High-Temperature Oxidation Behavior of Elemental Powder Metallurgy Processed TiAl-Mn-Mo-C Alloys with Yttrium Addition

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Effects of yttrium addition on the formation of oxide scales and the oxidation resistance of elemental powder metallurgy (EPM) processed TiAl-Mn-Mo-C alloys were studied. The Y-containing TiAl-based alloys (0.1~0.6 at%Y) showed better oxidation resistance than Y-free alloy oxidized in air at 800°C for 350 h. The Y-containing alloys showed a significantly reduced weight gain, especially for 0.6 at%Y-added alloy. In the Y-free alloy, the scale formed during extended air-exposure at 800°C consisted of TiO₂ and α -Al₂O₃. For 0.6 at%Y-added alloy, however, the oxide scale was composed of a complex mixture of TiO₂, α -Al₂O₃, Y₂O₃ and Al₅Y₃O₁₂. The formation of multi-phase (Y, Al)O-type oxides layer in a transitional Y-rich subscale close to the substrate and an increase of the amount of α -Al₂O₃ in the mixture oxide layer in the Y-added alloys were the main contributor to improving the oxidation resistance of the alloys. The reduction of oxygen content in the substrate also had a beneficial effect on the oxidation resistance of the Y-containing TiAl-based alloys.

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1. Introduction

Structural materials used for advanced aircraft engines and gas turbine blades at high temperature are required to show good oxidation resistance. The performance of TiAl-based alloys as new structural materials depends strongly on their oxidation resistance.¹⁾ Inadequate oxidation resistance limits the use of current TiAl-based alloys above about 800°C, however, because the external layer formed on the substrates is not a protective Al₂O₃ scale, but a TiO₂ scale or a mixture of these two oxides.²⁾ Some of the methods are developed to improve the oxidation resistance of TiAl alloys: alloying by adding ternary and quaternary elements,³⁻⁸⁾ surface coating^{9,10)} and ion implantation of alloy elements.^{11,12)} In the case of alloying, a strong resistance to the oxidation of TiAl-based alloys is sought by forming a protective Al₂O₃ layer or a new barrier layer that can block diffusion of titanium ions on the oxide interface, thereby preventing the rapid growth of TiO₂ scale. Although a great deal of research has already been reported to improve the oxidation resistance by alloying elements such as Nb, Mo, Si, Ta, Sb, Ag, W, Cl, F, P and others, it should be mentioned that some elements which improve oxidation resistance in many cases have a negative effect on the mechanical properties.^{3-8,13-18)} In our previous studies, it has been found that yttrium is a good alloying

element to improve the mechanical properties and oxidation resistance without sacrificing the ductility of TiAl-based alloys.^{19,20)} Also several investigators have studied the effect of yttrium addition as a metallic constituent, and the high temperature oxidation behavior of alloy systems other than TiAl²¹⁻²⁵⁾ and have found that yttrium addition is beneficial. Therefore, yttrium is an attractive element with which to study the oxidation resistance of TiAl-based alloys.

The aim of this paper was to determine the oxidation behavior of elemental powder metallurgy (EPM) processed TiAl-Mn-Mo-C alloys containing various amounts of yttrium (0.1~0.6 at%), focusing on the oxidation kinetic as well as the composition and microstructural evolution of oxide scales.

2. Experimental

Oxidation tests were conducted on four TiAl-based alloys. Table 1 shows the chemical compositions of these alloys in which the yttrium content was changed from 0 to 0.6 at% while the contents of the alloying elements of Mn, Mo and C remain constant. The present materials were fabricated by EPM, the processing details of which are described elsewhere.²⁶⁻²⁹⁾ Prior to the oxidation tests, the extruded rods were heat treated in an argon atmosphere. The heat treatment

Table 1 Chemical composition of the experimental alloys.

