

Oxidation Behavior of TiAl Coated with a Fine-Grain Co-30Cr-4Al Film

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Received October 6, 1992; revised January 1993

The oxidation behavior of TiAl coupons coated with a fine-grain Co-30Cr-4Al (mass %) film of about 30- μ m thickness has been studied at 1100–1400 K in a flow of purified oxygen at atmospheric pressure for up to 500 ks. Three oxidation stages were recognized: initial transient, parabolic, and accelerated stages. However, at 1100 K a parabolic stage continues for more than 800 ks. The activation energy for parabolic oxidation agrees with reported values for the oxidation of alumina-former alloys, although the mass gains during the parabolic stages are relatively small at 1200 and 1300 K. Micropores developed mainly at the scale/coating and coating/substrate interfaces as oxidation proceeded. This is attributable to recrystallization of the coating during oxidation and a Kirkendall effect due to preferential diffusion of Co into the substrate. The accelerated oxidation can be explained in terms of the formation of rutile mounds on the scale.

KEY WORDS: high temperature; oxidation behavior; TiAl; Co-Cr-Al coating; alumina scale; pore formation.

INTRODUCTION

The intermetallic compound TiAl is receiving considerable attention¹ because of its high specific strength^{2,3} at elevated temperatures. Its application to aircraft or automobile engines is thought to be very beneficial,

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provided that the degradation by its environment is overcome. However, it has been reported⁴⁻⁷ that protective alumina scales are not formed on TiAl in ordinary oxidizing atmospheres in spite of its high Al content. Therefore, several studies^{4,8,9} involving alloying additions and surface treatments have been performed to enhance the formation of protective alumina scales. However, no sufficiently successful results have been reported yet.

The present study deals with the oxidation resistance of TiAl, which has been much improved by applying a fine-grain Co-Cr-Al coating of about 30- μm thickness. The fine-grain structure was expected to enhance the formation of alumina scales.

EXPERIMENTAL PROCEDURES

Specimen Preparation

Coupon specimens measuring about $20 \times 10 \times 1$ mm and $15 \times 10 \times 1$ mm were machined from a TiAl ingot which had been annealed at 1473 K in a vacuum of 0.013 Pa for 86.4 ks. The specimens of the former size were used for kinetics tests and those of the latter size for metallographic examination.

The coupon specimens were mechanically polished with a series of SiC polishing papers up to #1000 and subsequently subjected to peening with glass balls. Then, they were coated with a Co-30Cr-4Al (mass %) film of 28- to 30- μm thickness by magnetron sputtering.

The chemical composition of the TiAl ingot and the conditions for the coating are shown in Tables I and II, respectively. A transmission-electron-microscopic study¹⁰ revealed that the coating consists of grains of around 0.2- μm size.

Table I. Composition of the TiAl Ingot (mass %)

Al	Fe	C	H	O	N	Ti
36.5	0.018	0.007	0.003	0.052	0.002	Balance

Table II. Sputtering Conditions

Vacuum before sputtering	6.7×10^{-3} Pa
Vacuum during sputtering	0.2 Pa
Sputtering voltage	570 V
Sputtering current	4.1 A
Substrate temperature	573 K
Thickness of coating	28-30 μm

Oxidation Tests

The isothermal kinetics behavior was followed using a thermobalance. After a specimen was hung with a thin Pt wire from a balance beam in a reaction tube, the atmosphere in it was replaced with oxygen which was purified by passing through silica gel, phosphorous pentoxide and alkali asbestos in this order. The oxidation run was started by switching on the furnace and the specimen mass was continuously recorded. The oxidation temperature ranged from 1100 to 1400 K. The duration was up to 500 ks, except for 800 ks at 1100 K. When a specified period was reached at temperature, the furnace was switched off, and the specimen was cooled in the furnace.

Metallographic Examination

The original and oxidized specimens were examined with X-ray diffractometry (XRD) using Cu-K α radiation at 40 kV and 30 mA. Structural and chemical features of the outer surfaces and fractured edges of the specimens were examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The specimen surface was coated with a thin layer of carbon or gold to prevent electron charging during observation or analysis. Optical microscopy (OM) was also used in a few cases.

RESULTS

Kinetics Tests

The oxidation curves are summarized in Fig. 1, which also includes the curve for an uncoated specimen oxidized at 1300 K for comparison. This figure shows that the coating is very effective in decreasing the oxidation rate. All the curves for the coated specimens show a parabolic manner after initial transition periods. However, some acceleration takes place later. The time at which the acceleration takes place is shown in Fig. 1 by arrows. The only exception is that parabolic oxidation continues for periods longer than 800 ks at 1100 K.

To clarify the presence of the parabolic period, parabolic plots of mass-gain squared vs time were constructed for all the temperatures. One such example is shown in Fig. 2, which clearly shows a linear part after an initial period of 50 ks. The mass gains during the parabolic stages are relatively small at 1200 and 1300 K.

Two or three runs were performed under identical conditions for confirming the reproducibility of the results. The reproducibility was found to be less than ten per cent, and it becomes poorer as temperature increases.

