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Oxidation behavior of titanium aluminides

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Abstract. — Results from an ongoing study of the high temperature oxidation of intermetallic compounds in the Ti-Al system are presented. The oxidation behavior of alloys based on TiAl (γ) has been found to be extremely complex depending on temperature and atmosphere composition. Protective alumina scales are formed in pure O₂ up to a critical temperature above which a mixed TiO₂/Al₂O₃ scale forms and grows at rates which are orders-of-magnitude faster than that of alumina. This phenomenon is believed to result from the formation of Al-containing internal oxides which coupled with the closeness in stability of alumina and the titanium oxides, prevents the alumina from becoming continuous. Continuous alumina scales were not observed, even at temperatures below 1000 °C, when N₂ was present in the oxidizing gas. The effect of the N₂ has been shown to be involved with the initial development of the reaction products.

1. Introduction.

Alloys in the Ti-Al system are of interest for high temperature systems such as aircraft engines because they have low density and substantial high temperature strengths. However, their resistance to oxidation and interstitial embrittlement is a concern. Those alloys which form alumina scales have excellent resistance while those which form titania-rich scales oxidize at rates which are unacceptably fast for most applications. The alloys based on γ -TiAl are generally regarded as having better oxidation resistance than those based on α_2 -Ti₃Al. The oxidation behavior of γ is the subject of this paper.

OXIDATION OF γ -TiAl. — Choudhury *et al.* [1] studied the oxidation of TiAl (50 at% Al) in O₂ and air over the temperature range 800-1200 °C. In O₂ cast TiAl which was abraded through 120 grit SiC formed alumina and exhibited k_p values $\approx 10^{-9}$ g²cm⁻⁴h⁻¹ at 950 °C but polished specimens formed TiO₂-rich scales and exhibited k_p values of about 10^{-5} to 10^{-6} g²cm⁻⁴h⁻¹. A Ti₃Al layer formed between the oxide and the alloy. Extruded TiAl formed alumina scales regardless of surface preparation. Choudhury *et al.* explained these differences in terms of macroinhomogeneities in the cast structure. Oxidation behavior in air at 950 °C was independent of specimen preparation or fabrication method with titania-forming kinetics (k_p about 10^{-5} - 10^{-6} g²cm⁻⁴h⁻¹) observed in all cases. The scales were similar to those formed on polished specimens in O₂ at 950 °C. Oxidation kinetics for all alloys, regardless of surface preparation, at 1100 and 1200 °C indicated TiO₂ formation. The transition from titania to alumina forming kinetics with decreasing temperature occurred at a higher temperature in O₂ with internal oxidation at the two higher temperatures. Experiments to determine the species responsible for the difference between exposure in O₂ and air indicated that CO, CO₂ and H₂O impurities were not responsible nor was the difference

in p_{O_2} . It was concluded that N_2 was responsible for the increased rate of oxidation in air although no N_2 -containing phases were identified in the scale or substrate. Several mechanisms were postulated including:

- 1) N_2 doping of an initial TiO_2 scale resulting in more rapid oxygen transport to the scale/ Ti_3Al interface;
- 2) The grain boundary diffusion of N_2 through the oxide to form AlN or possibly $AlON$ at the scale/ Ti_3Al interface;
- 3) N_2 grain boundary diffusion through the scale to the scale/ Ti_3Al interface with a subsequent stabilization of the Ti_3Al layer with the reduced Al activity at the interface promoting the growth of TiO_2 .

Mendiratta and Choudhury [2] reported that varying the Al -content of $TiAl$ (50, 53, and 54 at %) did not affect the oxidation behavior. Appalonia *et al.* [3, 4], however found that:

- 1) Alloys containing 50, 53, and 56 at % Al formed continuous alumina in oxygen at 800 °C with the Ti -56 at% Al alloy continuing this behavior up to 1000 °C. Between 1000 and 1100 °C, however, k_p increased by a factor of 10^6 for the 56 at% Al alloy as the result of a transition from alumina to *titanina* formation;

- 2) Alloys containing 50, 53, and 56 at% Al underwent accelerated oxidation in air with the rate independent of Al content at 800 °C.

