Improvement in Oxidation Resistance of TiAl by Preoxidation at 1200 K in a Pack Mixture of Cr_2O_3 and Cr Powders

Shigeji Taniguchi*, Toshio Shibata* and Shigetoshi Sakon**

* Department of Materials Science and Processing,
Faculty of Engineering, Osaka University

** Graduate School, Department of Materials Science and Processing,
Faculty of Engineering, Osaka University

The cyclic-oxidation resistance of a TiAl coupon at 1300 K was significantly improved by the preoxidation at 1200 K for 100 ks in a pack of a mixture of 70 mass% Cr_2O_3 and 30 mass% metallic Cr powders. This is attributable to the formation of a thin dense scale of about 1 μm thickness consisting mainly of $\alpha\text{-Al}_2\text{O}_3$. The scale contains small amounts of TiO_2 and Cr_2O_3 , and a very small amount of metallic Cr on its surface. The scale became thicker very slightly after ten-cycle oxidation (720 ks) with no significant structural changes. Other combinations of temperature (1100, 1200, and 1300 K) and pack composition (100, 70, and 30% Cr_2O_3 with balance of metallic Cr) lead to the formation of poorly protective scales. There is a general trend; when temperature is low or the amount of Cr_2O_3 in the pack is small, thin defective scales very rich in Al are formed, while when temperature is high or the Cr_2O_3 content is large, thick porous scales consisting of TiO_2 and Al_2O_3 are developed. The above can be explained in terms of the rate of oxygen supply.

Key words: high temperature, oxidation resistance, TiAl, preoxidation, chromia pack

1. Introduction

The intermetallic compound TiAl is of considerable interest for high temperature systems such as aircraft or automobile engines, because it has a low density and substantially high specific strengths^{(1)~(8)} at elevated temperatures. However, its oxidation resistance^{(4)~(8)} is very poor in air or oxygen atmospheres above about 1000 K. It is almost impossible to form protective Al_2O_3 scales on TiAl by simple oxidation procedures in spite of its high Al content.

The oxide scale formed by the oxidation above 1000 K was found^{(6), (7)} to have a three-layered structure; the outermost layer consists predominantly of TiO_2 (rutile), the intermediate layer is very rich in Al_2O_3 (α -type), and the innermost layer consists of a porous mixture of TiO_2 and Al_2O_3 grains. There are several large pores at the interface between the outermost and intermediate layers. The boundary between the intermediate and innermost layers is vague in some cases, because the amount of Al_2O_3 grains in the intermediate layer continuously

decreases toward the innermost layer.

Therefore, we cannot expect any protective oxidation under ordinary oxidation conditions. Several surface treatments^{(7)~(11)} and alloying additions^{(12), (13)} have been carried out to improve the oxidation resistance of TiAl. However, none of them seems so successful, if a protective duration of several hundred hours at 1300 K or higher is requested.

The present paper describes a surface treatment which brought about a sufficient oxidation resistance to TiAl. The treatment is to pre-oxidize the specimen packed in a mixture of Cr_2O_3 and metallic Cr powders which gives a very low oxygen partial pressure. This pressure would enhance the preferential oxidation of Al which is prerequisite for the formation of a protective Al_2O_3 scale.

2. Fundamental Aspects

Treatments under low oxygen partial pressures have been studied by Kobayashi *et al.*⁽⁹⁾ They showed that it was possible to form a scale very rich in Al_2O_3 on TiAl by heating it at low oxygen partial pressures which can be

*,** 2-1, Yamadaoka, Suita, Osaka 565, Japan.

attained by a vacuum pump. However, such specimens showed breakaway oxidation after certain protective periods. This was accounted for by the formation of small cracks due to thermal stresses arising from the temperature cycling. Another possible reason for this is inclusion of very small amount of TiO_2 in the scale, which will form channels for fast growth of TiO_2 during later oxidation periods and thus spoils the mechanical integrity of the preformed protective scale. Moreover, their oxidation temperature was less than 1223 K, which is considerably lower than 1300 K. Studies in which the oxidation temperature is higher than 1300 K are quite few.

