

Reactivity and interface characteristics of titanium-alumina composites

RICHARD E. TRESSLER*, TERRY L. MOORE†, ROBERT L. CRANE
Metals and Ceramics Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio, USA

The reaction kinetics between α -Ti alloys and single crystal sapphire, the phase composition and morphology of the reaction-zone, and the phase compatibility in the system Ti-Al-O were investigated as part of a study to determine the feasibility of fabricating useful Al_2O_3 -reinforced titanium matrix composites. In the temperature range 650 to 1000°C titanium reduces Al_2O_3 to form a complex reaction layer consisting of two distinct zones; an inner zone adjacent to the Al_2O_3 of a TiO phase containing isolated particles of $(\text{Ti}, \text{Al})_2\text{O}_3$, presumably, and an outer zone of a Ti_3Al phase adjacent to the Ti matrix. The isothermal growth of the reaction layer follows a parabolic rate law. The temperature dependence of the rate constants fits an Arrhenius equation yielding activation energies of 50 to 52 kcal/mol. The high Al alloys, except Ti-6Al-2Sn-4Mo-2Zr,‡ reacted more rapidly than pure Ti indicating that Al diffusion through the reaction zone may be the rate-limiting step.

1. Introduction

The very desirable uniaxial specific tensile properties of filament-reinforced metals, particularly at elevated temperatures, has been demonstrated by many investigators [1, 2]. These materials are receiving attention for application as rotating structural components in air-breathing propulsion systems. Boron- and SiC-coated boron-(Borsic[®]) reinforced titanium alloy composites are being actively studied for use at temperatures up to 538°C. However, significant problems still exist with these materials. Boron and Borsic[®] filaments have pre-existing flaws which promote filament splitting and, therefore, limit the transverse strength of the composite [3]. Strength-degrading chemical reactivity in the case of titanium/Borsic composites limits the temperatures for fabrication and use of this material [4].

The advent of substrateless, single crystal sapphire (Al_2O_3 /alumina) filaments with desirable mechanical properties, suggested titanium/sapphire composites as an alternative material

for high performance applications. In an earlier paper [5] the feasibility of fabricating alumina-reinforced pure titanium and Ti-6Al-4V composites was discussed. That study documented the growth of a complex reaction layer as a function of temperature for these composites. However, preliminary mechanical property data indicated that this composite system warranted further investigation. Filament strength retention and the time-dependent mechanical behaviour of this material is dependent on the rate of reaction and the interfacial structure. In this paper we describe the reaction rates of two other technologically useful titanium alloys (Ti-8Al-1V-1Mo and Ti-6Al-2Sn-4Zr-2Mo) with single crystal sapphire and the interface morphology and phase constitution developed during annealing of pure Ti/ Al_2O_3 under conditions which simulate fabrication and use temperature regimes. A cursory examination of ternary compatibility triangles in the system Ti-Al-O at 870°C is discussed to elucidate the phase constitution of the reaction zone.

*Present address: Department of Materials Science, Pennsylvania State University, University Park, Pennsylvania, USA.

†Present address: Avco Systems Division, Industrial Park, Lowell, Massachusetts, USA.

‡All alloy compositions are given in weight percentages.

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2. Experimental procedure

Reaction couple specimens were fabricated by vacuum diffusion-bonding *c*-axis sapphire filaments between cleaned and etched titanium alloy foils; typically, at 815°C for $\frac{1}{2}$ h and 1×10^{-5} torr [5]. All heat-treatments were performed in a resistance-heated vacuum furnace with an operating vacuum of 1×10^{-6} torr. The couples were all furnace-cooled and reaction times were recorded as time at temperature.

The width of the gross reaction layer, as described later, was measured using a calibrated eyepiece and photographs of the polished and etched couples which had been sectioned in a plane perpendicular to the filament axes. The technique used to polish the couples has been described earlier [6]. Great care was taken to achieve relief at the alumina-reaction layer interface of less than 1 μm . Polished samples were etched with the standard titanium etchant (90 vol % H_2O , 8 vol % HNO_3 , and 2 vol % HF).

To provide sufficient quantities of reaction products for X-ray diffraction and electron microprobe analyses, a large single crystal of alumina ($1.5 \times 1.5 \times 0.4$ cm) was completely encapsulated in pure titanium by diffusion bonding at 815°C for $\frac{1}{2}$ h. The sample was subsequently annealed at 981°C for a total time of 940 h. The rationale for using this specimen for detailed interface characterization is presented in the results and discussion section.

X-ray diffraction experiments using this large crystal specimen were performed with a Norelco high-angle diffractometer using nickel-filtered copper radiation. Peak positions, 2θ values, taken from the diffractometer traces were used as input to a least-squares programme for refining unit cell dimensions. In this manner the presence of various solid solutions was inferred from the altered unit cell dimensions of pure elements or compounds.