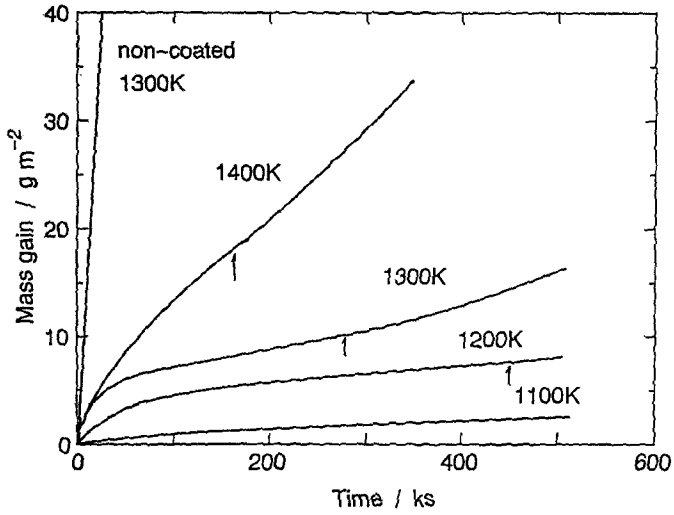


Fig. 1. Oxidation curves for TiAl coupons coated with a Co-30Cr-4Al film and for an uncoated TiAl coupon. The arrows show the time at which deviations from the parabolic manner start.

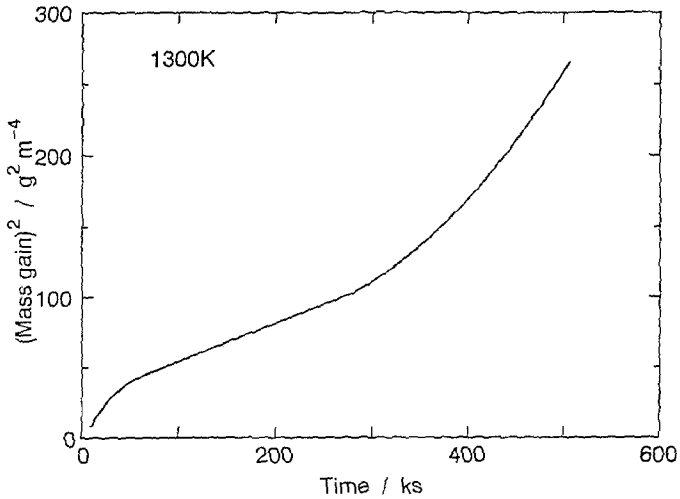


Fig. 2. Parabolic plot of the oxidation curve at 1300 K.

The parabolic rate constants, k_p , obtained from the linear intermediate periods are summarized in Fig. 3 in a form of Arrhenius plot. They can be expressed by the following equation.

$$k_p = 1.71 \times 10^5 \exp(-214,000/RT) \quad (\text{g}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1})$$

where R is the gas constant and T is the temperature. The activation energy obtained was $214 \text{ kJ} \cdot \text{mol}^{-1}$. This value agrees with a few reported values for alumina-former alloys.¹¹⁻¹³ An example of k_p obtained by other researchers¹² is shown in the figure for comparison. These values were obtained for the oxidation of Ni_3Al which forms rate-controlling alumina layers. The absolute value of k_p in this study is slightly larger than results obtained by other researchers. However, the formation of alumina scales were confirmed by the metallographic examinations, which will be shown next.

Metallographic Examination

An example of an XRD chart is shown in Fig. 4 for the specimens oxidized at 1300 K. The results of XRD are summarized in Table III, which shows that the major oxidation product is alpha alumina at all the temperatures. Very small amounts of CoAl_2O_4 (spinel) were also found. The spinel

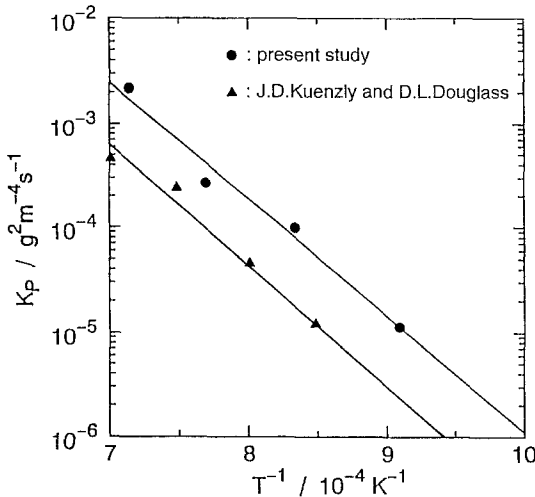


Fig. 3. Summary of the parabolic rate constants for the oxidation of TiAl coupons coated with a Co-30Cr-4Al film (circles) and those for the oxidation of Ni_3Al by Kuenzly and Douglass¹² (triangles).

