Oxidation Behavior of Binary Ti–Al Alloys in High Temperature Air Environment[†]

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The oxidation behavior of binary Ti–Al alloys containing 20 to 63 mass%Al was studied in air at 1073 to 1173 K. For alloys containing less than 51%Al multi-layered scale was formed accompanying internal oxidation zone in the base metal giving smaller oxidation resistance, while for 63%Al alloy protective scale was formed. The relationship between the scale morphology and the oxidation behavior was examined and the breakaway oxidation behavior observed in the alloys was interpreted by the stability in the continuity of the second from outer Al_2O_3 scale layer. The internal oxidation behavior was examined and discussed in terms of various influences on the overall oxidation behavior.

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I. Introduction

The TiAl intermetallic compound has received an increasing interest as an attractive light weight heat resistant material potentially to be used in the advanced transport systems such as space planes and next generation engines. In recent years, as a result of various efforts, the room temperature ductility has been improving and attempts toward practical application have been started. However, it has been well known that the oxidation resistance of TiAl would not be sufficient at temperatures above 1100 K. Although it contains 50 at%Al, the alloy does not form a protective Al_2O_3 scale. During the past couple of years, the number of research papers on its oxidation behavior has been increasing^{(1)–(4)}.

According to the present knowledge, oxidation rate of TiAl compared by the parabolic rate constant is approximately several orders of magnitude greater than an Al_2O_3 forming alloy (e.g. Ni_3Al) and is the order slightly better than a conventional 304 stainless steel, although the rate is much smaller than that of a pure titanium⁽⁵⁾. In order to overcome this defect, various attempts to improve the oxidation resistance have been conducted. Pre-oxidation treatment under a low oxygen potential atmosphere and addition of elements such as Si, Nb, W, Mo have been known to be effective for increasing its oxidation resistance^{(1)–(5)}. However, mechanism of oxidation in the Ti–Al alloys are not yet understood well. Even the rate controlling layer in the stratified scale is not clear.

In the present paper, oxidation behavior of binary Ti–Al alloys with varying Al content was studied with particular interest in the change in the scale structure as the Al content and test conditions are varied.

II. Experimental Procedure

Alloys were produced as small ingots of approximately 120 g by a non-consumable argon arc furnace, using titanium sponges and aluminum granules (or platelets) as raw materials. Double melting was conducted by the same furnace. Chemical composition of the alloys produced is shown in Table 1. Aluminum content was widely changed to cover the composition range between Ti_3Al and TiAl_3 . Those ingots were heat treated at 1473 K for 86.4 ks before being sliced to obtain rectangular specimens $10 \times 30 \times 2$ mm in size. In the cases when an ingot was too brittle to obtain a regular size specimen, smaller size specimens were used. Specimens were polished on SiC paper up to 600 mesh, degreased and weighed before being tested.

Continuous oxidation tests were conducted in static laboratory air at temperatures between 1073 and 1173 K, for up to 360 ks. Each specimen was placed in an alumina crucible and when test time was finished the crucible was removed and immediately covered to keep all oxide scales in the crucible even if spallation occurred.

After those oxidation tests, the mass gain including spalled scale of each specimen was measured. Cross sections were examined by an optical and a scanning electron microscopes and by an electron probe microanalyser.

Table 1 Chemical composition of test materials (mass%).

Al	N	O	Ti
20.7	0.005	0.05	bal.
34.9	0.004	0.05	bal.
36.3	0.004	0.04	bal.
38.0	0.003	0.04	bal.
51.3	0.002	0.05	bal.
63.1	0.003	0.03	bal.

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III. Results

1. Mass change behavior

Variations in mass gain with Al content is shown in Fig. 1. As Al content was increased, the mass gain was decreased. Although the trend was almost as expected, it was worth noting that the mass gain varied quite markedly in the Al content range of 34.9 to 38.0 mass%. Particularly at 1073 K, the mass gain values of alloys containing Al greater than 36 mass% were almost the same.

Time dependent behavior of the mass gain is shown on log-log axes in Fig. 2. Both the 20.7 and 34.9 mass%Al alloys exhibited a break in the curve, suggesting that a change in the oxidation kinetics was occurring from approximately parabolic in the beginning to linear in the

later stage (we would like to call this 'breakaway' as is often used in the Zr oxidation). For the 63.1 mass%Al alloy, no such break was observed, showing a constant parabolic growth.