Nominal	Analysis (at%)					
	Ti	Al	Mn	Mo	C	Y
Ti-46.6Al-1.4Mn-2Mo-0.3C	50.18	46.21	1.32	1.98	0.31	—
Ti-46.6Al-1.4Mn-2Mo-0.3C-0.10Y	49.99	46.30	1.31	2.01	0.30	0.09
Ti-46.6Al-1.4Mn-2Mo-0.3C-0.33Y	50.56	45.56	1.29	2.02	0.29	0.28
Ti-46.6Al-1.4Mn-2Mo-0.3C-0.60Y	49.32	46.48	1.30	2.06	0.29	0.55

*The average concentration of oxygen in the samples was approximately 1500 ppm regardless of the compositions.

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Fig. 1 Micrographs showing (a) fully lamellar microstructure of aligned $\alpha_2 + \gamma$ platelets and (b) Y_2O_3 particles formed in γ platelets in EPM Ti-46.6Al-1.4Mn-2Mo-0.3C-0.33Y alloy heat treated at 1400°C/1 h/AC + 800°C/12 h/AC.

cycles consisted of a solution treatment at 1400°C for 1 h followed by air cooling (AC) and an aging treatment at 800°C for 12 h. Microstructural analysis of the specimens was performed by optical microscopy and an H-800 transmission electron microscope operated at 200 kV. Metallographic examinations revealed that microstructures consisted predominantly of full lamellae of aligned $\alpha_2 + \gamma$ platelets and minor amounts of oxide precipitates of Y_2O_3 particles, in γ platelets as shown in Figs. 1 (a) and (b), respectively. The presence of Y_2O_3 precipitates in the alloys with higher content of yttrium was also evidenced by the results of X-ray diffractometry (XRD) as shown in Fig. 2. The peak of Y_2O_3 in (222) at $2\theta = 29.2^\circ$ was detected in 0.6 at%Y-added alloy (Fig. 2(b)). As reported previously,¹⁹⁾ the concentration of internal oxygen of the EPM TiAl alloys was reduced by additions of yttrium and the oxides of Y_2O_3 precipitated by the reaction of yttrium with the internal oxygen which was introduced during EPM processing of the experimental alloys. Because there is strong binding between yttrium and oxygen atoms,³⁰⁾ and because the average oxygen concentration of EPM experimental alloys is 1500 mass ppm, which

Fig. 2 XRD diffraction spectra of Ti-46.6Al-1.4Mn-2Mo-0.3C alloy prior to oxidation: (a) Y-free and (b) 0.6 at%Y-added alloys.

is about ten times higher than the solubility limit of 128 mass ppm,³¹⁾ supersaturated oxygen is prone to react with yttrium to form the Y_2O_3 particles.

Specimens ($5 \times 9 \times 2 \text{ mm}^3$) were cut from rod materials, polished with emery papers of up to 1200 mesh finish and ultrasonically cleaned for an additional 15 min in ethanol. Isothermal oxidation tests of the specimens were conducted using a thermo-balance in laboratory air at 800°C for up to 350 h. After these tests, the oxidation products formed were examined by XRD using Cu (K_α) target. Surface and cross-sectional morphologies of the oxides were observed by a scanning electron microscope (SEM). Distributions of elements in the cross-section of the oxides were analyzed by energy-dispersive X-ray spectrometry (EDS) in SEM and also by an electron probe micro-analyzer (EPMA).

3. Results

3.1 Isothermal oxidation kinetics

Figure 3 shows the mass gain per unit surface area of TiAl-based alloys oxidized in laboratory air as a function of exposure time at 800°C. The mass gain apparently decreased with increasing yttrium content. The mass gain of 0.6 at%Y-added alloy was approximately 1/3 that of Y-free alloy and Ti-50Al alloy³²⁾ after 350 h exposure. All of the oxidation kinetic curves consisted of two stages: a linear and a

Fig. 3 Effect of yttrium on the oxidation kinetics of EPM Ti-46.6Al-1.4Mn-2Mo-0.3C-*x*Y alloys in air at 800°C. Samples were heat treated at 1400°C/1 h/AC + 800°C/12 h/AC. Refer to Table 2 for the quantitative kinetics data.

parabolic stage. Results of the isothermal oxidation tests are summarized in Table 2, in which the parabolic rate constant, K_p , from the second stage of the oxidation curves, the mass gain and the thickness of oxide scale for each alloy after 350 h exposure at 800°C are found to be closely related to the yttrium content. In addition to the oxidation rate, the values of K_p and thickness of the oxide scale became smaller as the quantity of yttrium added was increased. Under these oxidation conditions, the addition of yttrium significantly improved the oxidation resistance of TiAl-Mn-Mo-C alloys.

