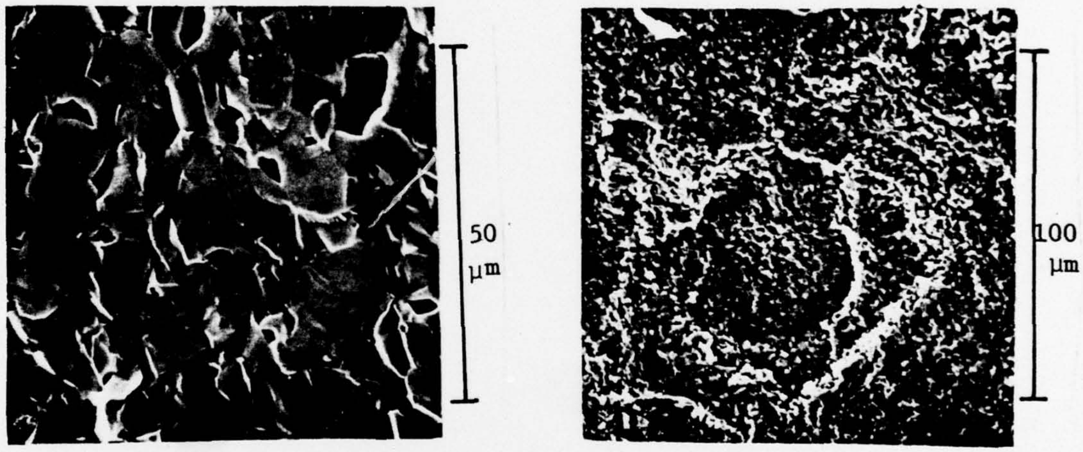
(c) 800°C

Figure 5. - SEM photographs of oxide surfaces developed on CP titanium heated at ~20°C/s in 200 torr O_2 and immediately quenched. Maximum temperature of exposure: (a) 600°C, (b) 700°C, and (c) 800°C.



External Surface

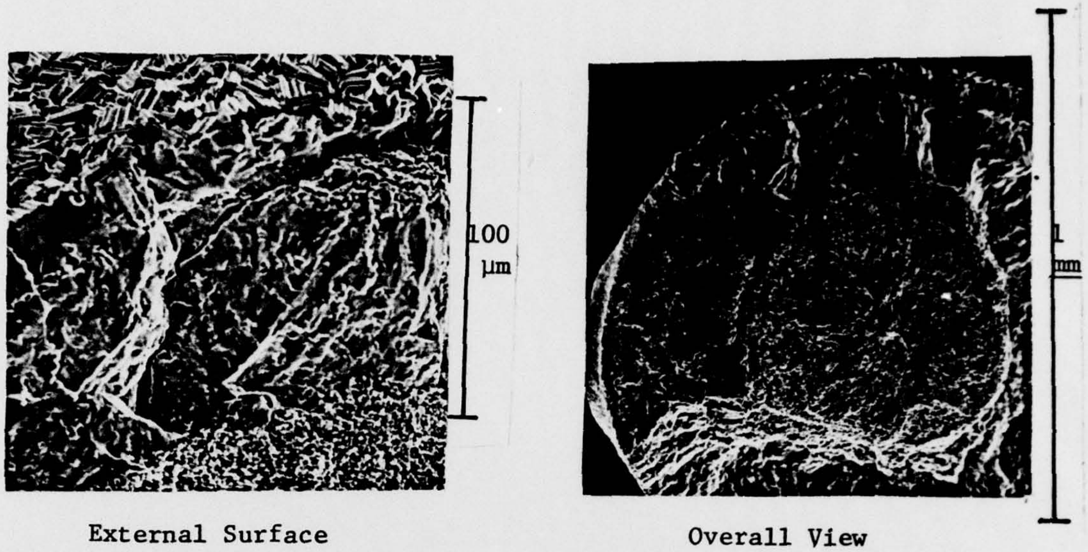
Overall View



Outer Zone F. S.

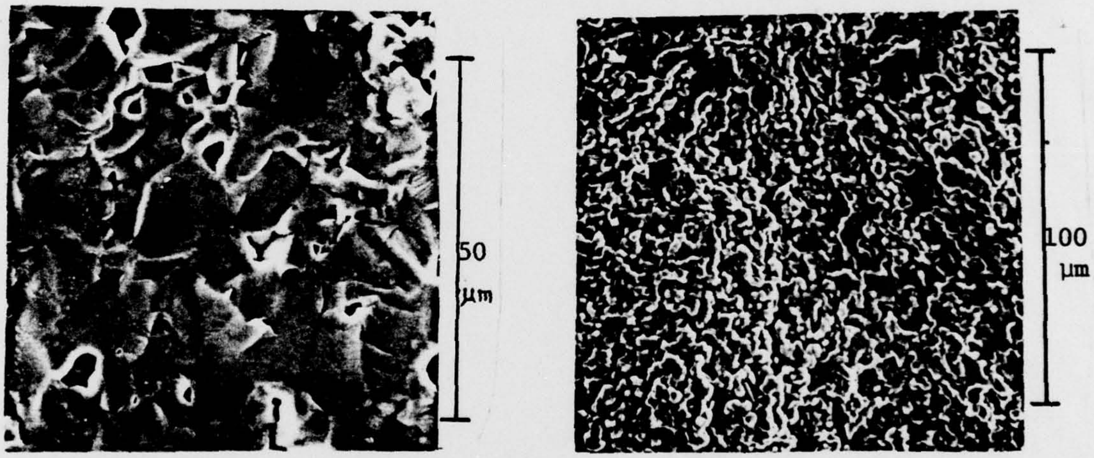
Center Zone F. S.