2. Observation in cross section

Oxide scales observed in cross section for typical alloys oxidized at 1173 K for 360 ks are depicted in Fig. 3. It was clear that the scale thickness was dependent on the Al content. Both the 20.7 and 34.9 mass%Al alloys showed a stratified multi-layered scale structure. The scale structure was analyzed to be in the order of $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2 + \text{Al}_2\text{O}_3/\text{internal oxides}$ in the Ti_3Al matrix from the outside, as has been reported previous-

Fig. 1 Variation of oxidation mass gain with Al content in Ti-Al alloys.

Fig. 2 Mass gain-time relationship obtained for several Ti-Al alloys at 1173 K.

Fig. 3 Cross-sections of oxide scale formed on typical alloys at 1173 K for 360 ks.

ly⁽¹⁾⁽²⁾⁽⁵⁾. The top two layers must be the “outer scale” growing outward and the $\text{TiO}_2 + \text{Al}_2\text{O}_3$ mixed oxide layer must be the “inner scale” growing inward. Also, it may be note worthy that pores tended to be observed along the top TiO_2 /second Al_2O_3 interface and in the inner, $\text{TiO}_2 + \text{Al}_2\text{O}_3$ mixed oxide region. As can be understood from the Fig. 4 as well, in the inner region relatively large pores appeared to grow along the TiO_2 -rich/ Al_2O_3 -rich region boundaries and relatively small pores were observed in the Al_2O_3 -rich region. On the other hand, the scale formed on the 63.1 mass%Al alloy was quite simple and uniform, the scale being a relatively thick TiO_2 layer in the outside and a very thin Al_2O_3 layer in the inside⁽⁵⁾. The Al_2O_3 layer was too thin to observe. In general, a protective Al_2O_3 usually formed on Ni and/or Fe based heat resistant alloys should be very thin under this temperature and time conditions, it being approximately $0.1\ \mu\text{m}$ according to the extrapolated calculation. The Al_2O_3 on the TiAl_3 alloy may be in the same order of thickness and must be quite protective. However, if the rate is assumed to be controlled by the growth of the Al_2O_3 , the total scale appeared to grow parabolically at the rate unexpectedly high (Fig. 2). Presumably, the parabolic rate observed may be the diffusion rate of Ti ions though the very thin Al_2O_3 layer, because the external TiO_2 appeared to grow with time to the thickness far greater than the Al_2O_3 layer.

In an attempt to understand what is occurring at the breakaway (Fig. 2), scales before and after the breakaway were compared. Figure 4 depicts the EPMA

results. Basically, the stratified scale structure was not changed. Only one clear change was observed in the second from outer Al_2O_3 layer. It was evident that the morphology of the Al_2O_3 layer, the second layer from outer, was different. Apparently, the layer was continuous before breakaway, but the layer lost the continuity after the breakaway. A similar observation was made for a Mn added TiAl ⁽⁶⁾. Thus, it may be concluded that the breakaway is definitely related with the loss of continuity in the second Al_2O_3 layer. This Al_2O_3 layer was far thicker than the Al_2O_3 formed on the TiAl_3 and, then, must be far less protective. However, this layer must be playing a protective role to keep the oxidation rate parabolic, probably by disturbing the air to have direct access to the metal-oxide interface. Figure 5 depicts the thickness change results for each layer in the stratified scale. After the breakaway, the top TiO_2 and the inner $\text{TiO}_2 + \text{Al}_2\text{O}_3$ layers increased its thickness rapidly.

The thickness of the each scale layer was also compared for the alloys with 34–38 mass%Al as shown in Fig. 6. It was understood that the composition in the scales changed significantly in this alloy composition range. The ratio of $\text{Al}_2\text{O}_3/\text{TiO}_2$ was markedly increased as Al increased a little.

3. Observation of internal oxidation

Along the scale/metal interface, an internal oxide zone and an aluminium depleted Ti_3Al phase layer were present. Figure 7 shows examples in the present study. At 1373 K, the internal oxide zone was clearly observed and

Fig. 4 Comparison of scale morphology between before and after breakaway (SEM-EPMA analysis; Ti-34.9 mass%Al).

Fig. 5 Thickness change of each oxide layer in the multi-layered scale with time, showing a rapid growth of the TiO_2 and the $\text{TiO}_2 + \text{Al}_2\text{O}_3$ layers.

Fig. 6 Variation of thickness of each oxide layer with Al content obtained for specimens oxidized at 1173 K for 360 ks.