2. Experimental.

Arc-melted $Ti-Al$ alloys with Al contents of 52 and 54 at% (γ) were studied. No substantial effect of heat treatment was observed on the oxidation behavior. Therefore, the data will be presented without specifying heat treatment. All specimens were polished through 600 grit SiC . Oxidation experiments were carried out in pure O_2 , air, tank argon containing O_2 impurities at $p_{O_2} \approx 10^{-4}$ atm, and various O_2 - N_2 mixtures at temperatures from 750 to 1100 °C. The oxidation kinetics were studied using a Cahn Model 2000 microbalance and the oxidation morphologies were studied using x-ray diffraction (XRD), Auger electron spectroscopy (AES), scanning electron microscopy, and energy-and wavelength dispersive x-ray analysis (EDS and WDS).

3. Results and discussion.

3.1 THERMODYNAMICS. — An important aspect of the oxidation of $Ti-Al$ alloys is the small difference in standard free energy of formation between alumina and the oxides of titanium which is accentuated by the negative deviation from ideal solution behavior in the $Ti-Al$ system. This is illustrated in figure 1 which is a plot of estimated activities *versus* composition in titanium-aluminum alloys at 1100 K. The aluminum activity is much smaller than unity in Ti_3Al and $TiAl$. In fact, combining these activities with standard free energy data for the oxides indicates that TiO is more stable in contact with the alloy than is Al_2O_3 for atom fractions of Al less than about 0.5. More detailed analyses of this situation are presented by Rahmel and Spencer [6] and Luthra [7]. Thus, Al_2O_3 is unstable in contact with binary α_2 and is only marginally more stable than TiO in contact with γ .

3.2 EFFECTS OF TEMPERATURE. — Weight change data for $TiAl$ are compared in figure 2 for exposures in air and in O_2 at a number of temperatures. In both atmospheres the weight gains are low at lower temperatures and then increase drastically over a narrow range of

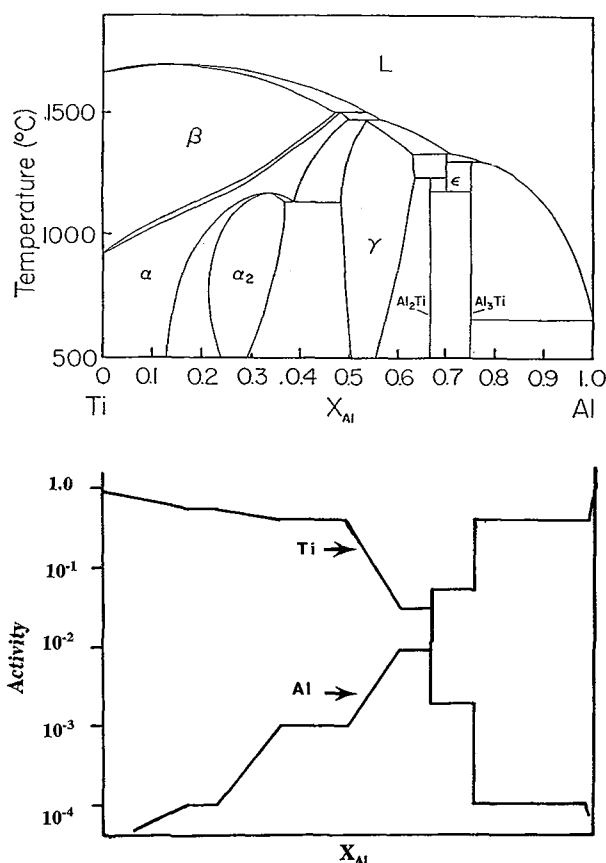


Fig. 1. — Binary phase diagram for the Ti-Al system (Ref. [5]) and estimated aluminum activities *versus* atom fraction of aluminum at 1100 K.