Here we postulate that if TiAl were oxidized at oxygen partial pressures between the dissociation pressures of TiO_2 and Al_2O_3 , only Al would be oxidized resulting in the formation of an Al_2O_3 scale. However, it is quite difficult to find the set of metal and its oxide which satisfies such conditions. The Ellingham diagram for oxides shows that the dissociation pressure decreases in the following order; $\text{Cr}_2\text{O}_3 > \text{TiO}_2 > \text{Al}_2\text{O}_3$. We therefore assumed that even the equilibrium oxygen partial pressure is slightly higher than the required pressure, it would be possible to oxidize Al only when the rate of oxygen supply is very small. Basing on this idea we chose the combination of Cr_2O_3 and Cr. The usage of Cr_2O_3 has another advantage. The presence of Cr in an Al_2O_3 scale has empirically been known¹⁴⁾ to improve its mechanical property.

3. Experimental Procedures

3.1 Specimen

A TiAl ingot was prepared in a form of

Table 1 Composition of the specimen (mass%).

	Al	Ti	Fe	C	H	O	N
TiAl	37.8	balance	0.010	0.006	0.002	0.044	0.011

cylinder having a diameter of 60 mm by plasma-skull melting. Its chemical composition is shown in Table 1. Coupons of about $15 \times 10 \times 1$ mm in size were cut out of the ingot and used for kinetic tests and metallographic examinations.

The coupon specimens were abraded with a series of SiC polishing papers of up to #1000, and washed ultrasonically in baths of acetone and alcohol.

3.2 Pack treatment

Three or four specimens were packed with Cr_2O_3 powder or a mixture of Cr_2O_3 and metallic Cr powders in an alumina tube having an inner diameter of 30 mm and a length of 140 mm. Reagent Cr_2O_3 and Cr powders were used. This tube was placed in a furnace tube, the atmosphere of which was replaced with Ar gas several times using a rotary pump. This assembly can provide oxygen partial pressures much lower than those given by a vacuum pump. Figure 1 shows the outline of the experimental assembly.

Then the pack was heated to 1100, 1200, or 1300 K in about 7.2 ks, held for 100 ks at temperature, and cooled to room temperature in the furnace tube. The pack composition had three levels: 100, 70 or 30 mass% Cr_2O_3 . They are called packs 1, 2, or 3 respectively. After the treatment the specimens were taken out of the pack and ultrasonically cleaned in a bath of alcohol, and subjected to mass measurement and metallographic examinations.

Fig. 1 Schematic drawings of the pack and the experimental assembly for the pack treatments.

3.3 Oxidation test

The oxidation resistance was assessed by a cyclic-oxidation test in a flow of purified oxygen at atmospheric pressure. An infra-red ray image furnace was used for providing the specified temperature pattern. Two specimens were placed on an alumina boat, which was then put in a transparent quartz tube. The specimen temperature was monitored with a Pt-13% Rh-Pt thermocouple attached to a dummy specimen placed very close to the specimen. The preliminary test showed that the maximum temperature difference between the two specimens was less than three degree.

The temperature pattern consisted of three steps; heating to 1300 K in about 3.6 ks, holding at temperature for 72 ks, and cooling to room temperature in about 5 ks. After each cycle the specimens were subjected to visual inspection and mass measurement, and were returned to the furnace again for the next oxidation cycle.

3.4 Metallographic examinations

The specimens before and after the oxidation were examined with X-ray diffractometry (XRD) using Cu-K α radiation at 40 kV and 30 mA. The outer surfaces, fractured edges, and polished sections of the specimens were examined with optical microscopy, pure scanning electron microscopy (SEM) equipped with an energy dispersive X-ray analysis (EDX) unit. Wavelength dispersive analysis (WDX) and X-ray photon electron spectroscopy (XPS) were also used in a few cases when they were necessary.

4. Results

4.1 Oxidation kinetics

The conditions of the pack treatment (temperature and composition), the nature of oxide

scales formed by the treatments and the oxidation behavior are summarized in Table 2 for convenience. The upper row shows the nature of oxide scales and the lower the oxidation behavior. Large and medium mass gains mean poor oxidation resistance, while the small mass gain means excellent oxidation resistance. The nature of the oxide scales will be shown later.