Al_2O_3 internal oxides were growing as stringers to the direction perpendicular to the scale-metal interface. In this case, the thickness of the Ti_3Al layer was almost same as the depth of the internal oxidation, i.e. the $\text{Ti}_3\text{Al}/\text{TiAl}$ phase boundary appeared to move at the same rate as the growth of the internal oxides. Another interesting observation was that the internal oxides were present penetrating into the inner $\text{TiO}_2 + \text{Al}_2\text{O}_3$ mixed oxide layer. This evidence suggests that the inner scale

(a) SEM (1173 K, 21.6 ks) 2 μm

(b) SEM (1173 K, 360 ks) 2.5 μm

Fig. 7 Examples of internal oxidation zone growth observed in the Ti-34.9 mass%Al alloy.

Table 2 Variation of the internal oxide layer thickness with Al content (1173 K, 360 ks). (μm)

Al	Internal oxide thickness
20.7	8
34.9	5~6
36.3	6
38.0	4~5
51.3	1~2
63.1	—

may be the mixture of oxides (mixture of TiO_2 and Al_2O_3) grown from the underlying Ti_3Al matrix and the Al_2O_3 originally formed as internal oxides. Therefore, the internal oxide morphology may affect the oxidation behavior via influencing the morphology of the inner scale. At 1173 K, the internal oxidation was much harder to be observed and penetration depth were occasionally uneven. As shown in Fig. 7, the internal oxide stringers were very thin. Table 2 shows the measured values of internal oxide depth for all alloys tested at 1173 K for 360

ks. As Al was increased, the depth was apparently decreased. Also, the depth of the Ti_3Al zone was no longer the same as the depth of the internal oxidation. In the case of the 34.9 mass%Al alloy, the thickness of the Ti_3Al layer was approximately $11\text{ }\mu\text{m}$, this being almost twice as deep as the internal oxidation. At 1073 K, internal oxides were not observed.

4. Observation by TEM

The oxide scales and the scale-metal interface were observed by a transmission electron microscope after preparing specimens by ion-thinning. Figure 8 depicts typical photographs obtained for outside part of the scale formed on the 34.9 mass%Al alloy oxidized at 1173 K for 360 ks. The top TiO_2 were very coarse grained and the second Al_2O_3 layer were of fine grained with

average grain size of $(0.5\text{--}2)\text{ }\mu\text{m}$. The inner mixed oxide zone was composed of fine and coarse oxides and micro-pores.

Figure 9 shows a feature of metal side at the scale-metal interface. Internal oxides were observed with leaving at the top of the foil. As shown from the photograph, the grains of the Ti_3Al layer were coarse and columnar and the phase boundary between the Ti_3Al and the TiAl was sharp and smooth.

IV. Discussion

1. Effect of Al content on the oxidation

As described in the previous chapter, the increased Al content resulted in a decreased oxidation rate, in general.

Fig. 8 Transmission electron microscopy of oxide scale formed on the Ti-34.9 mass%Al alloy at 1173 K for 360 ks.

Fig. 9 Transmission electron microscopy of the metal adjacent to the scale-metal interface for the Ti-34.9 mass%Al alloy oxidized at 1173 K for 360 ks.

However, the behavior of the alloys in the concentration range of 34–38 mass%Al was somewhat different. In this range, the effect of Al concentration was greater than any other concentration range. This range correspond almost exactly to the TiAl single phase region. Also, as shown in Fig. 6, the $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio increased sharply in this range. Presumably, the preference of alloys for the formation of either Al_2O_3 or TiO_2 may be changing in this concentration range. According to the thermodynamic study on the Ti-Al-O system by Rahmel *et al.*⁽⁷⁾, the equilibrium oxygen partial pressure-Al content curves for Ti/TiO and for Al/ Al_2O_3 intersect in the TiAl single phase region, suggesting that Al_2O_3 would be more stable for the alloys with higher Al content and vice versa. The present experimental observation is in quite good agreement with the thermodynamic prediction.

2. On the breakdown of the second Al_2O_3 layer

It has been understood in the present study that the second from outer Al_2O_3 layer plays a protective role in the early stage of oxidation, although the layer is far less protective in comparison with the protective Al_2O_3 formed on heat resistant super-alloys. When continuity of the layer was lost, a breakaway oxidation behavior was observed. Therefore, the continuity of the layer is most important in this case. The reasons for the breakdown (loss of continuity) have not been discussed.