temperatures. In O_2 , at temperatures of 1000 $^{\circ}C$ and lower, a thin alumina scale (Fig. 3a) develops and the oxidation rates are correspondingly slow. However, on raising the temperature by only 25 $^{\circ}C$ the rate increases markedly as a result of the development of the oxidation morphology illustrated in figures 3b, c, d. The scale consists of an outer rutile layer over a layer which is an intimate mixture of rutile and alumina. An internal oxidation zone is observed below the scale. The cause of the transition is not completely understood but may well be associated with the internal oxides which are not observed at temperatures below 1000 $^{\circ}C$, even when the alumina is not continuous. The internal oxides are indicated by EDS to contain both Al and Ti which suggests they are $TiAl_2O_5$. This oxide cannot form below the eutectoid temperature in the TiO_2 - Al_2O_3 system which is reported to be 1010 $^{\circ}C$ [6]. At lower temperatures internal oxidation is not possible because Al_2O_3 would have to form and it is likely that the Al activity would not be high enough for this phase to form. The formation of internal $TiAl_2O_5$ would deplete the alloy of Al since two moles of Al react for each mole of Ti. Therefore, since the alumina is only marginally more stable than TiO , the internal oxidation would prevent an alumina scale from forming. Further experiments are needed to ascertain if the above mechanism is correct or if the internal oxidation is in fact the result, rather than the cause, of a continuous alumina scale not forming.

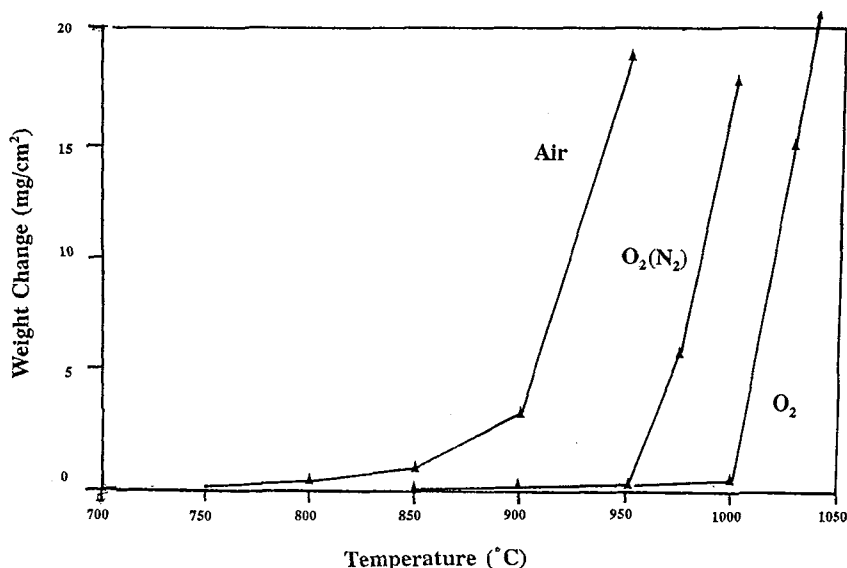


Fig. 2. — Weight change *versus* temperature for TiAl oxidized for 58 hours in air, oxygen, and oxygen which is contaminated with a small amount of nitrogen. Air and O₂(N₂) curves are for 54 at% Al and O₂ curve is for 52 at% Al.

3.3 EFFECTS OF ATMOSPHERE. — Protective alumina scales form on TiAl, exposed in O₂, up to 1000 °C (Fig. 2). However, the same exposures conducted in air result in the formation of TiO₂-rich scales which grow at rates orders of magnitude faster than pure alumina scales and even trace amounts of N₂ lower the critical temperature for the transition from alumina to titania formation, as indicated by the line labelled O₂(N₂) in figure 2. This effect is illustrated in figure 4. The rate of oxidation increases continually as increasing amounts of N₂ are added to pure O₂. Figure 5 shows that addition of 10% N₂ to O₂ results in the formation of nodules of intermixed TiO₂ and Al₂O₃ interspersed with thin areas of protective Al₂O₃ which would cover the entire surface in the absence of N₂. The area density of these nodules increases as the concentration of N₂ increases (Fig. 6) until the surface is completely covered with the mixed oxides when the gas contains 90% N₂. The effect of N₂ appears to involve the nucleation and initial growth of the scale since preoxidation in argon, which contains O₂ impurities, develops an alumina scale which remains protective during subsequent exposures in air (Fig. 7). Kobayashi, *et al.* [8] have also reported that preformed alumina scales formed on TiAl at reduced O₂ pressure remain protective during subsequent exposures in air, even under cyclic conditions.