The results of kinetic tests are summarized in Fig. 2. The numbers in the figure correspond to those shown in Table 2 and are also used as the specimen numbers. Here, $\Delta m \cdot A^{-1}$ means the mass gain per unit area of the original specimen.

The specimens treated at 1100 K (Nos. 1 to 3) show large mass gains even after the first cycle of oxidation. Their mass gains are comparable to that of the untreated specimen. Therefore, we can conclude that the pack treatments under conditions 1 to 3, or treatment at 1100 K, are ineffective.

The oxidation behavior of the specimens treated at 1200 K (Nos. 4 to 6) varies widely with the pack composition. The treatment with pack 1 (No. 4) leads to very large mass gain. Contrary to this, that with pack 2 (No. 5) results in very good oxidation resistance with the mass gain being very small. Further, that with pack 3 (No. 6) results in a surface layer which is slightly protective for several cycles after which breakaway oxidation sets in.

The oxidation resistance of the specimens treated at 1300 K (Nos. 7 to 9) is poor, because they show medium mass gain, large mass gain followed by spallation, or large mass gain respectively.

4.2 Metallographic examinations

The XRD for the oxidized specimens showed

Table 2 Correlation of the nature of surface scale formed by the treatment with oxidation properties.

	1100 K	1200 K	1300 K
Pack 1 100% Cr ₂ O ₃	No.1 thin defective scale large mass gain	No.4 thick porous scale large mass gain	No.7 thick porous scale medium mass gain
Pack 2 70% Cr ₂ O ₃	No.2 thin defective scale large mass gain	No.5 thin dense scale small mass gain	No.8 defective scale of medium thickness large mass gain and spalling
Pack 3 30% Cr ₂ O ₃	No.3 thin defective scale large mass gain	No.6 thin defective scale large mass gain and breakaway	No.9 thin defective scale large mass gain

Fig. 2 Cyclic-oxidation curves of the TiAl specimens treated under conditions 1 to 9 and of the untreated specimen.

Fig. 3 XRD charts for specimens (a) 5 and (b) 4, after the oxidation for 10 cycles at 1300 K.

that the oxides formed under all the conditions were α - Al_2O_3 and TiO_2 (rutile). Figure 3 shows examples of XRD charts. (a) shows specimen 5 after the oxidation for ten cycles. The major oxide is Al_2O_3 and the peaks corresponding to TiO_2 are very low indicating that very small amount of TiO_2 is formed. The formation of

Ti_3Al phase is noteworthy. This corresponds to the SEM and EDX examinations which will be shown later. The formation of Ti_3Al phase beneath the oxide scale has commonly been seen.^{(6), (7)}

On the other hand, (b) shows specimen 4 after the oxidation test. The extensive formation of

Fig. 4 Characteristic features of outer surfaces (a, c) and fractured edges (b, d) of TiAl treated under condition 5 (1200 K, 70% Cr_2O_3 and 30% Cr), before (a, b) and after the 10 cycle oxidation at 1300 K (c, d).

TiO_2 can be understood from high peaks corresponding to it. This coincides with the kinetic result.

Detailed metallographic examinations were performed for all the specimens and the results for specimens 4 to 6 will be shown below, because they showed typical cases.

They were treated at 1200 K before the oxidation test, however kinetic behavior was very different among them.

Figures 4 (a) and (b) show an outer surface and a fractured edge respectively of the specimen treated under condition 5, which gave the best oxidation resistance, while (c) and (d) similarly show the specimen oxidized for 10 cycles at 1300 K.

The white particles in (a) and (c) were identified as Cr_2O_3 with EDX and XPS. The XPS also showed the presence of small amount of metallic Cr on the surface in (a). It is natural that some Cr_2O_3 and metallic Cr powders can stick to the surface even after the pack treatment. The fractured section (b) clearly shows that the specimen surface is covered with a thin layer of about 3 μm thickness developed during the treatment. Close examinations with EDX line scan and spot analysis, and XRD revealed that the layer consists of an outer Al_2O_3 scale of about 1 μm thickness and an inner modified alloy layer of about 2 μm thickness. An example

Table 3 EDX analysis of areas (1) to (6) (at.%).

area	Al	Ti	Cr
(1)	45.9	52.6	1.5
(2)	81.6	4.2	14.2
(3)	39.1	60.9	—
(4)	37.1	62.9	—
(5)	45.0	55.0	—
(6)	46.9	53.1	—

Fig. 5 Concentration profiles of Ti and Al across the fractured section shown in Fig. 4 (d).

of the composition of the modified alloy layer (1) is shown in Table 3. This table indicates a small decrease in the Al content and association of Cr in the layer.