Figure 6. - SEM photographs of 0.079 cm CP titanium wire completely oxidized at 800°C in air for 2760 hours. Fracture Surface (F. S.) illustrated.



External Surface

Overall View



Outer Zone F. S.

Center Zone F. S.

Figure 7. - SEM photographs of 0.079 cm CP titanium wire completely oxidized at 1000°C in air for 89 hours. Fracture surface (F. S.) illustrated.

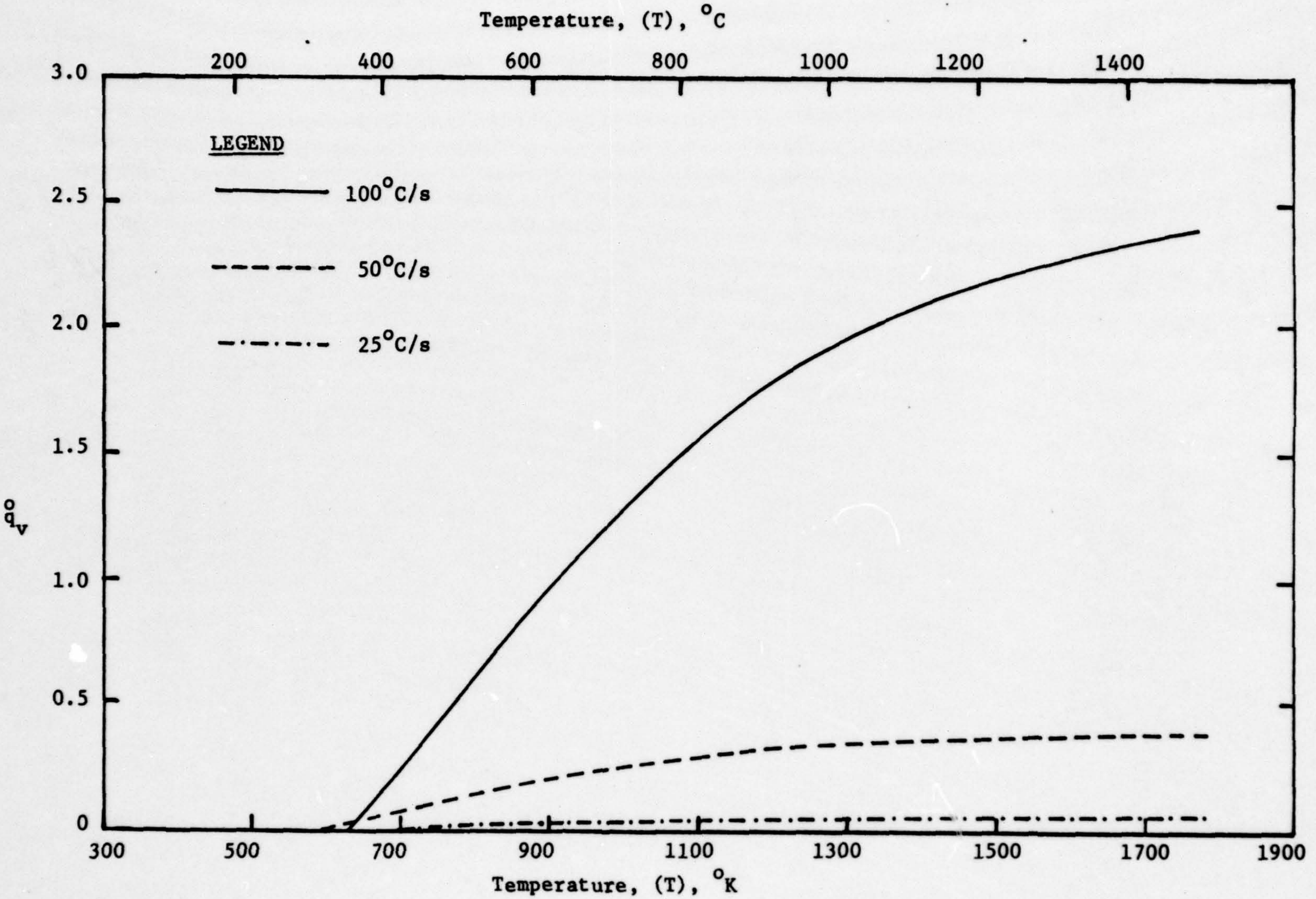


Figure 8. - Calculated dependence of the heat delivery parameter upon heating rate for the case of 0.010 cm thick CP titanium in 200 torr oxygen.

