Long Term Oxidation of Model and Engineering TiAl Alloys

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ABSTRACT

The purpose of this research was to characterize the oxidation behavior of several model (TiAl, TiAl-Nb, TiAl-Cr, TiAl-Cr-Nb) and engineering alloys (XD, K5, Alloy 7, WMS) after long-term isothermal exposure (~7000 h) at 704°C, and after shorter time exposure (~1000 h) at 800°C in air. High-resolution field emission and microprobe scanning electron microscopy were used to characterize the scales formed on these alloys. Similarities and differences observed in the scales are correlated with the various ternary and quaternary microalloying additions.

INTRODUCTION

Titanium aluminides (TiAl) are of great interest for intermediate-temperature (600°C-850°C) aerospace, automotive, and power generation applications because they offer significant weight savings compared to today's nickel-based alloys. TiAl alloys are being investigated for low-pressure turbine (LPT) blade applications, exhaust nozzle components and compressor cases in advanced subsonic and supersonic engines [1-2], and exhaust valves in automobiles [2-4]. Significant progress has been made in understanding the fundamental aspects of the oxidation behavior of binary TiAl alloys [5-12]. However, most of this work has concentrated on shorter term (< 1000 hours), higher temperature (900°C-1000°C) exposures. Much less data is available in the literature regarding the oxidation behavior of the quaternary and higher order engineering alloys under the long term, low temperature conditions likely to be encountered in near term structural applications [5-6,11,13]. The present investigation was undertaken to characterize the long-term oxidation behavior of various model and advanced engineering titanium aluminides at 704°C in air. Some engineering alloys were also exposed to 800°C in air for 1000 h. Of particular interest for this study was the formation of nitrides, which have been linked to disruption of alumina scale formation in air [12,14], and the formation of brittle oxygen- and titanium- enriched, aluminum-depleted phase(s) at the metal scale interface, termed by various researchers as Z, X or NCP phase (new cubic phase) [14-18].

EXPERIMENTAL PROCEDURES

The alloys included in this investigation are listed in Table 1. All compositions presented in the paper are reported in atomic percent. Alloys were cast, hot isostatically pressed and heat treated to produce a duplex microstructure of γ -grains and $\alpha_2 + \gamma$ lamellae. Several alloys were isothermally exposed to 704°C for 7000 hours and 800°C for 1000 hours in static air. All samples had a 600-grit finish. Back-scattered electron (BSE) images and elemental maps of polished cross-sections were obtained by electron probe microanalysis (EPMA) equipped with a wavelength dispersive x-ray spectrometry (WDS) using pure element standards for Ti, Al, Cr, Nb, and a pure MgO standard for O. A high-resolution field emission electron microscope (FE-SEM) equipped with BSE and low angle secondary electron (SE) detectors and an energy dispersive x-ray spectrometer (EDX) was used to resolve and analyze the fine multiple layers observed in the metal/scale interface formed in these alloys. Total weight gain was measured before and after exposure using an analytical balance. The scale thickness was measured at three different locations in regions that were not in contact with the supporting alumina boat.

Results and Discussion

Oxidation at 704°C – 7000 h – in Air

Typical alloy compositions, the specific weight changes and the total scale thickness measured for each alloy after exposure to 704°C for 7000 h in air are included in Table 1. The weight gain results are presented in Fig. 1. The binary TiAl alloy is the only one where the scale was not adherent and tended to spall-off. The TiAl-2Cr alloy showed significant weight gain, the thickest scale of all the alloys studied, and was the only alloy that reacted with the supporting alumina boat during the exposure treatment. Therefore, the weight gain values for TiAl and TiAl-2Cr obtained may be inaccurate. The presence of Nb as a ternary or quaternary addition was extremely beneficial, minimizing the weight gain

even when Cr was present in the alloy. A phosphoric acid surface treatment [19] on the Ti48Al-2Cr-2Nb alloy had a pronounced beneficial effect resulting in a further reduction in the weight gain and scale thickening. The advanced engineering alloys, K5, XD-TiAl, Alloy 7 and WMS showed the smallest weight gain. A description of the complex scales that formed in these alloys during the exposure follows.