Scanning electron microscope (SEM) photographs of selected specimens were taken for qualitative assessment of the reaction layer features using a Jeolco JSM-3 SEM. Samples were polished and etched but not coated before examination. Carbon replicas of selected reaction couples were examined with a JEM-6A transmission electron microscope (TEM) in order to observe the fine structure of the reacted region. A reflection diffraction experiment was performed with this instrument on the large crystal specimen described above. The very thin reaction layer adhering to the sapphire crystal has been

tentatively identified as described below.

Electron microprobe analyses of polished and carbon-coated specimens were performed in order to determine the compositions of various regions of the reaction zone. Fixed time point count determinations were made at 5 μm intervals across the interfacial zone. Standards of pure Ti, Ti_3Al , Al_2O_3 were used in correcting the microprobe data. Raw intensity data were used as input to the computer program MAGIC (Version III) [7]. Corrections were made for backscatter electron loss, mean ionizational potential, fluorescence, and detector dead time. Since the instrument used could not detect oxygen, this element was determined by difference.

As part of this study nine compositions in the system Ti-Al-O were selected for annealing experiments to determine the compatibility relations at 870°C. Mixtures of Ti, TiO_2 , and Al powders were carefully mixed and cold pressed into pellets. Each specimen was wrapped in Ta foil and sealed in quartz capsules under a vacuum of 10^{-5} torr. The capsules were annealed for various lengths of time at $865 \pm 5^\circ\text{C}$ and water-quenched. Phases present were determined using the X-ray diffractometer. When equilibrium was not reached, its position was inferred from the changing ratios of peak heights.

3. Experimental results and discussions

3.1. Interface characteristics

The microstructural features of the "gross" reaction layers for the pure Ti/ Al_2O_3 and the α -Ti (alloy)/ Al_2O_3 reaction couples were almost identical. In Fig. 1, the region termed the "gross" reaction layer, region of new phase formation, is clearly defined as lying between the sapphire (dark, quarter circle area) and the large grain size, high reflectivity α -Ti matrix. In addition to the new phases being formed, a wide band of hardened, recrystallized α -Ti has formed adjacent to the unaltered matrix [5]. The deleterious effect that this embrittled region can have on composite properties has been considered elsewhere [5].

Since the morphology of the interfacial reaction zone and the reaction rates for pure Ti and the four alloys considered were very similar, the detailed characterization study was conducted with the simplest possible system, i.e., pure Ti/ Al_2O_3 . The use of pure metal/filament reaction couples to identify reaction products and describe their morphology and the extrapolation of these results to dilute alloy/filament

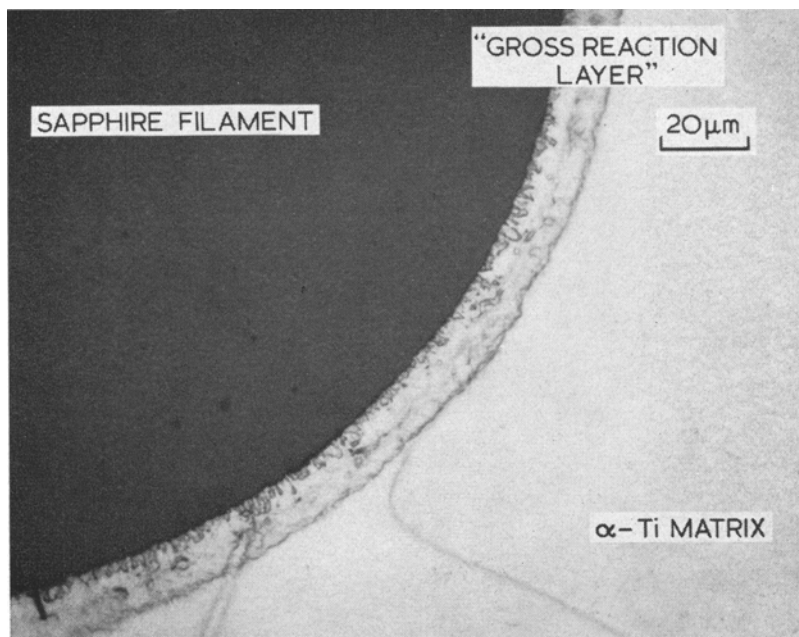


Figure 1 Ti/Al₂O₃ interaction layer after 60 h at 1600°F (871°C) [5].

systems has been shown to be a valid method of characterization, if certain precautions are taken [4]. Each dilute alloy/filament system must be examined for the formation of new intermetallic compounds which may form by one or both of two possible mechanisms. First, new compounds may form as the result of a reaction between the filament and the solute additions. Second, new compounds may form between the solute and solvent as a result of concentration of solute rejected ahead of the growing reaction layer. The four Ti alloys considered contained only minor solute additions, so it seemed quite reasonable to extrapolate the phase constitution and nominal composition data for the pure Ti/Al₂O₃ interfacial reaction products to these more complex alloys. The most serious deviation expected from phase-diagram data was the rejection of β -stabilizing elements such as V and Mo ahead of the growing interface and the formation of Ti intermetallics with these elements. No evidence of such compounds was found from either micrographs or microprobe data.