3.2 Composition and surface morphology of oxide scale

Through analysis of the phases in scales by XRD, a difference between the Y-free alloy and Y-containing alloys was identified as shown in Table 2. Figure 4 shows the XRD diffraction spectra of the oxide scales formed in TiAl-based alloys exposed at 800°C for 350 h. Basically four different oxide phases were distinguishable, TiO_2 (rutile), $\alpha\text{-Al}_2\text{O}_3$, Y_2O_3 and $\text{Al}_5\text{Y}_3\text{O}_{12}$. The XRD diffraction spectra obtained from Y-free TiAl alloy (Fig. 4(a)) and 0.1 at%Y-added alloy (Fig. 4(b)) after longer exposure time only contain peaks from the mixture of the TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ phases. However, the oxide scales in 0.33 at%Y-added and 0.6 at%Y-added alloy were significantly thinner than those of the former alloys from the SEM observation. Moreover the scales

consisted of all four oxide phases as shown in Figs. 4(c) and (d), although the amounts of Y_2O_3 and $\text{Al}_5\text{Y}_3\text{O}_{12}$ phases were slightly higher in the 0.6 at%Y-added alloy.

Figure 5 shows the XRD diffraction spectra at the incident beam angle of 1° of the oxide scales formed in Y-free TiAl alloy at 800°C after various periods of isothermal exposure. After 1 h oxidation at 800°C (Fig. 5(a)) a thin oxide scale was found to be a mixture of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$. Some peaks of TiAl from the underlying material were also determined. With increasing oxidation time up to 48 h (Fig. 5(b)) and 100 h (Fig. 5(c)), the oxide scales grew thicker but no crystallographic phase change occurred except for change in the relative peak heights of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$.

The appearance of Y_2O_3 and $\text{Al}_5\text{Y}_3\text{O}_{12}$ phases in the alloy containing 0.33 at%Y or 0.6 at%Y was detected only after an extended exposure at high temperature. The progress of oxidation with exposure time of the 0.33 at%Y-added alloy is illustrated in Fig. 6. At oxidation for 1 h, only TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ phases appeared. Due to the minimal thickness of the oxide scale, the substrate TiAl phase was also detectable in the XRD spectrum. Formation of Y_2O_3 and $\text{Al}_5\text{Y}_3\text{O}_{12}$ phases was noticed after exposures for 48 h and 100 h, respectively, so that all four phases were present thereafter.

SEM examination of the oxidation process of the TiAl-based alloys revealed an interesting development of morphological features and variation in chemical composition of the oxide scales that is consistent with the XRD result of Fig. 4. The oxide scales of all the specimens at 800°C after 350 h isothermal exposure showed a common feature of granular oxide particles. However, the Y-containing alloys (0.33 at%Y or 0.6 at%Y) were associated with a greater amount of aluminum and yttrium in the oxide scales compared to the Y-free or Y-lean (0.1 at%Y) alloys.

In accord with the XRD analysis results of Y-free alloy in Fig. 5, the surface microstructural evolution as a function of oxidation time under SEM observation showed that the oxide layer consisted of granular phases, and the average size of individual grains varied from $0.5\mu\text{m}$ to about $5\mu\text{m}$ with exposure time of 1 h and 350 h, respectively. With increasing oxidation time, the number of coarse-grained oxides increased on the scales of the surface. The oxide scale was enriched only with Ti and oxygen at all the periods of exposure. Especially to be noted was that the spallation problem occurred in the Y-free alloy after oxidation at 800°C for 350 h.