The Al_2O_3 is moderately permeable for both Ti ions and oxygen ions, since the outer TiO_2 and the inner mixed oxide zone continued to grow in the presence of continuous Al_2O_3 . This permeation may be occurring along intergranular zones, because in-grain transport must be smaller by several orders of magnitude. Therefore, the present authors speculate the following mechanism. Figure 10 shows a schematic illustration of the mechanism. First, there may be micro-intergranular channels which are the transport paths. Along the channels, transport of Ti ions outward and oxygen ions inward may be occurring in a diffusional manner in the early (parabolically growing) stage. As time elapses, TiO_2 may

Fig. 10 Schematic illustration for the proposed mechanism on the breakdown of the second Al_2O_3 layer.

precipitate along the channels and eventually form continuous TiO_2 paths bridging the top TiO_2 and the inner oxide zone, transport being predominantly along the TiO_2 giving a linear rate growth. Then, the Al_2O_3 layer, which has lost its continuity, may break up into islands in the porous TiO_2 sea. In the case of TiAl alloys containing ternary alloying elements, the Mn addition definitely shortened this breakdown and retarded the breakdown, as the present authors have shown⁽⁶⁾⁽⁸⁾. Mn may promote and disturb this tendency by enhancing the growth of TiO_2 and by reducing the supply of Ti ions from the metal-oxide interface, respectively.

3. Internal oxidation

The internal oxidation occurring in the present alloy system may be handled as the first limiting case in the Wagner's categories⁽⁹⁾⁽¹⁰⁾. As was described previously⁽⁵⁾, it is morphologically so. Also, the roughly estimated diffusion and solubility parameters fall into this case. At 1373 K, D_{O} in $\text{Ti}_3\text{Al} = 3.4 \times 10^{-13} \text{ m}^2/\text{s}$ (calculated from $\alpha\text{-Ti}$ data⁽¹¹⁾), D_{Al} in $\text{Ti}_3\text{Al} = 8 \times 10^{-15} \text{ m}^2/\text{s}$ ⁽¹²⁾. Then, $D_{\text{Al}}/D_{\text{O}} = 0.02$. On the other hand, N_{O} may be in the order of 0.01–0.02 and N_{Al} may be in the order of 0.1, resulting in $N_{\text{O}}/N_{\text{Al}} = 0.1$. Therefore, $D_{\text{Al}}/D_{\text{O}} \ll N_{\text{O}}/N_{\text{Al}} \ll 1$, which is the mathematical condition for the first limiting case. In the first limiting case, enrichment of solute can not be expected and high solute content may be necessary for the internal to external transition to occur. However, as temperature decreases, the thickness of the Ti_3Al layer became greater than the depth of internal oxides and then some Al enrichment may be expected.

It may be worthwhile to discuss the morphology of the internal oxides. They grew as stringers to the direction perpendicular to the interface. This type of alumina growth has been oftenly observed in Ni-Cr-Al alloys⁽¹³⁾⁽¹⁴⁾ and it has been explained as a result of Al diffusion control. However, a most important characteristic of this alloy system is that the internal oxidation occurs even with the high Al content. The most important reason for this may be the large oxygen solubility. Probably because of this, the solubility product for Al_2O_3 must be large. Anyway, the matrix of metal at the scale-metal interface is Ti_3Al and the oxidation at the interface

occurs as an oxidation of Ti_3Al , which is much less oxidation resistant. Therefore, the internal oxidation occurrence is one of the cause for the poor oxidation resistance of this alloy system.

As temperature was decreased, the internal oxidation was hard to observe. This may be due to the relatively slow growth of internal oxides in comparison to the recession rate of the interface. Probably, at temperatures lower than 1100 K, internal oxides, even once formed, may be incorporated into the inner scale within a short time.

V. Conclusion

After the study on the high temperature oxidation behavior of Ti-Al binary alloys ranging from Ti_3Al to TiAl_3 , the following conclusions were drawn.

(1) On alloys containing less Al than 51 mass%, multi-layered scales composed of the $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2 + \text{Al}_2\text{O}_3$ /internal oxide (Al_2O_3 in the Ti_3Al matrix) zone were formed and oxidation resistance of those alloys were not sufficient. Among those alloys, effect of Al was observed most sharply in the TiAl single phase composition range. While on a 63 mass%Al alloy (TiAl_3), a uniform protective scale composed of $\text{TiO}_2/\text{Al}_2\text{O}_3$ without the internal oxide zone was obtained.

(2) The breakaway oxidation behavior was observed in the alloys which formed the multi-layered scale and was interpreted by the stability in the continuity of the second from the outer Al_2O_3 layer.

(3) Internal oxidation of Al_2O_3 stringers growing inward perpendicular to the interface was observed particularly clearly at relatively high temperatures. Due to the

internal oxidation, matrix metal at the interface was changed to Ti_3Al which is less oxidation resistant.

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