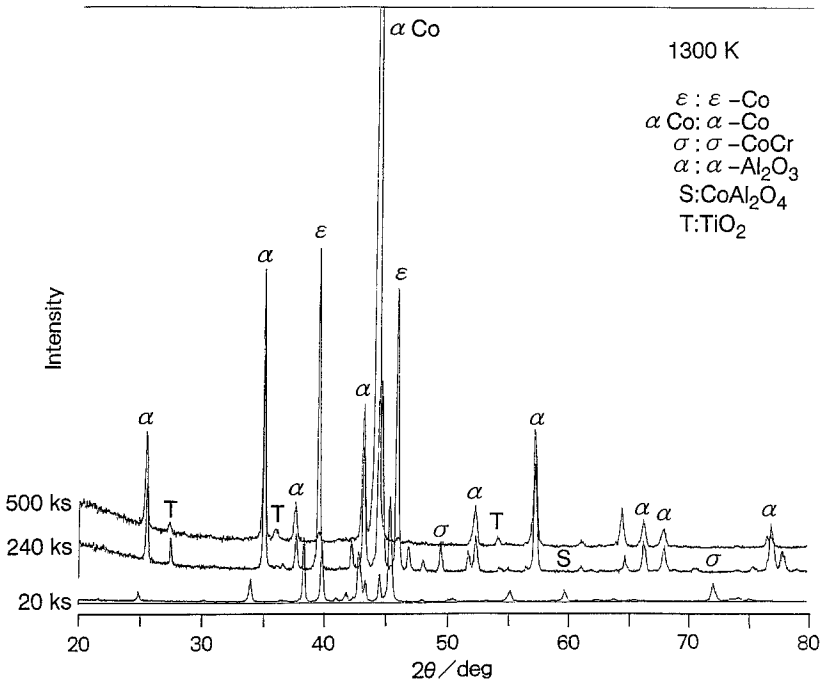


Fig. 4. XRD charts for coated TiAl coupons oxidized at 1300 K for 20, 240, and 500 ks.

oxide seems to have been formed mainly during the initial transient-oxidation periods, because peaks corresponding to it showed very little change with oxidation time.

It is noteworthy that the oxidation at higher temperatures and for longer periods leads to the formation of rutile in small amounts.

Figure 5 shows an outer surface (a, b) and a fractured edge (c, d) of a coated specimen before oxidation. The grain size of the coating was found¹⁰ to be around 0.2 μm . This is understood in (b). However, the coating consists of columns almost normal to the coating/substrate interface (C/S interface) (c). There are micropores in each column (d).

The oxidation at 1100 K for 20 ks results in a very thin scale on the coating as shown in Fig. 6 (a) and (b). Many micropores are developed mainly at the interfaces between the columns (b). Relatively large pores were developed near the C/S interface.

After the 500 ks oxidation the outer surface shows little change; the oxide grains became slightly larger (c). The columnar structure of the coating is still maintained (d). However, relatively large pores formed within the

Table III. Summary of XRD Data^a

As received		ϵ -Co (hcp)		(s)	
20 ks		α -Co(fcc)		(w)	
		β -CoAl		(w)	
500 ks					
1100 K	ϵ -Co	(m)	ϵ -Co (s)		
	α -Co	(s)			
	σ -CoCr	(s)	σ -CoCr (s)		
	α -Al ₂ O ₃	(s)	α -Al ₂ O ₃ (s)		
				CoAl ₂ O ₄ (vw)	
240 ks					
1200 K	ϵ -Co	(m)	ϵ -Co	(s)	ϵ -Co (s)
	α -Co	(m)	α -Co	(m)	α -Co (m)
	σ -CoCr	(s)	σ -CoCr	(s)	σ -CoCr (s)
	α -Al ₂ O ₃	(w)	α -Al ₂ O ₃	(s)	α -Al ₂ O ₃ (s)
	CoAl ₂ O ₄	(vw)	CoAl ₂ O ₄	(vw)	CoAl ₂ O ₄ (vw)
					TiO ₂ (w)
240 ks					
1300 K	ϵ -Co	(s)	ϵ -Co	(s)	ϵ -Co (w)
	α -Co	(s)	α -Co	(s)	α -Co (s)
	σ -CoCr	(s)	σ -CoCr	(m)	σ -CoCr (vw)
	α -Al ₂ O ₃	(w)	α -Al ₂ O ₃	(s)	α -Al ₂ O ₃ (s)
	CoAl ₂ O ₄	(vw)	CoAl ₂ O ₄	(vw)	
			TiO ₂	(m)	TiO ₂ (m)
125 ks					
1400 K	ϵ -Co	(s)	ϵ -Co	(w)	
	α -Co	(s)	α -Co	(s)	α -Co (s)
	σ -CoCr	(s)			
	α -Al ₂ O ₃	(s)	α -Al ₂ O ₃	(s)	α -Al ₂ O ₃ (s)
	CoAl ₂ O ₄	(vw)	CoAl ₂ O ₄	(vw)	CoAl ₂ O ₄ (vw)
			TiO ₂	(w)	TiO ₂ (w)
320 ks					

^a(s) = strong, (m) = medium, (w) = weak, and (vw) = very weak.

coating and near the C/S interface (d). This kind of pore formation is a general occurrence at all the temperatures.