Figure 7 shows SEM micrographs of the surface morphology of Ti-46.6Al-1.4Mn-2Mo-0.3C-0.6Y alloy oxidized isothermally at 800°C for different exposure times of 1 to

Table 2 Results of isothermal oxidation of the experimental alloys at 800°C for 350 h.

Alloy	K_p ($\text{g}^2\cdot\text{m}^{-4}\text{h}^{-1}$)	Mass gain ($\text{g}\cdot\text{m}^{-2}$)	Scale thickness (μm)	Oxides detected
Ti-46.6Al-1.4Mn-2Mo-0.3C	2.4	29.12	24–30	TiO_2 , Al_2O_3
Ti-46.6Al-1.4Mn-2Mo-0.3C-0.1Y	1.1	19.65	20–25	TiO_2 , Al_2O_3
Ti-46.6Al-1.4Mn-2Mo-0.3C-0.33Y	0.6	14.61	13–17	TiO_2 , Al_2O_3 , Y_2O_3 , $\text{Al}_5\text{Y}_3\text{O}_{12}$
Ti-46.6Al-1.4Mn-2Mo-0.3C-0.6Y	0.3	10.30	10–15	TiO_2 , Al_2O_3 , Y_2O_3 , $\text{Al}_5\text{Y}_3\text{O}_{12}$

Fig. 4 XRD diffraction spectra of the oxide scales formed at 800°C after 350h isothermal exposure in EPM Ti-46.6Al-1.4Mn-2Mo-0.3C alloy: (a) Y-free, and alloys containing (b) 0.1 at% Y, (c) 0.33 at% Y and (d) 0.6 at% Y.

100h. No spallation of oxide particles was observed after cooling. The size of oxide crystals increased gradually with exposure time. EDS results indicated that the outer part of the oxide scale, formed after 1 h (Fig. 7(a)) at 800°C was composed mainly of titanium and oxygen. Aluminum in the oxide layer was slightly detected after 1 h exposure but was unmistakably identified after 48 h of oxidation. After 48 h (Fig. 7(b)) of isothermal oxidation the surface of the alloy was covered with oxide particles enriched with titanium and aluminum. The intensity of yttrium was weak at 48 h of exposure but was clearly evident after 100 h of oxidation. After 100 h exposure, the overall scale was enriched with a large number of oxide particles of titanium, aluminum or yttrium. However, the oxides in Fig. 7(c) showed a pillar-like feature, indicating the formation of TiO_2 crystal in the outmost layer.

3.3 Cross-sectional microstructures

Figure 8 shows typical micrographs of a cross-section through part of the scale formed on Ti-46.6Al-1.4Mn-2Mo-0.3C alloy for different isothermal exposure times at 800°C. The EDS results in Table 3 show that the structure of the scales is relatively simple and consists in the order of Mo-rich Ti_3Al layer (II)/Mixed layer (III)/ TiO_2 crystal (V) from the inside. With increase in the exposure time from 48 h (Fig.

8(a)) to 350 h (Fig. 8(b)), the thickness of oxide scales increased. The outer scale consisted of large TiO_2 crystals followed by a mixed oxide scale. Furthermore, it is presumed from EDS analysis that this layer consisted predominantly of TiO_2 and minor amounts of Al_2O_3 . Pores and voids were observed within this oxide layer. The oxide next to the substrate was Mo-rich Ti_3Al layer with bright contrast under SEM. After 350 h of oxidation, in addition to the thickening of the oxide scale, it was also observed that some microscopic cracks were seen to have formed within the oxide layer as shown in Fig. 8(c); these originated from either a residual stress build-up due to the thick scale or inherent poor cohesion between the scale and the substrate.