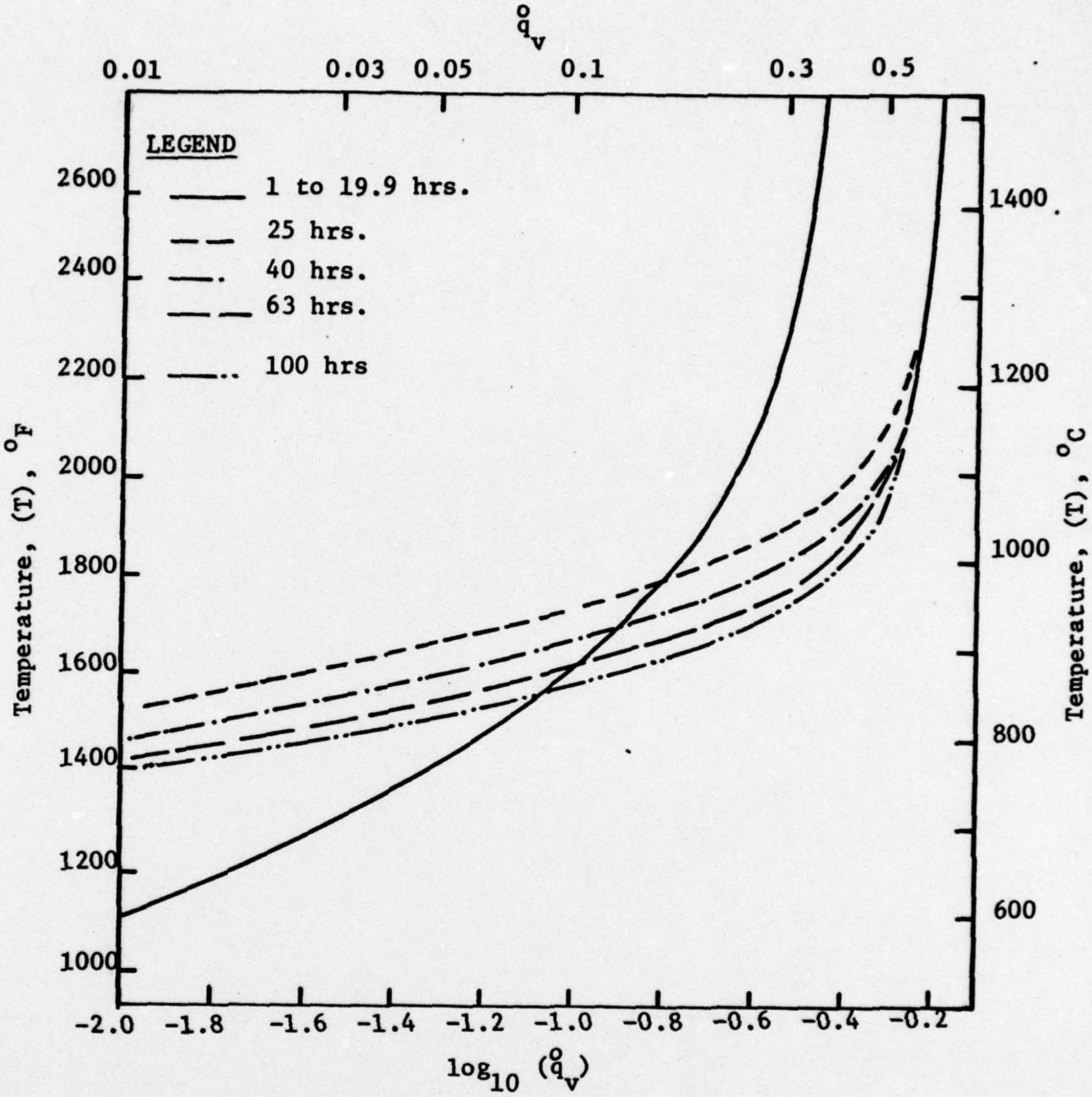


Figure 9. - Model calculation intended to analog a titanium turbine compressor "surged" after various exposure times in air at 900°F.

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The objective of this research has been to provide from laboratory experiments and analyses a capability for the prediction of oxidation-associated ignition of reactive metals; especially titanium and its alloys. Emphasis was placed upon the generation of basic information for subsequent application to technical problem areas where high rates of heating prevail or are suspect, as in engine fires and laser-assisted ignition.

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