Table I. Compositions, weight gain, and scale thickness for model and engineering TiAl alloys exposed to 700°C for 7000 hours in static air

Alloy Comp. (at.%)	Al	Ti	Cr	Nb	W	Mo	Mn	Wt. Change/area (mg/cm ²)	Scale ² Thickness (μm)
TiAl ³	47.31	52.69	-	-	-	-	-	4.28 ¹	20
TiAl-2Cr ⁴	46.58	51.43	1.99	-	-	-	-	10.29 ¹	150
TiAl-2Nb	47.67	50.35	-	1.98	-	-	-	1.43 ¹	12
TiAl-2Cr-2Nb	48.19	47.95	1.94	1.92	-	-	-	2.04 ¹	15
TiAl-2Cr-2Nb + Surf. Treat.	48.19	47.95	1.94	1.92	-	-	-	0.57 ¹	6
K5	46.5	47.2	2	3	0.2	-	-	1.1	6
Alloy 7	46	48	-	5	1	-	-	0.41 ¹	5
XD-TiAl	47	51	-	2	-	-	2	0.86	9
WMS	47	49	-	2	0.5	0.5	1	0.61 ¹	4

¹ Average of 2 samples; ² Average of 3 regions; ³ Including spall

⁴ Reacted with Al₂O₃ boat

Model Alloys: Ti-48Al -- A typical cross section of the scale (20 μm thick) formed and a series of microprobe elemental maps, which show the distribution of Ti, Al, N, and O in the different regions of the scale, are presented in Figure 2. The scale has fractured in the middle of the intermixed layer composed of TiO₂ and some Al₂O₃. Typically rutile (TiO₂) needles/platelets are observed on the scale surface, followed by a discontinuous Al₂O₃ layer and an intermixed Al₂O₃/TiO₂ region. Two other layers at the subscale, next to the metal, are clearly visible. The first layer, next to the metal is very rich in Al; microprobe analyses indicate that this rich phase has chemistry close to TiAl₂; the second layer is rich in Ti and N and Al. An Al-enriched zone below the scale has also been reported for Nb and Mo-containing alloys [5,20]. A Microprobe linescan that reflects the changes in chemistry for the multiple layers that formed at the metal/scale sub-surface is included in Fig. 2. It should be noted that such extensive nitride formation and Al enrichment at the metal/scale interface does not appear to occur under shorter term, higher temperature exposure conditions. For example, Dettenwanger et al. [14] report Al depletion and Z/X phase formation at the metal/scale interface for oxidation of Ti-50Al at 900°C in air, which suggests a change in oxidation mechanism between 900°C and 700°C for binary γ-TiAl alloys. On the other hand, Magnan et al., on nitridation of TiAl at 1000°C reported the formation of a surface nitride scale and an Al-enriched subscale [21].

TiAl-2Cr -- Figure 3 (a) shows an image and corresponding maps for the TiAl-2Cr sample after the 7000 hr exposure. Large blocky rutile crystals (30-40 μm thick) are observed on the outer part of the scale followed by a large area of porosity, probably left by the preferential outward growth of TiO₂. A discrete Al₂O₃ layer is detected, followed by finer porosity in a thin TiO₂ region. An extended region of alternating layers of Al₂O₃ / TiO₂ is beneath that layer. The appearance of this layered intermixed region is very atypical compared to the binary TiAl and other TiAl alloys, where a spottier intermixed region is generally observed. This intermixed region is followed by a bright Al-depleted (Ti-rich)/O-rich layer right at the metal/scale interface; its average microprobe chemistry is 58 Ti, 28 Al, 10.8 O and 2.3 Cr. This layer is speculated to be the Z/X phase described in [12-14]. No N-enrichment was detected at the subscale, although Haanappel et al. [8,22] reported the presence of Ti-nitrides after 150h at 700°C in Ti48Al-2Cr. Higher FE-SEM magnification images, shown in Figure 3 (b), provide some fine details of the scale/metal interface. Alternating vertical channels (pipes) of Al₂O₃/TiO₂ connect the bright Ti-rich/O-rich layer to the scale. A few Cr rich particles are also present in the channeled region. This channeled region morphology may be a form of internal oxidation and is reminiscent of that reported by Doychak et al. [23] for the accelerated oxidation of NbAl₃ and Brady et al. [24] for the rapid oxidation of a Ti modified σ-Nb₂Al alloy. Observation of the intermixed Al₂O₃/TiO₂ region suggests that the channel morphology occurred throughout the course of oxidation. The detrimental effects of small Cr additions on the oxidation of TiAl have generally been postulated to result from doping effects of Cr on TiO₂ growth rate [25]. However, the present results suggest that Cr may also promote this channel form

Figure 1. Specimen weight gain for model and advanced γ-TiAl alloys after isothermal exposure to 704°C for 7000 h in air.