Fig. 2 is an electron micrograph of a replica from the interface region of the sample seen in Fig. 1. The rather featureless area to the left is the filament. The reaction-zone interface with α -Ti is the distinct boundary running nearly

vertically on the right hand side of the photograph. A faint, irregular line roughly parallel to the other interface boundaries divides the reaction zone into a slightly larger outer zone and a narrower inner zone with isolated second phase particles clustered near the alumina boundary. Fig. 3 is a higher magnification micrograph illustrating these isolated particles more clearly. The tentative identification of these small grains is discussed below.

Efforts to obtain phase composition data for the complex reaction layer from the Ti/Al₂O₃ (filament) specimens were frustrated by the extreme difficulty in exposing a sufficient volume of the unknown phases to radiation necessary for X-ray diffraction analysis. The large crystal specimen described in the experimental procedure was selected to obtain sufficient quantities of reaction products in a useful geometry for diffraction analysis. The sample was annealed above the α - β Ti transition temperature to accelerate the growth of the reaction layer after initially diffusion bonding well below the α - β transition temperature. The analysis results are directly applicable to the specimens that were annealed below the transition temperature since the reaction layer exhibited no microstructural differences for the two cases. This conclusion is

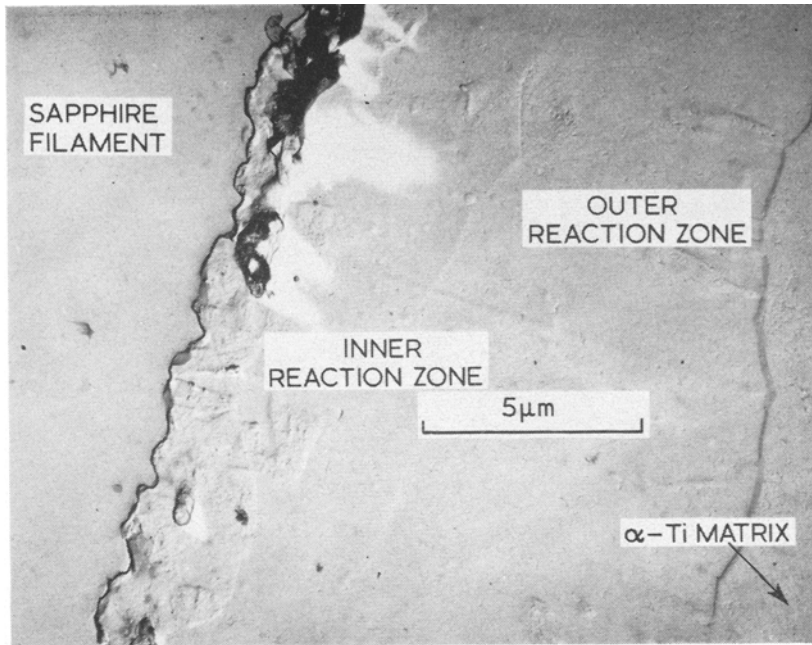


Figure 2 Electron micrograph of the reaction layer of the sample as shown in Fig. 1.

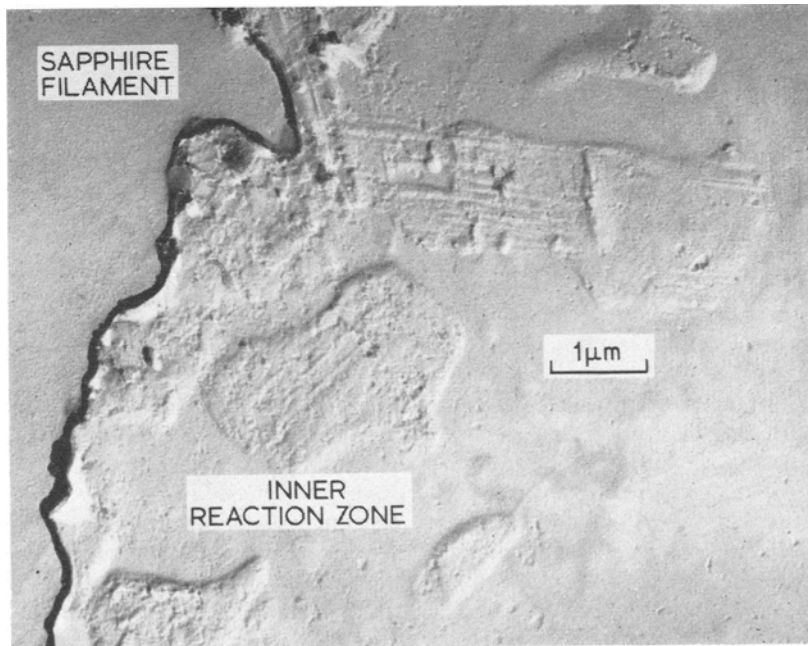


Figure 3 Electron micrograph of same sample as Fig. 2 showing the inner zone of the reaction layer.