These characteristic features were maintained when the temperature was raised to 1200 K as shown in Fig. 7. The oxide grains on the outer surface of the scale became slightly larger than those in samples oxidized at 1100 K, (a) and (c). Small pores developed at the scale/coating interface (O/C interface: O referring to oxide scale) and the C/S interface.

Cross sections (b, d) clearly show that continuous scales having thicknesses less than 1 μ m are definitely formed and that the coating has many phases in accordance with the results of XRD (cf. Table III). An SEM micrograph (Fig. 8) of a polished and etched section clearly shows the appearance of a multi-phase structure.

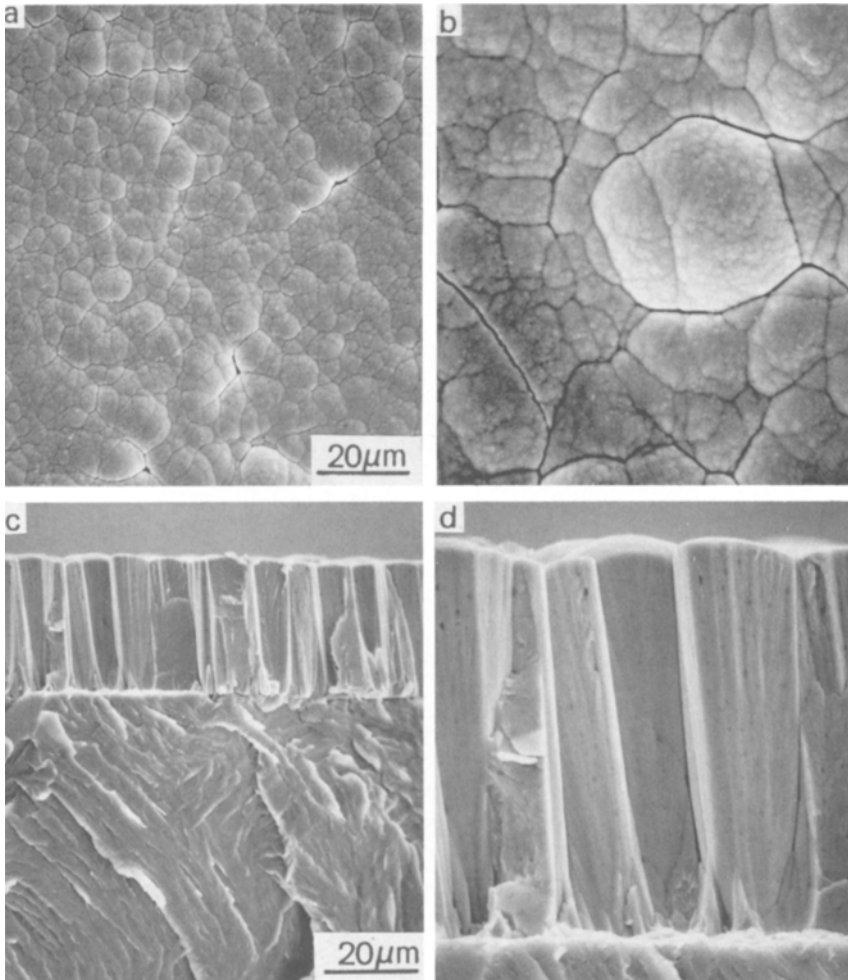


Fig. 5. Surfaces (a, b) and fractured edges (c, d) of a TiAl coupon coated with a Co-30Cr-4Al film, before oxidation. The film shows a columnar structure almost normal to the substrate.

At 1300 K the scale was thicker and slightly convoluted as shown in Figs. 9b and d. The coating seems to have almost completely recrystallized, because its columnar structure becomes very vague (b). Several pores developed mainly near and at the O/C and C/S interfaces (b). This behavior became very pronounced when oxidation period was extended to 240 ks (d).

The convoluted scales indicate the generation of oxide-growth stresses.^{14,15} However, the scale having a uniform thickness seems to be well maintained (d).