Figure 2. Typical microstructure, microprobe elemental maps and line scans observed in a binary γ -TiAl alloy after exposure to 704 °C for 7000 hr in air.

Figure 3. (a) Typical microstructure, microprobe elemental maps and line scans observed in a TiAl-2Cr alloy after exposure to 704 °C for 7000 hr in air. (b) Higher magnification of the scale/metal interface showing the alternating vertical Al₂O₃/TiO₂ channels that connect the Ti-Al-O rich layer to the scale.

of internal oxidation, possibly by increasing oxygen solubility in the alloy, although it is difficult to distinguish whether the channel morphology is a consequence of the more rapid oxidation with Cr additions or the cause of it. It is somewhat consistent with the mechanism forwarded by Shida and Anada [25], which interpreted beneficial or detrimental effects of ternary additives to TiAl in terms of oxygen solubility and internal/external oxidation and its effect on alumina morphology.

TiAl-2Nb -- A nearly continuous Al_2O_3 scale (~2 μm thick), containing a few spots of TiO_2 was observed near the gas/scale interface with a few discontinuous TiO_2 needles at the surface. The remainder of the scale as observed in the other alloys consisted of the intermixed $\text{TiO}_2/\text{Al}_2\text{O}_3$ richer in TiO_2 . A thin discontinuous Ti(Al)-N rich layer was formed at the metal/scale interface. No Al-enriched or depleted layer was distinguished.

Ti48Al-2Cr-2Nb -- Detailed description of the scale formed in this system has been reported earlier [5,6]. Typically, the scale consisted of an outer layer of TiO_2 and an inner intermixed layer of $\text{Al}_2\text{O}_3/\text{TiO}_2$. Observations after 6000 h revealed that a nearly continuous layer of Al_2O_3 separated these regions. A continuous Ti(Al)-N rich layer nearly 1 μm thick was formed at the alloy/scale interface. Discontinuous Cr/Nb-enriched phases decorated this layer. These results are consistent with results reported by Sunderkotter for the oxidation of Ti-48Al-2Cr-2Nb after exposure for 150 h at 800 °C [26]. The alloy ahead of this layer was significantly depleted in Ti and enriched in Al by approximately 10 at.% each. Based on the composition analyses, the N containing layer consisted of the TiN phase (with a minor amount of Al), and the Ti-depleted/Al-enriched layer consisted of the TiAl_2 phase.

Engineering Alloys: XD-TiAl -- The scale formed in the advanced engineering alloys is more complex than that observed on the model alloys with regards to the structure at the metal/scale interface. Figure 4 shows a typical cross section of the scale (~9 μm thick) formed on the XD-TiAl alloy. A few TiO_2 whiskers are observed at the surface followed by a nearly continuous Al_2O_3 layer. Next is the typical intermixed $\text{Al}_2\text{O}_3/\text{TiO}_2$ layer. The metal/scale interface consists of two fairly well defined layers. The one next to the matrix (white contrast) is very rich in Mn and also enriched in Nb; typical microprobe chemistry is 31.6 Ti, 34.5 Al, 5.4 Nb, 15.3 Mn, 6.5 O, 6.8 N. The layer next to the intermixed region (gray contrast) is Ti and N-enriched; typical chemistry is 37.7 Ti, 17 Al, 2.3 Nb, 4 Mn, 22 N, 17 O. Large TiB_2 particles can be observed in the matrix. A FE-SEM line scan showing the chemistry variation across the metal scale interface is included in Fig. 4.

Alloy K5 -- Figure 5 shows a typical cross section of the scale (~6 μm thick) formed on alloy K5. Similarly to the XD-alloy, a few TiO_2 whiskers are observed at the surface followed by a nearly continuous Al_2O_3 layer. The typical intermixed $\text{Al}_2\text{O}_3/\text{TiO}_2$ layer follows. The metal/scale interface is more complex. Higher magnification observations revealed at least two main layers. The layer next to the metal (white contrast) is Cr and Nb enriched. A Ti and N-enriched layer (gray contrast), interrupted by pockets of Al_2O_3 , is observed next to the intermixed region. Microprobe chemistry for both layers are, 31.3 Ti, 30 Al, 4.2 Nb, 3.1Cr, 0.2 W, 6.9 O, 23.9 N and 37.7 Ti, 5.3Al, 1Nb, 2.1 Cr, 51.7 N, 0.3 W, respectively. Since these layers are much less than 1 micron thick, chemical contribution from neighboring regions is occurring. Also in certain areas (not shown in Fig. 5), a discontinuous Al-enriched layer was observed next to the metal. Typical microprobe chemical analysis for the matrix is 47.9 Ti, 47.4 Al, 2.6Nb, 1.9 Cr, 0.16 W, which is comparable to the bulk alloy composition.