quite reasonable when one realizes that the Ti matrix material adjacent to the reaction layer is α -Ti whether annealed below the transus or at 985°C because the contaminants Al and O are

both α -stabilizing elements and increase the transition temperature very sharply so that even at 985°C the reaction zone is in fact growing by reaction with α -Ti producing the same sequence

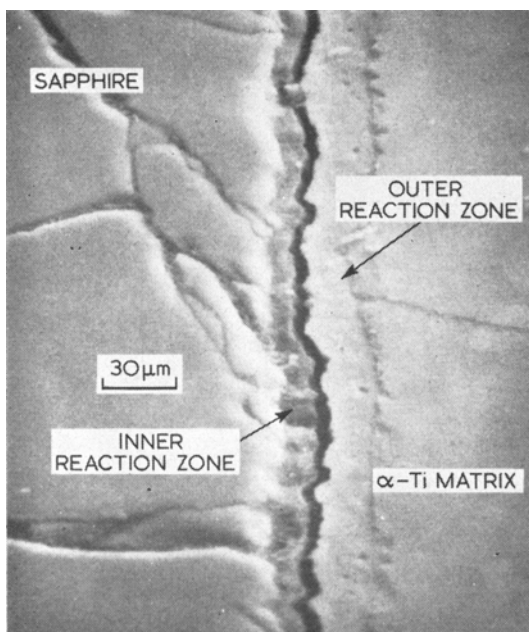


Figure 4 SEM photograph of the Ti-Al₂O₃ reaction couple annealed at 1800°F (981°C) for 940 h.

of new phases in the reaction zone. Admittedly the composition will be slightly different in the samples annealed at 985°C from those annealed at lower temperatures.

Fig. 4 is a scanning electron micrograph of the interface region of the large crystal/titanium couple after being lightly etched. The sapphire crystal is on the left; the two major zones of the "gross" reaction layer are conveniently parted by a crack, presumably due to differential thermal strains, which appears as the dark shadow running top to bottom just to the right of the middle of the photograph. To the left of the crack is the inner reaction zone adhering to the sapphire crystal; to the right is the outer zone tightly bonded to the α -Ti. The separation of the couple along this crack allowed the direct analysis of the two zones by diffraction experiments. X-ray diffractometer traces were obtained for the reaction-zone adhering to the Ti portion of the above specimen. The observed pattern is listed in the left hand side of Table I. The pattern was indexed with a Ti₃Al type unit cell as shown in Table I [8]. The observed pattern represents a Ti₃Al phase with a range of compositions because of the nature of the specimen, and possibly with a preferential orientation. As a result, the pattern is not an ideal fit to the

TABLE I X-ray diffraction data from the outer reaction zone of a Ti-Al₂O₃ reaction couple

$d_{\text{obs}}(\text{\AA})$	I/I_0 (obs)	d_{calc}^* for Ti ₃ Al (\AA)	$(hkl)_{\text{calc}}$	I/I_0 [8]	(hkl) [8]
4.17	100	4.20	101	40	101
3.75	25	3.78	210	20	210
3.40	10	3.40	201	60	201
2.809	20	2.78	310	20	310
2.501	20	2.505	400	60	400
2.315	80	2.318	002	100	002
2.204	50	2.204	401	100	401
1.995	40	2.004	500	—	—
1.7024	20	1.7024	402	80	402
1.3186	20	1.3196	522	100	403
1.2279	20	1.2274	442	100	442
1.2096	10	1.2095	801	80	802
0.9748	10	0.9746	514	80	803
0.9279	10	0.9279	841	80	841
0.9068	10	0.9086	922	80	444

*Based on hexagonal unit cell dimensions $a_0 = 11.57\text{\AA}$, $c_0 = 4.64$ [8].

computer matched Ti₃Al pattern. The observed d -spacing at 1.995Å is not listed in the published pattern for Ti₃Al [8]. However, the peak corresponds to an allowed reflection for the compound but has not been observed to date. The $d = 1.995\text{\AA}$ peak also closely matches the (200) peak for TiAl. However, no microstructural evidence is apparent for the existence of TiAl in the outer reaction zone. The Ti₃Al zone was carefully removed in several stages with X-ray diffraction patterns from the new surface taken at each stage. However, the only other phase revealed by this procedure was α -Ti with an expanded unit cell dimension relative to the pure α -Ti.

Attempts to determine the identity of the inner reaction zone which adhered to the sapphire side of the large reaction couple (Fig. 4) using standard X-ray diffractometer techniques were unsuccessful. No diffraction pattern other than alumina could be detected. However, the reflection electron diffraction technique revealed a diffraction pattern which could be indexed on a NaCl type cubic unit cell with an $a_0 = 4.35\text{\AA}$ as shown in Fig. 5. This unit cell is somewhat larger than the unit cell of the NaCl-type TiO phase. However, this effect may be expected if the compound contained a substantial amount of Al ions.