The influence of N₂ on the initial scale development has been investigated using Auger spectra collected while sputtering through scales formed for short times in O₂ and air. The results are summarized in figure 8. The scales on specimens which were cooled as soon as they reached 900 °C (0 min) were 2000-3000 Å thick with AES profiles which were consistent with intermixed transient oxides of Al and Ti. However, specimens exposed in air were found to have a N₂-rich layer at the scale/alloy interface. This layer is indicated as TiN in figure 8 but is still to be unequivocally identified. The scales on specimens which were held in O₂ at 900 °C for 15 minutes were quite different from those in air. The AES profiles indicated that a continuous layer of aluminum oxide was forming below the mixed transient oxide in

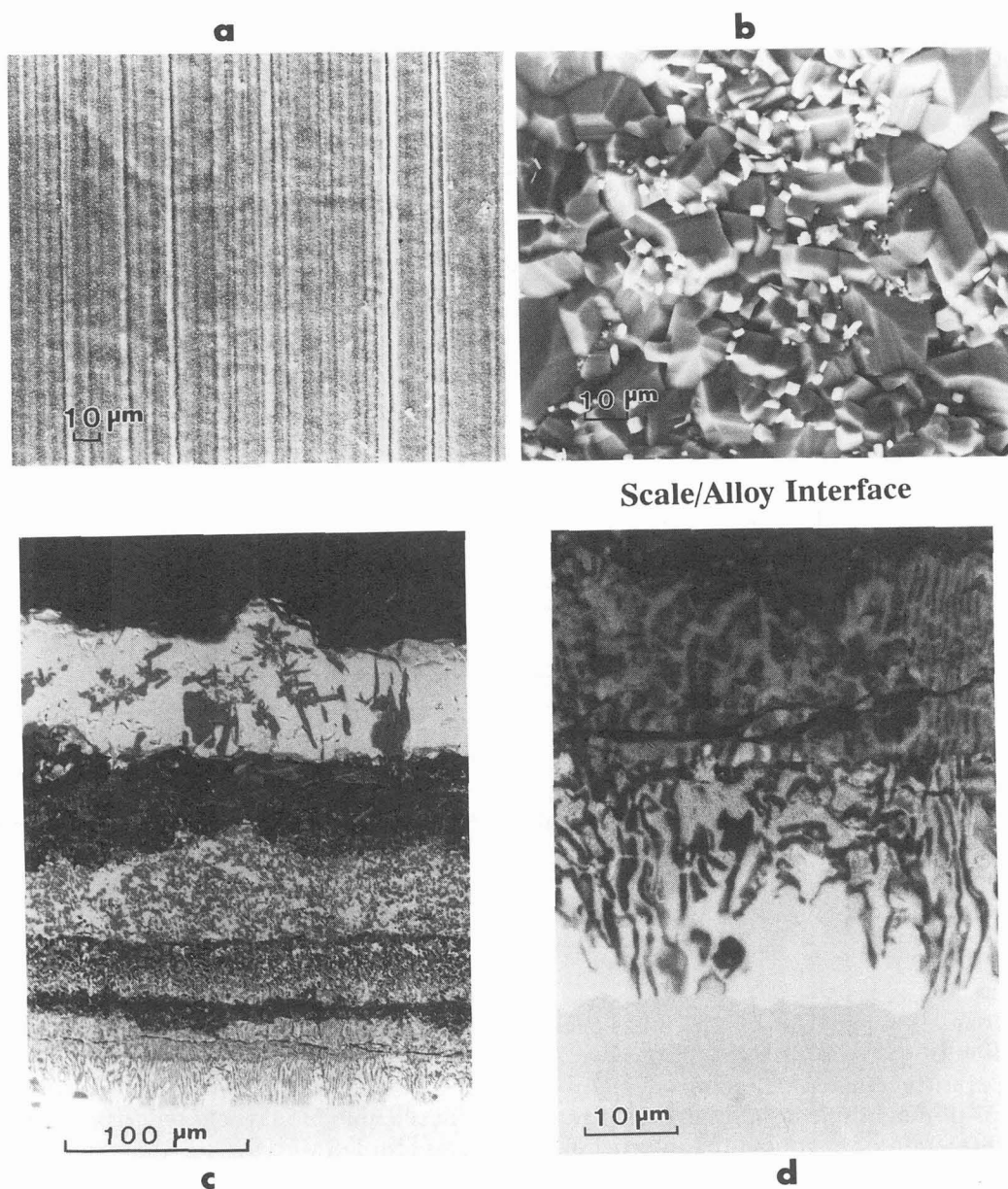


Fig. 3. — Surfaces and cross-sections of TiAl (52 at%) oxidized for 160 hours in oxygen: a) surface, 900 °C; b) surface, 1050 °C; c) and d) cross-section, 1050 °C.

O₂ while in air the scale consisted only of intermixed Ti- and Al-oxides and was almost ten times as thick as that in O₂. Therefore, it appears that a major effect of the N₂ is in forming a nitride layer which prevents alumina from developing continuity. However, the presence

