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Shigeji Taniguchi, Toshio Shibata, Naoyuki Asanuma, Hanyi Luo, Fuhui Wang, et al.. Oxidation resistance of TiAl improved by a CoCrAl coating. Journal de Physique IV Proceedings, 1993, 03 (C9), pp.C9-403-C9-410. 10.1051/jp4:1993942 . jpa-00252382

HAL Id: jpa-00252382

<https://hal.science/jpa-00252382>

Submitted on 1 Jan 1993

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Oxidation resistance of TiAl improved by a CoCrAl coating

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Abstract. — The oxidation behavior of TiAl coupons coated with a fine-grained Co-30Cr-4Al (mass %) layer of about 30 μm thickness was 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 acceleration stages. However, at 1100 K a parabolic stage continues for more than 800 ks. The parabolic rate constants agree well with the reported values for alumina-former alloys. Voids are developed mainly at the scale/coating and coating/substrate interfaces as the oxidation proceeds. This is attributable to a slightly loose structure of the coating, its recrystallization 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 microcracks in convoluted scales. At 1400 K the growth of rutile on the scale seems to be additionally contributing to the acceleration.

1. Introduction.

Intermetallic compound TiAl is receiving considerable attention [1] because of its high specific strength [2, 3] at elevated temperatures. Its application to aircraft engines is thought to be very beneficial, provided that the degradation by its environment is overcome. However, it has been reported [4-6] that protective alumina scales are not formed on TiAl in ordinary oxidizing atmospheres in spite of its high Al content. Therefore, several trials [7, 8] including alloying additions and surface treatments have been performed to enhance the formation of protective alumina scales. However, no sufficiently successful results have yet been reported.

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

2. Experimental procedures.

2.1 SPECIMEN PREPARATION. — Specimens measuring about 20 $\times$ 10 $\times$ 1 mm and about 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 kinetic tests and those of the latter size for metallographic examinations. The specimens were mechanically polished in the ordinary way with SiC polishing papers up to 1000 and subsequently subjected

to peening with glass balls. Then, they were coated with a Co-30Cr-4Al (mass %) layer of 28-30 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.

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. — *Conditions for the sputtering.*

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

2.2 OXIDATION TESTS. — The isothermal kinetic behavior was followed by a thermobalance. After a specimen was hung from a balance beam in a reaction tube, the atmosphere 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 1100 K at which it was longer than 800 ks.

2.3 METALLOGRAPHIC EXAMINATIONS. — The original and oxidized specimens were examined with X-ray diffractometry (XRD) using Cu- K_{α} radiation at 40 kV and 30 mA. Outer surfaces and fractured edges of the specimens were examined with scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). Optical microscopy (OM) was also used.

3. Results.

3.1 KINETIC TESTS. — The oxidation curves are summarized in figure 1, which includes the curve for the uncoated specimen oxidized at 1300 K for comparison. This figure shows that the coating is very effective to decrease the oxidation rate. All curves for coated specimens show a parabolic manner after initial transition periods. However, some acceleration takes

Fig. 1. — Oxidation curves of TiAl coated with the Co30Cr4Al film and uncoated TiAl.

place later. To clarify this, parabolic plots were performed and an example is shown in figure 2. The only exception is that parabolic oxidation continues for periods longer than 800 ks at 1100 K. The time at which the acceleration takes place is shown in figure 1 by arrows.

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

The parabolic rate constants, k_p , obtained from the parabolic periods are summarized in figure 3 in the form of Arrhenius plot. The activation energy obtained was 220 kJ mol^{-1} . The values of k_p and the activation energy agree well with the reported values for alumina-former alloys [9]. This coincides with the observation that the main oxide formed is α -alumina. This observation will be shown in the next section.

Fig. 3. — Summary of parabolic rate constants for TiAl coated with the Co30Cr4Al film.

3.2 METALLOGRAPHIC EXAMINATIONS. — The results of XRD are summarized in table III, which shows that the major oxidation product is α -alumina at all the temperatures. Very small amounts of CoAl_2O_4 (spinel) were also found. The spinel seems to have been formed mainly during the initial transient oxidation periods, because peaks corresponding to it showed very little change with oxidation time. The oxidation at 1300 K for 240 ks and at 1400 K for 320 ks gave rutile in small amounts.

Figure 4 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 found to be around $0.2 \mu\text{m}$ [10]. 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 and the contact between columns seems somewhat loose (b, d).

The oxidation at 1100 K for 20 ks results in a very thin scale on the coating (Figs. 5a, b). Many micropores have developed mainly at the interfaces between the columns (b). After the 500 ks oxidation the outer surface shows a little change such that oxide grains become slightly larger (c). The columnar structure of the coating is still maintained (d). However, relatively large voids have formed within the coating and near the C/S interface (d). This kind of void formation is general occurrence at all the temperatures.