A fixed-time point-count electron microprobe technique was employed on the above sample

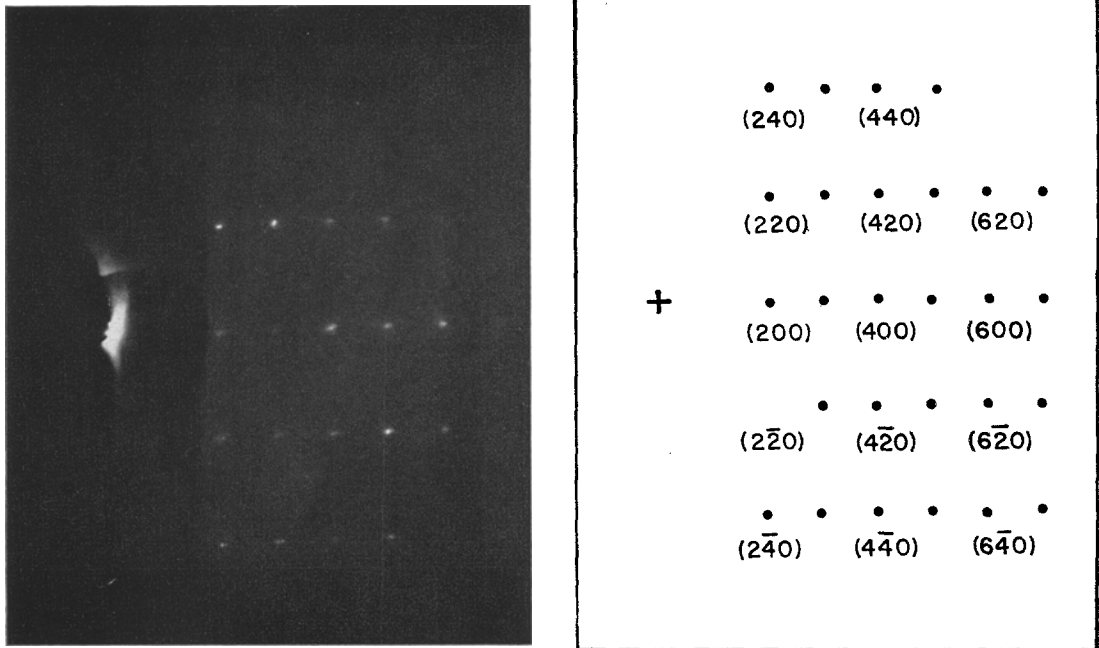


Figure 5 Reflection electron diffraction pattern from inner zone of the Ti/Al₂O₃ reaction layer. Lattice parameter is $a_0 = 4.35 \text{ \AA}$.

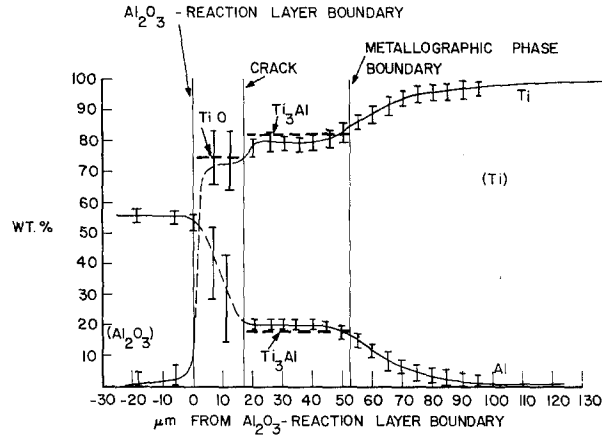


Figure 6 Summary diagram of microprobe data for the Ti/Al₂O₃ reaction couple annealed at 1800°F (981°C) for 940 h.

(before etching) to determine the elemental composition of the reaction products. The point-analyses for Ti and Al are shown in Fig. 6 as a function of distance from the sapphire-reaction layer interface. Each point on the curves is the average of seven point-counts taken at two different locations along the interfacial region. In these experiments the electron beam was

stepped at 5 μm intervals in a line perpendicular to the interface. The location of microstructural features and the compositions of Ti₃Al and TiO are indicated in this figure. The relief at the sapphire reaction layer interface and the crack between the two distinct reaction zones prevented the acquisition of quantitative data for the inner reaction zone, hence, the dotted line. There has

been considerable diffusion of Al into the Ti matrix. The analysis for oxygen by difference indicated a similar composition versus distance curve as would be expected since the diffusion rates of Al and O in α -Ti are almost identical over a wide temperature range [9, 10]. This diffusion of both Al and O causes a wide band of hard, recrystallized α -Ti around alumina filaments as discussed in an earlier paper [5]. The outer reaction zone clearly corresponds in composition to the Ti_3Al phase. The reaction layer of a Ti-6Al-4V/ Al_2O_3 reaction couple was examined in a similar manner and the composition of the outer reaction zone likewise corresponds to Ti_3Al .