The Al_2O_3 scale is in good contact with the modified alloy layer which is in turn in good contact with the substrate. There are no large differences between (b) and (d) except slight increases in thickness of the scale and the modified alloy layer formed during the oxidation test.

The presence of a sound Al_2O_3 scale after the oxidation test can be understood by the profiles of Ti and Al shown in Fig. 5. The two layers remained very sound. We can therefore conclude that the excellent oxidation resistance is resulted from the thin and very sound Al_2O_3 scale developed by the treatment. Further, the results of EDX of areas (2) to (6) in Fig. 4 (d) are shown in Table 3. The high Ti concentrations at areas (3) and (4) indicate the formation of Ti_3Al phase during the oxidation test. This is in good agreement with the result of XRD

Fig. 6 Characteristic features of outer surfaces (a,c) and fractured edges (b,d) of TiAl treated under condition 4 (1200 K, 100% Cr_2O_3), before (a, b) and after the 10 cycle oxidation at 1300 K (c, d).

(Fig. 3 (a)). The origin of Cr present in the oxide scale is attributable to the Cr_2O_3 particles stuck to the surface by the pack treatment.

Figures 6 (a) and (b) show an outer surface and a fractured edge respectively of the specimen treated under condition 4, which resulted in poor oxidation resistance. The outer surface is very rich in TiO_2 (a) and the scale is thick and very porous (b). Here, the presence of TiO_2 was confirmed by XRD and EDX. It is readily understood that the large mass gain during the oxidation test (cf. curve 4 in Fig. 2) is due to the formation of the porous scale during the treatment. The porous scale cannot be protective.

Figures 6 (c) and (d) show corresponding views after the oxidation. The grain size of the outer TiO_2 layer becomes very large during the oxidation, indicating considerable sintering and grain growth taking place. The fractured edge (d) shows large voids in the outer TiO_2 layer, beneath which there is a porous layer consisting of a mixture of TiO_2 and Al_2O_3 grains. These features are quite similar to those of the specimen⁽⁶⁾ oxidized without any treatment.

It should be emphasized that pack 1, 100% Cr_2O_3 , was used in this case, while the treatment temperature was the same for the specimen shown in Fig. 4.

Figures 7 (a) and (b) show an outer surface and a fractured section of the specimen treated

Fig. 7 Characteristic features of outer surfaces (a,c) and fractured edges (b,d) of TiAl treated under condition 6 (1200 K, 30% Cr_2O_3 and 70% Cr), before (a, b) and after the 10 cycle oxidation at 1300 K (c, d).

under condition 6, which resulted in a thin scale (right end in (b)). However, this scale is associated with several small cracks. This is understood by comparing it with Fig. 4 (b).

After the oxidation test extensive growth of TiO_2 can be seen on the specimen surface (c) and the fractured section (d) shows a structure very similar to that for untreated specimens.

The above results indicate that thermodynamic equilibrium was not maintained at least when packs 2 and 3 are used, because Al predominantly oxidized by the treatment.

When the pack treatments were performed at 1100 K, very thin or thin and defective scales were developed, the structure of which were similar to that shown in Fig. 7 (b). Further, when the treatments were performed at 1300 K, porous scales similar to that in Fig. 6 (b) were formed, except for the case where pack 3 was used. In the latter case a thin scale was developed.

The results of the detailed metallographic examinations are summarized in Table 2.

4.3 Correlation of scale structure with oxidation kinetics

The correlation of the characteristic features of oxide scales formed by the pack treatments with the oxidation behavior is summarized in Table 2.

In general, the thin defective scales and thick

porous scales result in large mass gains, i.e. poor oxidation resistance. Only condition 5 gave thin dense scale, which brought about very good oxidation resistance such that the oxide scale after 10 cycles is still very sound and protective.