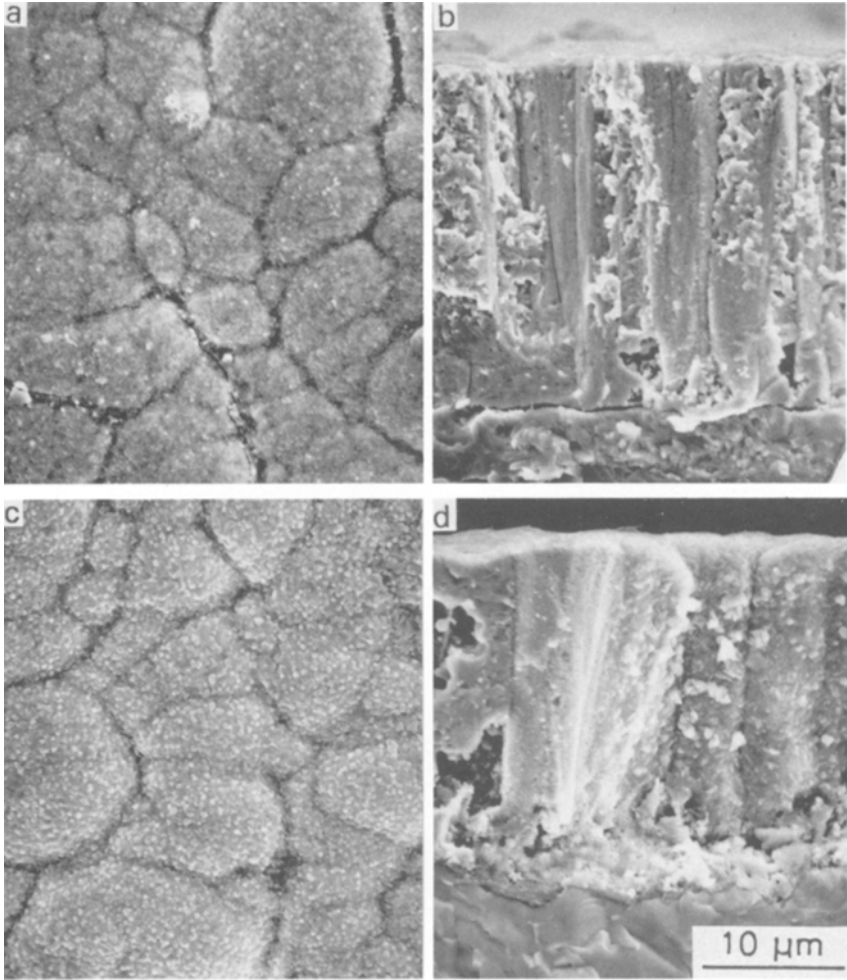


Fig. 6. Surfaces (a, c) and fractured edges (b, d) of a TiAl coupon coated with a Co-30Cr-4Al film, oxidized at 1100 K for (a, b) 20 and (c, d) 500 ks.

On the other hand, the oxide grains on the outer scale surface become larger as shown in (a) and (c).

At 1400 K pore formation at the O/C and C/S interfaces, and scale convolution become more pronounced as shown in Figs. 10b, d, and f. The change in surface features of the scale and its deformation seem rather rapid at this temperature.

Closer observation revealed that the alumina scale has columnar grains almost normal to the coating as shown in Figs. 7, 9, and 10.

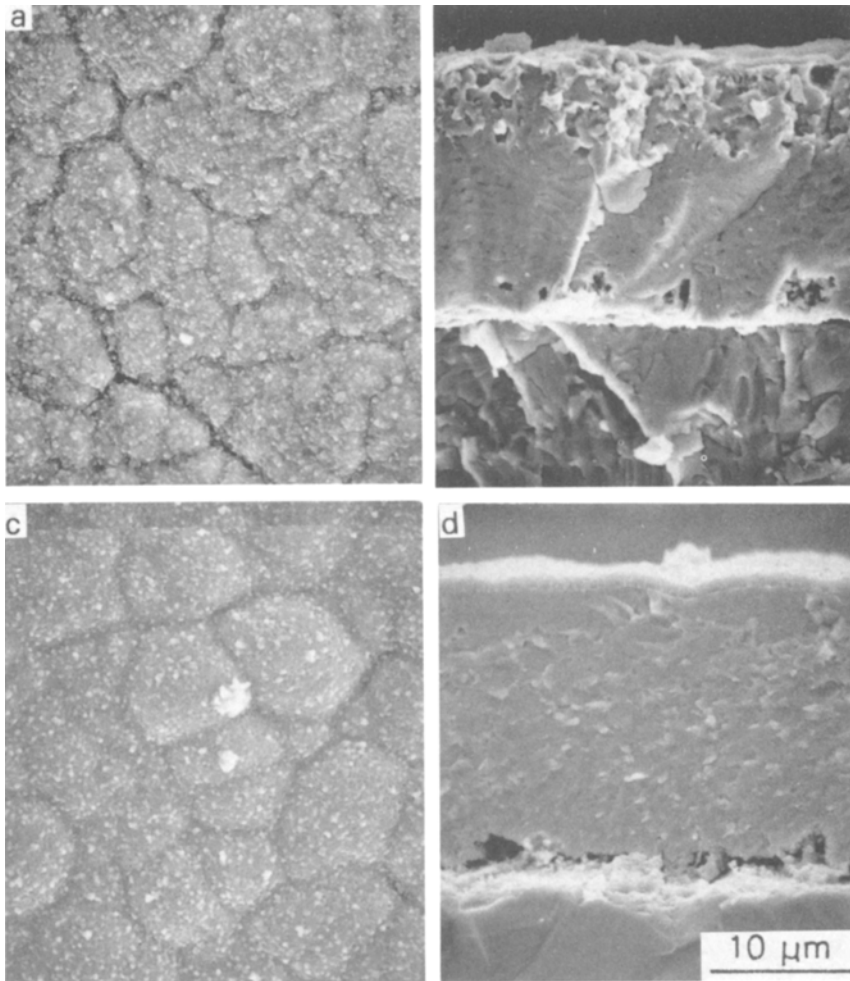


Fig. 7. Surfaces (a, c) and fractured edges (b, d) of a TiAl coupon coated with a Co-30Cr-4Al film, oxidized at 1200 K for (a, b) 20 and (c, d) 500 ks.