3.2. Phase compatibility

The fact that Ti and Al_2O_3 are not the end-members of a binary join in the ternary system Ti-Al-O is obvious from the fact that the phases in the reaction-layer, i.e., Ti_3Al and TiO, do not lie on the line connecting Ti and Al_2O_3 . However, insufficient data exist to construct the compatibility triangles in this system at 865°C. If these compatibility relations could be constructed, then a clue to the identity of the isolated particles in the TiO phase could be obtained. Assuming that the phases in the reaction zones are in equilibrium,

the results of the phase identification experiments could be checked by an independent method. From the binary phase relationships in the Ti-Al system [8, 11, 12], Ti-O system [13-15], Al-O system [16], and the join Al_2O_3 - TiO_2 [17] many ternary compatibility triangles are possible. Ternary phase relations in the Ti-Al-O system have been studied to a limited extent in the Ti-rich corner of the diagram above 1200°C [18].

As a part of this study nine compositions in the Ti-Al-O system (Fig. 7) were selected for annealing experiments at 865°C to establish the compatibility relations. No attempt was made to define accurately phase fields in this isothermal section. The Ta wrapped, quartz encapsulated pellets were annealed for various lengths of time at $865 \pm 5^\circ C$ and water-quenched. After annealing, each specimen was checked for Ta contamination using an X-ray fluorescence technique - none was observed. Samples 6 to 9 reached equilibrium, as determined by the unchanged ratios of equilibrium phases and the disappearance of metastable phases, after 4 weeks at 865°C. Sample 5 reached equilibrium after an additional anneal for 6 weeks. However, samples 1 to 4 did not reach equilibrium as indicated by the presence of more than three phases. The equilibrium condition shown in

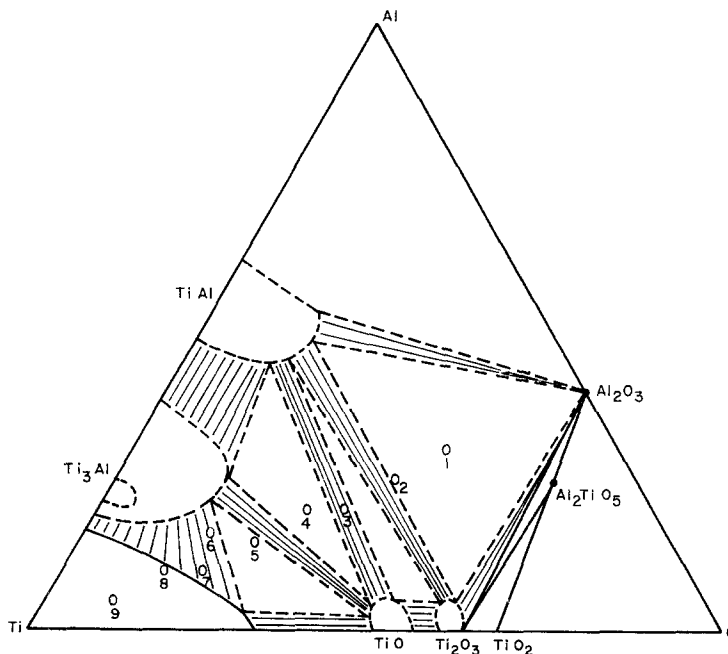


Figure 7 First of two possible phase diagrams for the system Ti-Al-O at 1600°F (871°C). Dotted lines indicate uncertainty as to exact compositions.

Fig. 7 was indicated by changing peak heights for these samples. Unfortunately, the equilibrium phase assemblage in the area of samples 3 and 4 could not be unequivocally established. As a result, Figs. 7 and 8 represent the two possible diagrams for the isothermal section of this system. Despite this ambiguity, the only possible phase in equilibrium with both TiO and Al_2O_3 is $(\text{Ti, Al})_2\text{O}_3$ in both diagrams. Thus, from the assumption of equilibrium it could be concluded that the second phase particles in the TiO phase of the reaction layer are $(\text{Ti, Al})_2\text{O}_3$. However, there is also the possibility that these second phase grains are either a nonequilibrium phase or a phase precipitated during cooling of the reaction couple, or possibly the result of diffusion across a two phase field along a path not parallel to a tie-line. Since all of these possibilities exist for the formation of these second phase grains, their identity can only be cautiously assumed to be $(\text{Ti, Al})_2\text{O}_3$.