of the N_2 is also required for the continued rapid growth of the scale since figure 7 indicates that switching the gas to O_2 after a one hour exposure in air caused the oxidation rate to decrease markedly.

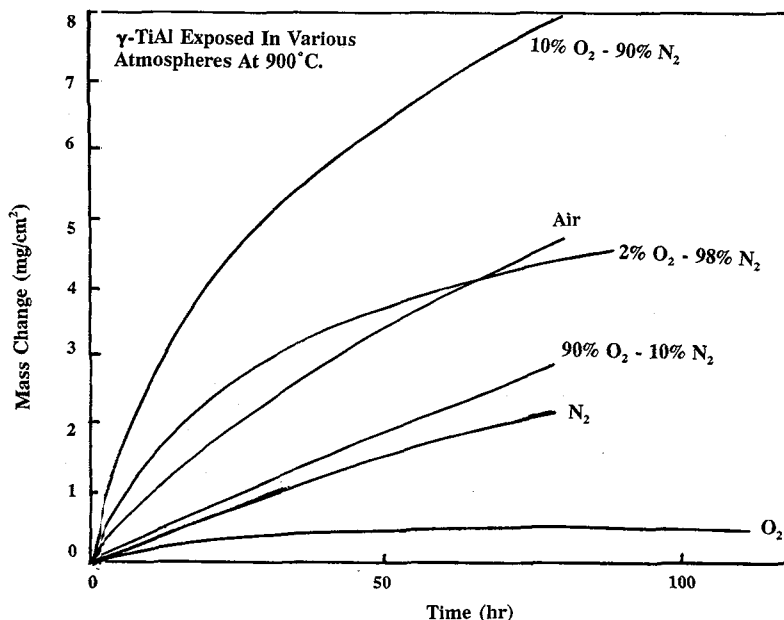


Fig. 4. — Weight change *versus* time data for TiAl (52 at% Al) oxidized at 900 °C in various atmospheres.

4. Summary.

The oxidation behavior of γ -TiAl has been found to depend on temperature and the composition of the oxidizing gas. Protective alumina scales formed in pure O_2 up to a critical temperature above which a mixed TiO_2/Al_2O_3 scale formed which grew at rates which are orders-of-magnitude faster than that of alumina. This phenomenon is believed to result from the formation of Al-containing internal oxides which, coupled with the closeness in stability of alumina and the titanium oxides, prevented the alumina from becoming continuous. Continuous alumina scales did not form at any temperature above 750 °C when N_2 was present in the oxidizing gas. The effect of the N_2 has been shown to be involved with the initial development of the reaction products.