An additional important finding is that small mounds of rutile formed on the scale after oxidation at higher temperatures and longer periods as shown in Fig. 11. This indicates that the transport of Ti through the coating and the oxide scale is rather rapid. There was no sign of sites on the scale for preferential growth of rutile crystals. The mechanism for this is a topic for further study.

Concentration profiles of metallic elements along the fractured sections were obtained using EDX, because pore formation at the C/S interface is

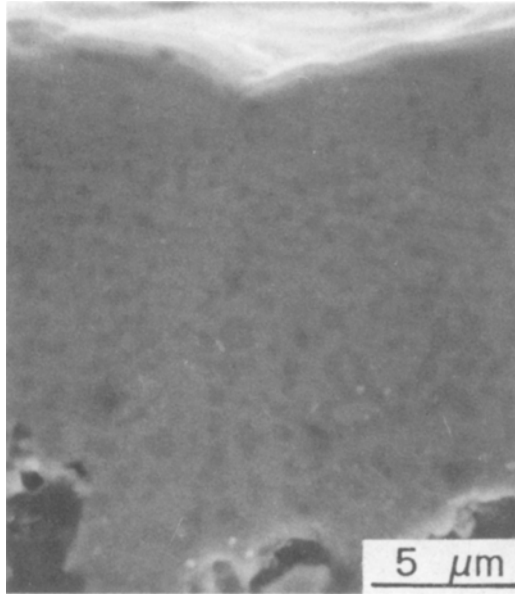


Fig. 8. SEM micrograph of the coated specimen oxidized at 1200 K for 20 ks. Etched with aqua regia for 60 s.

thought to be at least partly due to a Kirkendall effect. An example of the results is shown in Fig. 12, which indicates that a certain amount of Co diffused into the substrate. Also small amounts of Ti and Al diffused into the coating.

The development of the diffusion zone was hinted at in SEM photos by a change in the structural features; for example, in Fig. 10b, the upper third shows the remaining coating and the scale, and the rest, except the very bottom area, shows a diffusion zone.

DISCUSSION

Two characteristic features were found in this study. First, the oxidation kinetics are similar to those of alumina-former alloys except for the accelerated oxidation at later periods and the initial periods too. Second, pores formed at the O/C and C/S interfaces. Therefore, we will discuss mainly these two points below.

It seems that once a protective alumina scale or at least a dense and continuous alumina layer is established on TiAl, it is not too difficult to maintain it during subsequent oxidation because of its high Al content. Application¹⁶ of a CVD alumina film to TiAl showed this possibility.

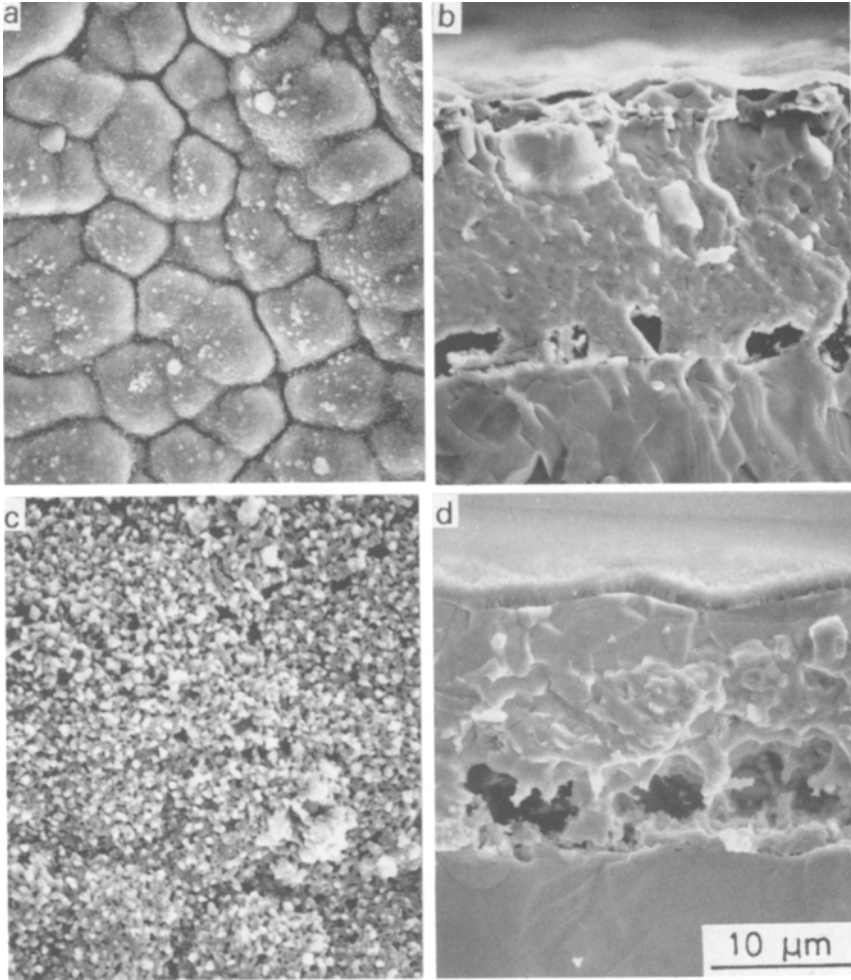


Fig. 9. Surfaces (a, c) and fractured edges (b, d) of a TiAl coupon coated with a Co-30Cr-4Al film, oxidized at 1300 K for (a, b) 20 and (c, d) 240 k.