3.3. Reaction kinetics

The reaction rate study reported for pure Ti and Ti-6Al-4V with alumina [5] was extended to include the two technologically important alloys Ti-6Al-2Sn-4Zr-2Mo and Ti-8Al-1Mo-1V which contain predominantly α -Ti. The growth of the

reaction zones between these alloys and alumina as a function of time at 925, 865, and 780°C were measured. The data are plotted in Fig. 9 as $x = K\sqrt{t}$, where x is the thickness of the "gross" reaction layer in microns, K is the parabolic rate constant, and t is reaction time in seconds at the respective temperatures. From the slopes of straight lines, as determined by a least squares technique, the K values were determined. Although the geometry of these reaction couples was cylindrical, the kinetics follow a parabolic rate law since the dimension of the growing layer is much smaller than the diameter of the cylinder. In the early stages of a finite and cylindrical reaction couple the growth of a product phase may follow the parabolic rate law [19]. Note that at zero on the time axis the extrapolated curves do not intersect the thickness axis at the "as bonded" reaction layer thickness of 1.5 μm . This is probably the result of somewhat different "heat-up" times to the annealing temperature and the fact that no correction is made for the heat-up times. If the lines are extrapolated backwards, they seem to intersect at $x = 1.5 \mu\text{m}$ and $t^{\frac{1}{2}} = -55 \text{ sec}^{\frac{1}{2}}$. If a "heat-up" correction is made by adding 55 $\text{sec}^{\frac{1}{2}}$ to all the anneal times, then the lines intersect at approximately 1.5 μm .

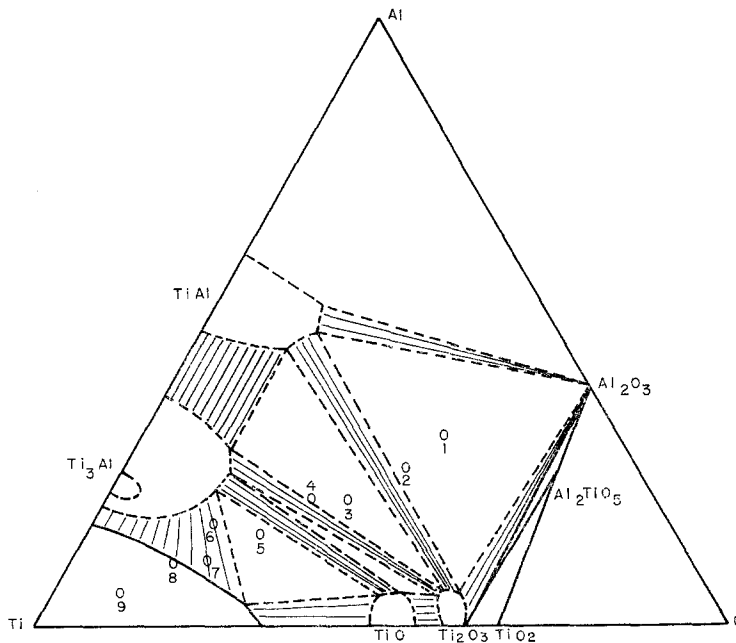


Figure 8 Second of two possible phase diagrams for the system Ti-Al-O at 1600°F (871°C). Dotted lines indicate uncertainty as to exact compositions.

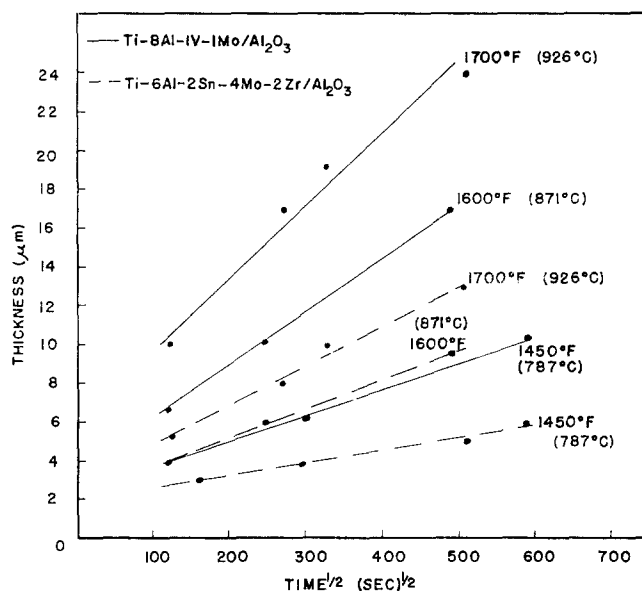


Figure 9 Growth of reaction layer thickness as a function of time and temperature.

The K values are plotted as a function of reciprocal temperature in Fig. 10 along with the previously published data [5]. As in the case of Ti-6Al-4V the slopes of the curves decrease at higher temperatures and deviate from the apparent activation energies which were determined for Ti/Al₂O₃ and Ti-6Al-4V/Al₂O₃. Because of the similarity in phase constitution of the alloys involved and the similarities in microstructural features of the reaction layers, it seems reasonable to assume that the lower temperature regions of these curves approach linearity and demonstrate apparent activation energies comparable to those shown by the Ti/ and Ti-6Al-4V/Al₂O₃ reactions. Attempts to verify this speculation at 648°C were unsuccessful because the growth of the reaction layer was too little to be measured accurately even after several anneals of 100 h each. The apparent activation energies shown in Fig. 10 were derived by multiplying the slopes by two in order to change the K values into units of cm²/sec; the commonly used units in diffusion experiments.