At 1300 K the scale becomes thicker and slightly convoluted (Fig. 6b). The coating seems to have recrystallized, because its columnar structure becomes less clear (b). Several voids have developed mainly near and at the scale/coating interface (S/C interface) and at the C/S interface (b). This fact becomes very pronounced when oxidation period is extended to 240 ks (d). The convoluted scale indicates the generation of oxide growth stresses. However, the scale having a uniform thickness seems to be well maintained (d).

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

At 1400 K the void formation at the S/C and C/S interfaces, and scale convolution become more pronounced. Additional finding is that small mounds of rutile were found on the scale after oxidation for 320 ks.

The concentration profiles of metallic elements across the coating were obtained using EDX, because the void formation at the C/S interface is thought to be partly due to a Kirkendall effect. An example of the results is shown in figure 7, which indicates that Co diffused into the substrate, and small amounts of Ti and Al into the coating.

Table III. — *Summary of XRD.*

As-Received		ϵ -Co (hcp) (s) α -Co (fcc) (w) β -CoAl (w)
	20ks	
1100K	ϵ -Co (m)	500ks ϵ -Co (s) σ -CoCr (s) α -Al ₂ O ₃ (s) CoAl ₂ O ₄ (vw)
	α -Co (s)	
	σ -CoCr (s)	
	α -Al ₂ O ₃ (s)	
1200K	ϵ -Co (m)	430ks ϵ -Co (s) σ -CoCr (s) α -Al ₂ O ₃ (w) CoAl ₂ O ₄ (vw)
	α -Co (m)	
	σ -CoCr (s)	
	α -Al ₂ O ₃ (w)	
	CoAl ₂ O ₄ (vw)	
1300K	ϵ -Co (s)	240ks ϵ -Co (s) σ -CoCr (s) α -Al ₂ O ₃ (s) CoAl ₂ O ₄ (vw) TiO ₂ (vw)
	σ -CoCr (s)	
	α -Al ₂ O ₃ (w)	
	CoAl ₂ O ₄ (vw)	
1400K	ϵ -Co (s)	320ks α -Co (s) α -Al ₂ O ₃ (s) CoAl ₂ O ₄ (vw) TiO ₂ (w)
	σ -CoCr (s)	
	α -Al ₂ O ₃ (s)	
	CoAl ₂ O ₄ (vw)	

(s).....Strong
(m).....Medium

(w).....Weak
(vw).....Very Weak

4. Discussion.

The following two characteristic features were found in this study. First, the oxidation kinetics is very similar to that of alumina-former alloys except for the accelerated oxidation at later periods. Second, voids are formed at the S/C and C/S interfaces. Therefore, we will discuss mainly these two points below.

It was found possible to improve the oxidation resistance of TiAl significantly by applying the CoCrAl coating. This is attributable to the formation of alumina scales on the coating at all the temperatures tested. This view is firmly supported by the results of XRD, kinetic tests, and metallographic examinations.

However, accelerated oxidation takes place above 1200 K. It is quite difficult to explain this acceleration now, because the metallographic examinations showed no useful information,

Fig. 4.

Fig. 5.

Fig. 4. — Surfaces (a, b) and fractured edges (c, d) of TiAl coated with the Co₃₀Cr₄Al film, before oxidation.

Fig. 5. — Surfaces (a, c) and fractured edges (b, d) of TiAl coated with the Co₃₀Cr₄Al film, oxidized at 1100 K for 20 ks (a, b) and 500 ks (c, d).

Fig. 6. — Surfaces (a, c) and fractured edges (b, d) of TiAl coated with the Co₃₀Cr₄Al film, oxidized at 1300 K for 20 ks (a, b) and 240 ks (c, d).

Fig. 7. — Profiles of Co, Cr, Al, and Ti across the coating, before and after oxidation.

except the growth of rutile at 1300 and 1400 K. One possible reason is the appearance of rutile, because rutile grows much faster than alumina and an increase in the number of sites for rutile growth will lead to accelerated oxidation.

Another possible reason is the formation of microcracks in the scale due to oxide stresses, because it is well known [11, 12] that the oxide scale is stressed during its growth. The convoluted scales indicate the generation of stresses.

The voids at the S/C interface can additionally contribute to the formation of microcracks, because stress concentration takes place in the scale above the void.

If relatively large cracks had formed in the scale, there would have been a sudden increase in the mass gain. However, this was not the case in this study.

On the other hand, the void formation at the two interfaces can be explained in terms of the structure of the original coating which is not completely dense and its recrystallization during oxidation.

The coalescence of these micropores and possible volume decreases due to the recrystallization can develop voids.

Additional possibility for the void formation at the C/S interface is a Kirkendall effect arising from preferential diffusion of Co into the substrate. The results of EDX (Fig. 7) support this view.

5. Conclusions.

The oxidation resistance of TiAl is much improved by applying the fine-grained Co-30Cr-4Al coating, which results in alumina scales formation. However, accelerated oxidation takes place after parabolic oxidation periods above 1200 K. The formation of voids at the scale/coating and coating/substrate interfaces is noteworthy.

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