5. Discussion

The main point in this study is to examine the possibility of forming oxide scales very rich in Al or Al_2O_3 scales by the treatment. The possibility was confirmed by condition 5 which resulted in very protective Al_2O_3 scales. However, other conditions gave unacceptable results. This means that there is a suitable combination of temperature and pack composition for the treatment.

Although oxidation behavior varied widely with the conditions of pack treatment, the oxidation resistance showed a strong dependence on the nature of the scales formed by the treatment as Table 2 shows. Thin defective scales and thick porous scales lead to the poor oxidation resistances. Only the thin dense scale gave the very good oxidation resistance.

Therefore, the discussion will be mainly concentrated on the influence of temperature and pack composition. The temperature is related to dissociation pressure of Cr_2O_3 which is the source of oxygen for the preoxidation, and oxidation rates of Al and Ti. On the other hand, the pack composition may change the rate of oxygen supply when the thermodynamic equilibrium is not maintained. The rate of oxygen supply would be higher for the pack of larger amount of Cr_2O_3 .

If the thermodynamic equilibrium were maintained during the treatment at 1200 K, both Ti and Al would be oxidized, because the Ellingham diagram shows that the dissociation pressure of Cr_2O_3 is high enough to form TiO_2 and Al_2O_3 . This is the case for pack 1, with which both Ti and Al were oxidized resulting in the thick porous scale consisting of TiO_2 and Al_2O_3 . However, when packs 2 and 3 were used, Al was oxidized predominantly. These differences are understood by the different structures of scales shown in Figs. 4 (b), 6 (b) and 7 (b). Therefore, we can conclude that the equilibrium was not maintained at least when packs 2 and 3 were used. This also means that the rate of oxygen supply is not sufficient to oxidize Ti.

It can also be concluded that pack 2 gives a

Table 4 A map showing the conditions under which scales of various protectiveness are formed.

	1100 K	1200 K	1300 K
100 % Cr_2O_3	A	C	C
70 % Cr_2O_3	A	B	C
30 % Cr_2O_3	A	A	A

Rate of oxygen supply A : too low, B : suitable
C : too high

suitable rate of oxygen supply, because very protective Al_2O_3 scales were established. Contrary to this, pack 3 gives insufficient oxygen supply, because the scale was thin but defective. This is attributable to the smallest amount of Cr_2O_3 .

When temperature is lowered to 1100 K, it becomes more difficult to attain the equilibrium and the oxidation rate of Al becomes low. These two are possible reasons for the thin defective scales (cf. Table 2) developed at this temperature by the treatment.

At 1300 K packs 1 and 2 resulted in the oxidation of both Ti and Al. This means the rate of oxygen supply is too high. This is due to the effect of temperature rise, which is favorable to attain the thermodynamic equilibrium. However, pack 3 resulted in the thin defective scale (cf. Table 2). This means again that the equilibrium was not maintained because of the smallest amount of Cr_2O_3 . Oxygen is thought to be consumed by the oxidation of Al before its partial pressure attains the equilibrium value.

The above considerations can be visualized in Table 4. Within areas A, the rate of oxygen supply is too low to develop sound Al_2O_3 scales, because of low temperature or the smallest amount of Cr_2O_3 or the both.

Contrary to this, in areas C the rate of oxygen supply is too high so that Ti oxidizes as well as Al. This is attributable to the higher temperatures or higher rate of oxygen supply. Area B, situating between areas A and C, shows the suitable combination of temperature and amount of Cr_2O_3 . This in turn means rates of oxygen supply and Al oxidation are very suitable for forming protective Al_2O_3 scales.

6. Conclusion

The TiAl coupons preoxidized in a mixture of 70% Cr₂O₃ and 30% metallic Cr powders at 1200 K for 100 ks show an excellent resistance to cyclic oxidation at 1300 K for at least 720 ks. The very good result is attributable to a thin and dense Al₂O₃ scale formed by the preoxidation. The preoxidation under other conditions of temperature and pack composition is ineffective. These results can be explained in terms of the rate of oxygen supply; lower temperature or smaller amount of Cr₂O₃ in the pack will lead to insufficient rate of oxygen supply, and vice versa.

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