The fact that the apparent activation energies for these complex reactions are similar suggests the possibility that there is a common rate controlling step for all the systems considered. Since the faster reacting alloys have high Al contents and the product layers have flat interfaces, it is possible that Al transport through the Ti₃Al layer is rate-controlling [19]. Thus, the

reaction rate would be accelerated in these alloy/sapphire systems relative to the pure Ti/alumina system, since the amount of Al that must be transported to form Ti₃Al at the growing interface is reduced. Presumably, the failure of the Ti-6Al-2Sn-4Zr-2Mo alloy to follow this behaviour is either due to alloying of Sn in the Ti₃Al phase thereby lowering the rate of Al diffusion or due to the build up of the rejected β -stabilizing elements Zr and Mo at the growing interface with the effect of lowering the Al content at the interface [4]. It is very difficult to rationalize these data without a complete analytical treatment of the problem using non-existent multicomponent diffusion coefficients as a function of composition, and solubility limits of the phases involved.

However, the practical value of the Arrhenius plot of Fig. 10 is in the comparison of the relative reaction rates for various Ti alloy composites during fabrication and use at high temperatures. At a desirable long-term use temperature of 540°C, the reaction rates are slow enough to consider the composite essentially "stable" during reasonable lifetimes. The data for Ti (40A)/Borsic^R has been included in the plot for comparison. With regard to total reaction, the Ti alloy/alumina systems are more reactive than Ti/Borsic^R except for the Ti-6Al-2Sn-4Zr-2Mo/alumina system. However, the effect of the total reaction layer thickness on the mechanical

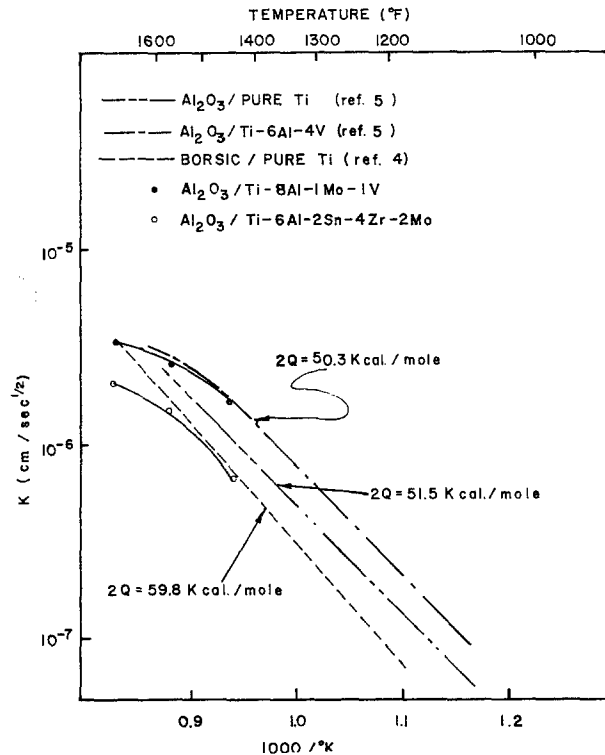


Figure 10 Parabolic rate constants as a function of reciprocal temperature.

properties of a composite material is the chief criterion for judgment and is the subject of current study.

4. Summary

The reactions of pure titanium and three important α -titanium alloys with sapphire were investigated and found to be very similar in the temperature range 650 to 925°C. The morphology and phase composition of the products in the reaction layer of a pure Ti/ Al_2O_3 reaction couple were examined in detail. The reaction layer consists of two zones. The zone adjacent to α -Ti was identified as Ti_3Al . The reaction zone adjacent to Al_2O_3 was identified as a TiO-type phase and contains second phase particles which were tentatively identified as $(\text{Ti}, \text{Al})_2\text{O}_3$. These results are extrapolated to the three Ti alloy/ Al_2O_3 reactions investigated based upon the similar morphologies of their reaction layers, microprobe data from a Ti-6Al-4V/ Al_2O_3 reaction couple, and data from other Ti alloy/filament systems.

The kinetics of the reaction of the two alloys Ti-6Al-2Sn-4Mo-2Zr and Ti-8Al-1V-1Mo with

sapphire were investigated and compared with the kinetics of pure Ti and Ti-6Al-4V/sapphire reactions from a previous study. The isothermal growth of the reaction layers follow a parabolic rate law. Since the Al-containing alloys, except Ti-6Al-2Sn-4Mo-2Zr, reacted more rapidly with Al_2O_3 than pure Ti it is possible that Al diffusion through the Ti_3Al zone is the rate controlling step. Presumably, the failure of the Ti-6Al-2Sn-4Mo-2Zr alloy to follow this behaviour is due to the higher Mo concentration and possibly the presence of Sn. This seems reasonable since the amount of Al that must be transported to the growing $\text{Ti}_3\text{Al}/\alpha$ -Ti interface would be less for the alloys that contain Al.

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