In addition to the effect of reducing the thickness of oxide, Y-addition also resulted in the formation of a transitional Y-rich subscale between the substrate and the Mo-rich Ti_3Al scale. Five different chemical compositions were identified for the oxide scales formed in the specimen containing 0.6 at% Y; the corresponding cross-sectional micrograph and the result of EDS analysis of these are presented in Fig. 9 and Table 3, respectively. Starting from the substrate, the oxides consisted of Y-rich oxide (I)/Mo-rich Ti_3Al (II)/Mixed scale (III)/Al-rich mixed scale (IV)/ TiO_2 (V). As evidenced by elemental distribution maps and line analysis by SEM-EPMA in Fig. 10 and Fig. 11, respectively, there was a transitional

Fig. 5 XRD diffraction spectra (at 1° angle of incidence) of the oxide scales formed in Ti-46.6Al-1.4Mn-2Mo-0.3C alloy after isothermal exposure at 800°C for: (a) 1 h, (b) 48 h and (c) 100 h.

oxide layer in the Y-enriched innermost region of the Y-containing alloy. The Y-content in this layer was about 1.42 mass% whereas that in the other layers was below the detection limit. The chemical composition of Mo-rich Ti_3Al -containing layer was identical to that formed in the Y-free alloy; the existence of the outermost TiO_2 layer is also common to both alloys. However, there was a significant difference in the microstructure of the intermediate layer in that a gradual transition occurred from TiO_2 to the Mo-rich Ti_3Al layer in the Y-containing alloy. The transition involved a mixture of Al-rich oxide in the outer layer immediately underneath TiO_2 crystals followed by another mixed oxide

Fig. 6 XRD diffraction spectra (at 1° angle of incidence) of the oxide scales formed in Ti-46.6Al-1.4Mn-2Mo-0.3C-0.33Y alloy after isothermal exposure at 800°C for: (a) 1 h, (b) 48 h and (c) 100 h.

layer. The distribution of alloying elements in the cross-sectional structure in Fig. 11 shows that a peak in the Al-content is contrasted by a decrease in Ti-content in the fourth layer of the oxide due to the formation of $\alpha\text{-Al}_2\text{O}_3$. Therefore, there are two additional layers, Y-rich subscale and Al-rich mixed scale, in the Y-containing alloys although the whole scale is quite thin compared to that formed in the Y-free or Y-lean alloys.

Fig. 7 SEM micrographs of the surface morphology of Ti-46.6Al-1.4Mn-2Mo-0.3C-0.6Y alloy after isothermal exposure at 800°C for: (a) 1 h, (b) 48 h and (c) 100 h.

4. Discussion

From the present study it is clear that Y-addition improves the oxidation resistance of EPM TiAl-based alloys. Similar studies were reported by several researchers in various alloy systems which support this conclusion.^{21–25} In most cases, Y-additions reduce the weight gain during oxidation and decrease the parabolic rate constant. Zhang *et al.*²¹ studied the oxidation resistance of a H13 steel implanted with yttrium or yttrium plus carbon, and concluded that yttrium provided a

Fig. 8 Cross-sectional SEM micrographs of Ti-46.6Al-1.4Mn-2Mo-0.3C alloy after isothermal exposure in air at 800°C for: (a) 48 h, (b) and (c) 350 h. Note: II-Mo-rich layer, III-Mixed layer, V-TiO₂ crystals.

barrier layer for hindering the oxygen diffusion along dislocations or grain boundaries during thermal oxidation. Tsai *et al.*²² found that yttrium atoms segregated along grain boundaries and hindered both anionic and cationic intergranular diffusion in Ni-30Cr alloy. In Ni₃Al-based alloys with yttrium additions, Han *et al.*²⁵ investigated the mechanism of improvement of high temperature isothermal oxidation resistance and indicated that this resistance of the alloy was substantially improved by the proper amount of yttrium. They demonstrated that the beneficial effects of yttrium on

Table 3 Comparison of chemical compositions on the oxides of Y-free and 0.6 at%Y-add alloys after isothermal exposure in air at 800°C for 350 h.