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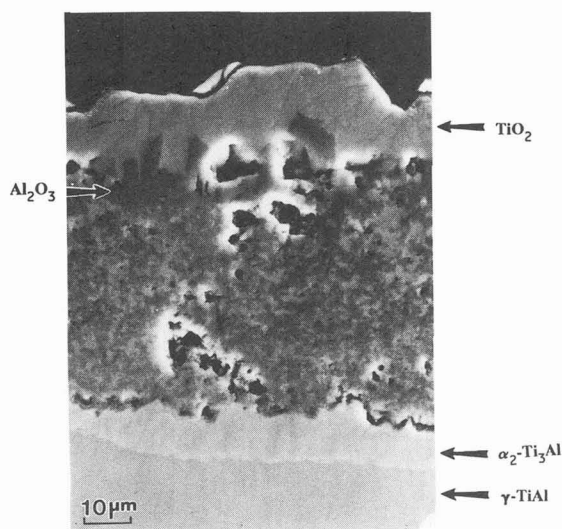
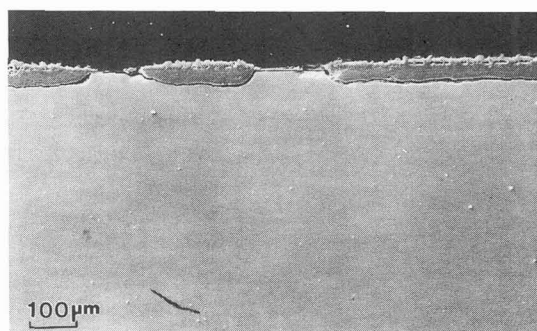
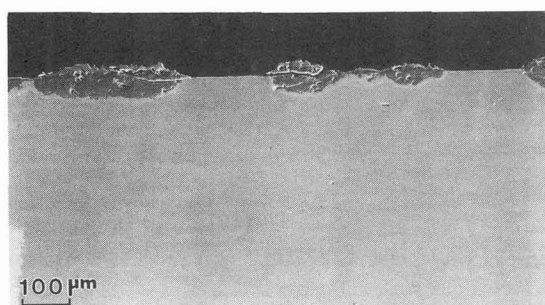


Fig. 5.

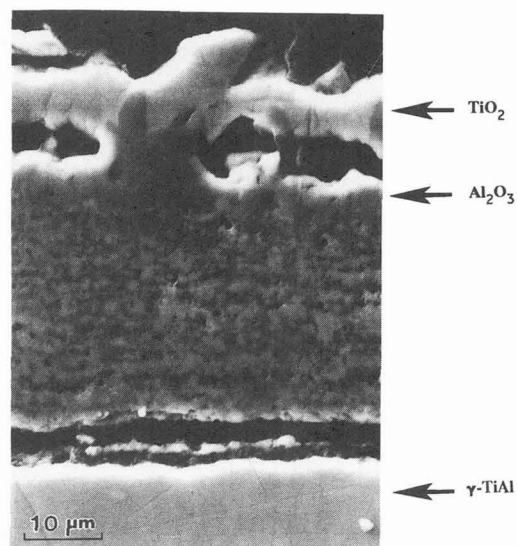


Fig. 6.

Fig. 5. — Cross-section of TiAl (52 at% Al) oxidized in 10% N₂ - 90% O₂ at 900 °C for 80 hours.

Fig. 6. — Cross-section of TiAl (52 at% Al) oxidized in air at 900 °C for 80 hours.