In the present study the application of a Co-Cr-Al alloy coating, which would produce alumina scales on oxidation, has been tried on a similar basis to the above.

It has been reported¹⁷⁻²⁰ that generally more than about 8 mass % Al is needed to form scales consisting predominantly of alumina on Co-Cr-Al alloys with Cr contents of 10 to 30 mass %. According to the oxide map obtained by Wallwork and Hed¹⁷ for Co-Cr-Al alloys, the composition of

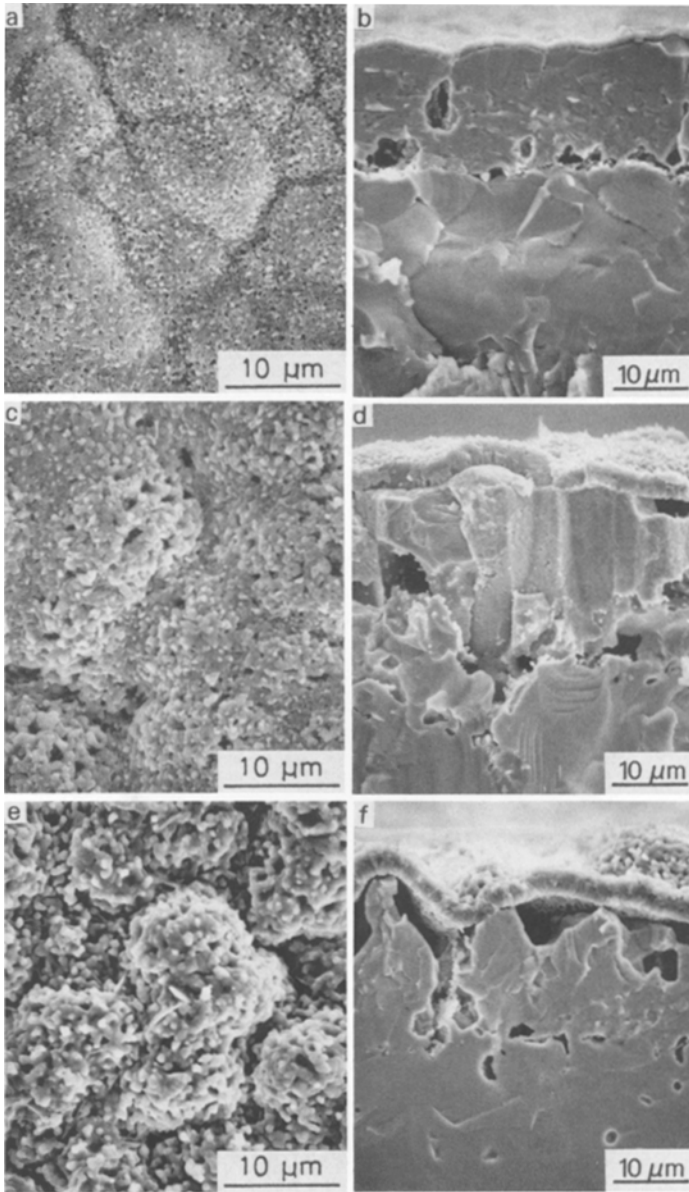


Fig. 10. Surfaces (a, c, e) and fractured edges (b, d, f) of a TiAl coupon coated with a Co-30Cr-4Al film, oxidized at 1400 K for (a, b) 20, (c, d) 125 ks, and (e, f) 320 ks.