Alloy 7 -- A typical cross section of the scale (~5 μm thick) formed on the Alloy 7 after exposure is presented in Fig. 6. This alloy, which contains 5 at.% of Nb, has very few TiO_2 whiskers at the surface and an almost continuous Al_2O_3 layer follows beneath. Next is an intermixed $\text{Al}_2\text{O}_3/\text{TiO}_2$ with apparently more Al_2O_3 compared to other alloys. A difficult to resolve thin Ti-rich nitride layer followed by a Nb-enriched region was observed. No Al-enriched or depleted layer at the metal/scale interface was detected.

Oxidation at 800°C-1000 hr-in Air

Ti48Al-2Cr-2Nb -- The appearance of the scale (~12 μm thick) formed on the Ti-48-2Cr-2Nb after the 800°C exposure is very similar to the long-term exposure at 704°C. Main differences occurred at the interface where multiple layers have formed at the metal/scale interface. A high magnification FE-SEM image, shown in Figure 7, reveals four main layers, beyond the intermixed region. First, an alumina region containing small discrete particles is observed beneath the intermixed region. This is followed by a Ti-N enriched region (white), a Nb-enriched region (grayish), and lastly (slightly darker) an Al-enriched region next to metal.

Alloy K5 -- The scale thickness formed on alloy K5 was approximately ~14 μm thick with features similar to the sample exposed to 704°C (Fig.5). Two well-defined bright regions, both enriched in Nb, were observed at the metal/scale interface (Fig.8 (a)). Oxygen was only detected in the Nb-enriched bright region next to

intermixed region. A third region, enriched in Ti and N, separates the two Nb-enriched regions. No Al-enriched layer at the metal/scale interface was detected in the regions investigated.

Alloy 7 -- Alloy 7 developed a 6 μm thick scale during the 800°C exposure. Alumina nodules lightly coated with TiO_2 were observed at the surface. The nodules seem to be connected by a thin but continuous Al_2O_3 layer above the intermixed layer. Figure 8 (b) shows a high magnification of the metal/scale interface. A Nb-enriched layer next to the metal precede a brighter and thick Ti-N enriched region which is interrupted by pockets of Al_2O_3 ahead of the intermixed region. W-rich particles have concentrated near the metal/scale interface.

Conclusions

This study shows the complex nature of the scale that can form on TiAl alloys during high temperature exposure in air. None of the alloys form a true continuous alumina layer and nearly all formed nitrogen enriched zones at the alloy/scale interface. Alloy 7 and alloy K5 show excellent oxidation resistance at 704 and 800°C. With the exception of binary TiAl and TiAl-2Cr, all the TiAl alloys exhibit good long-term isothermal oxidation resistance at 704°C in air, the scale thickness only varying from 5 to 15 μm . The scales formed on the engineering γ -alloys are not identical and extremely complex, in particular with regards to the phases formed at the metal/scale interface. To some extent these results are at odds with generalizations made for protective behavior at higher temperatures. That is, very good behavior is observed here for 704°C oxidation of the engineering alloys, which do exhibit a nitride interlayer but not the brittle oxygen- and Ti-enriched, Al-depleted Z/X phase interlayer reported during oxidation above 900°C. While at high temperature, it appears that continuous alumina scales occur primarily when the Z/X phase is formed and the nitride layer and $\alpha_2\text{-Ti}_3\text{Al}$ layers are absent [27]. Much of the environmental concern for the TiAl engineering alloys stems from an embrittlement perspective - most do not form excessive scales, but may have compromised mechanical properties if a brittle surface layer forms. It is not yet clear whether the Z/X, nitride, or oxygen-saturated $\alpha_2\text{-Ti}_3\text{Al}$ phases are equally problematic.

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Figure 4. Typical microstructure, and FE-SEM elemental linescans observed in a XD-TiAl alloy after exposure to 704°C for 7000 hr in air.

Figure 5. Typical microstructure, and FE-SEM elemental linescans observed in alloy K5 after exposure to 704°C for 7000 hr in air.

Figure 6. Typical microstructure observed in alloy 7 after exposure to 704°C.

Figure 7. Typical microstructure observed at the metal/scale interface in TiAl-2Cr-2Nb after 800°C.

Figure 8. Typical microstructure observed at the metal/scale interface for (a) Alloy K5, (b) Alloy 7 after 800°C - 1000h.