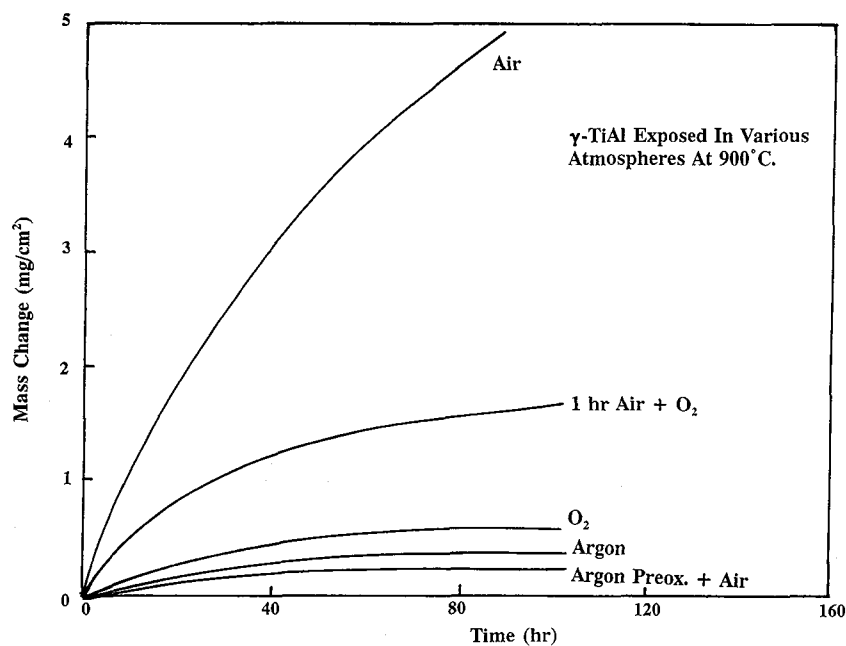


Fig. 7. — Weight change *versus* time curves showing the effect of various pretreatments on the oxidation behavior of TiAl (52 at% Al) at 900 °C.

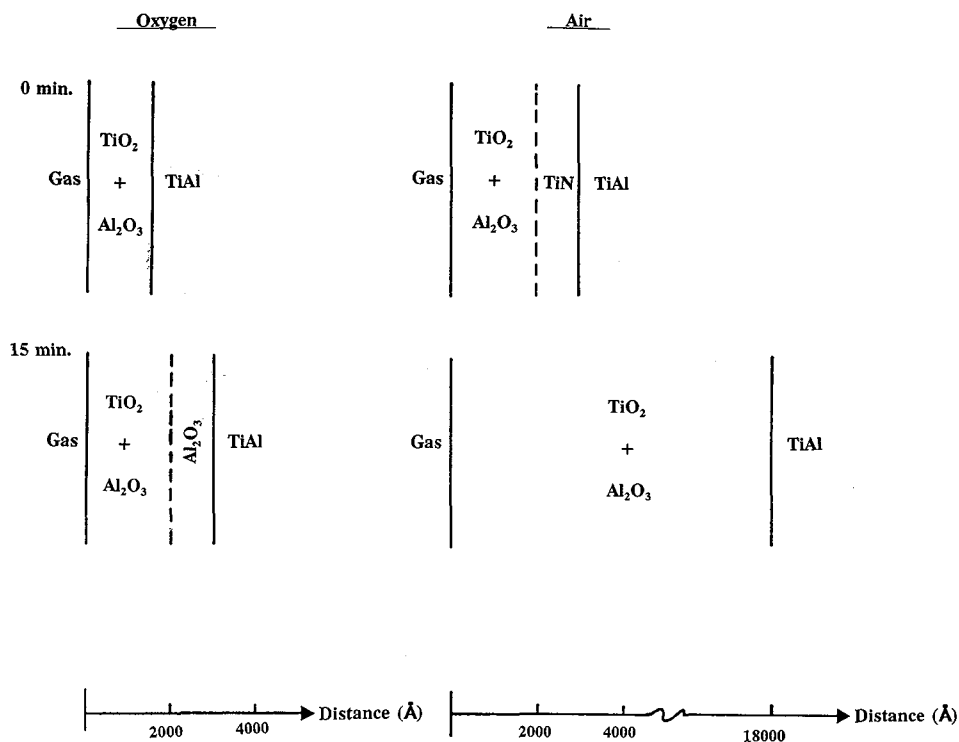


Fig. 8. — Summary of initial scale growth sequence on TiAl in air and oxygen inferred from Auger sputter profiles.