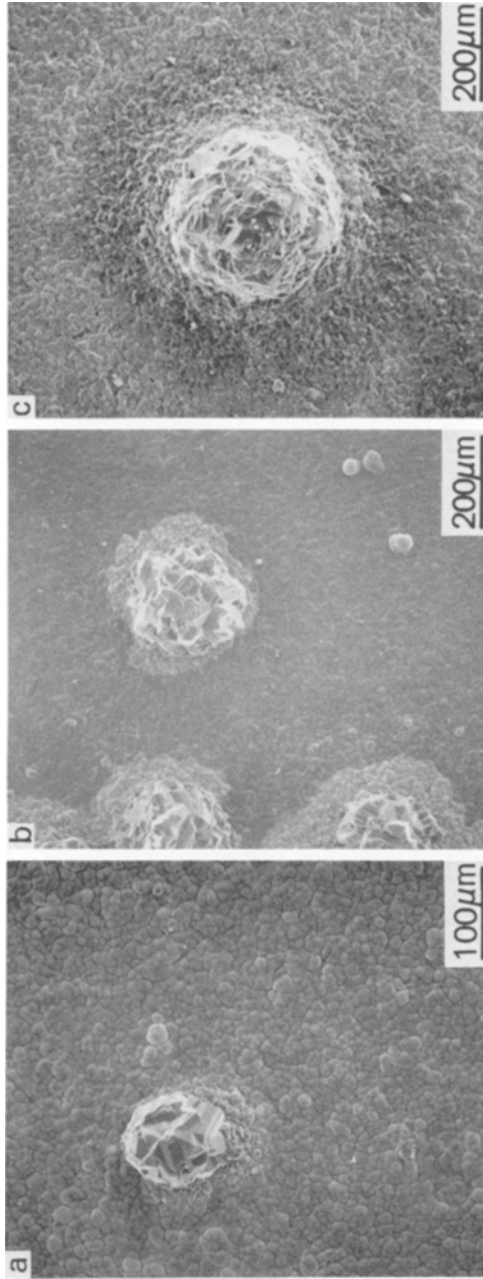


Fig. 11. Specimen surfaces showing mounds of rutile, oxidized at 1300 K for (a) 240 and (b) 500 ks, and (c) at 1400 K for 320 ks.

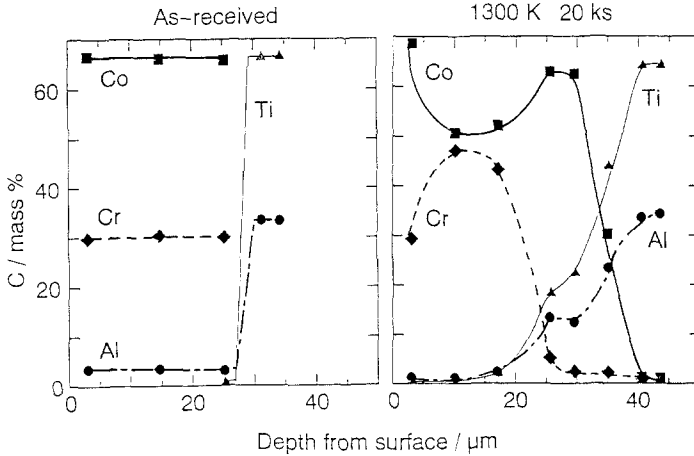


Fig. 12. Profiles of metallic elements along the fractured section of the specimens before and after oxidation at 1300 K for 20 ks.

the coating of the present study will form spinel oxide as the main oxide. However, the results of SEM, XRD and EDX showed that the oxide scales are virtually only alumina. This indicates that the fine-grain structure of the present coating is very effective to form alumina scales. This can be explained by the fine-grain structure of the coating which is expected to enhance the diffusion of Al, leading to establishment of the alumina layer. This effect cannot be expected for conventional cast alloys.

However, accelerated oxidation takes place above 1200 K. Metallographic examination showed that the onset of the acceleration coincides approximately with the appearance of rutile mounds on the scale (cf. Table III and Fig. 11). Therefore, the acceleration can be explained in terms of the appearance of rutile which grows much faster than alumina and by an increase in the number of sites for rutile growth.

The formation of convoluted scales indicates the generation of stresses during oxidation, because it is well known^{14,15} that the oxide scale is stressed during its growth.

However, these stresses seem not sufficiently large to break the scales. If the scale breaks, oxides other than alumina are expected to form owing to aluminum depletion as shown in Fig. 12, and scales will show non-uniform thicknesses. There were no such signs of scale fracture found in the present study.

The fact that the values of k_p in this study are slightly larger than others is partly attributable to the convoluted scales because they give larger actual oxidation surface areas than the geometrical area of the specimen.

Now, we extend our discussion to pore formation during oxidation. During the oxidation at 1100 K micropores tended to develop at the interfaces between columns all through the coating. This can be explained by its recrystallization during oxidation which results in a volume decrease. This can lead to pore formation. The interfaces between the columns may have provided sites for precipitation of pores.

As the oxidation temperature increases and/or the oxidation period becomes longer, these micropores can move to the two interfaces and form larger pores by their coalescence.

An additional possibility for pore formation at the C/S interface is the Kirkendall effect arising from preferential diffusion of Co into the substrate. The results of EDX (Fig. 12) support this view.

CONCLUSIONS

The oxidation resistance of TiAl is much improved by applying a fine-grain Co-30Cr-4Al coating, which results in alumina scales on oxidation. However, accelerated oxidation takes place after parabolic periods above 1200 K owing to the formation of rutile mounds on the scale.

The formation of pores at the scale/coating and coating/substrate interfaces is noteworthy at higher temperatures and longer oxidation periods.

ACKNOWLEDGMENTS

The authors are grateful to Mr. J. Nakata of Department of Materials Science and Processing, Osaka University for his partial assistance in the experimental work. The TiAl ingot was kindly supplied by Osaka Titanium Co. Ltd. A part of this work was supported by the Grant-in-Aid of the Ministry of Education, Science, and Culture of Japan.

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