Alloy	Layer	Elements (mass %)						
		Ti	Al	Mn	Mo	Y	O	C
Y-free	Substrate	64.19	25.68	2.14	7.02	—	0.18	0.79
	II Mo-rich Ti_3Al	57.73	17.09	1.61	18.92	—	4.63	0.02
	III Mixed scale	56.76	29.24	0.15	3.73	—	10.06	0.09
	V TiO_2 crystals	58.15	9.00	2.29	0.22	—	30.29	0.05
0.6 at%Y-added	Substrate	65.24	26.48	1.97	5.22	0.21	0.17	0.71
	I Y-rich	63.21	27.79	1.96	5.06	1.42	0.55	0.01
	II Mo-rich Ti_3Al	58.19	24.13	3.88	11.43	—	2.35	0.02
	III Mixed scale	51.69	21.53	0.16	2.76	—	23.69	0.17
	IV Al-rich mixed scale	44.66	41.61	1.07	0.21	—	12.39	0.06
	V TiO_2 crystals	52.48	18.61	1.13	0.20	—	27.51	0.07

Fig. 9 Cross-sectional SEM micrographs of Ti-46.6Al-1.4Mn-2Mo-0.3C-0.6Y alloy after isothermal exposure in air at 800°C for: (a) 48 h and (b) 350 h. Note: I-Y-rich layer, II-Mo-rich Ti_3Al layer, III-Mixed layer, IV-Al-rich mixed layer, V- TiO_2 crystals.

high temperature oxidation resistance included: (a) inhibiting the cationic transportation and decreasing the depth of the diffusion layer, (b) promoting the selective oxidation of aluminum and (c) promoting the formation of a fine and closely-packed oxide grain structure. In the present case, the

improvement of the oxidation resistance through Y-modification can surmise the effect of yttrium on the microstructure of the oxide scale, *i.e.*, the formation of a transitional Y-rich layer and the increase in the amount of $\alpha\text{-Al}_2\text{O}_3$ in outer oxides layer.

The alloys with Y-additions showed smaller mass gain and smaller parabolic rate constant. The XRD diffraction spectra showed that in 0.33 at%Y-added alloy (Fig. 4(c)) and 0.6 at%Y-added alloy (Fig. 4(d)) exposed at 800°C for 350 h, thin oxide scales composed of a mixture of TiO_2 , $\alpha\text{-Al}_2\text{O}_3$, and subscales Y_2O_3 and $\text{Al}_5\text{Y}_3\text{O}_{12}$ were formed. However, in the case of the Y-free alloy, the surface oxides contain only a mixture of TiO_2 and $\alpha\text{-Al}_2\text{O}_3$ (Fig. 4(a)) even after long exposure. In Y-containing alloys, however, the chemical composition of the oxide was modified at 800°C for an extended period. Especially for the 0.6 at%Y-added alloy, both yttrium and internal oxides existed due to intrinsic oxygen and excess yttrium in the sample (Fig. 2(b)). During the exposure at high temperature yttrium reacted with internal and external oxygen and formed the Y_2O_3 until the presence of the (Y, Al)O-type subscales.²⁰⁾

In the second stage, oxidation curves of all TiAl-based alloys obeyed the parabolic rate law that was represented by the equation of $(\Delta M)^2 = K_p t$, where ΔM , K_p and t are mass gain, parabolic rate constant and time, respectively. This process was controlled by cation and oxygen transport through the scale. In the present EPM TiAl alloys, two specific sources of oxygen, namely, oxygen inside the intermetallic compound and oxygen in the environment should be considered during the isothermal oxidation at high temperature. Because of the limited solubility of yttrium in TiAl and the strong affinity of yttrium to oxygen, the supersaturated oxygen atoms form Y_2O_3 (Fig. 1(b)), and thereby the oxygen-scavenging effect of yttrium is realized. Because Y_2O_3 is stable up to 2009°C in TiAl,³⁰⁾ the oxide is not decomposed during exposure at 800°C in air. The quantity of Y_2O_3 formed inside TiAl is proportional to the quantity of yttrium added. In fact the quantity of Y_2O_3 increased in the high-Y alloy with exposure time at 800°C. The content of oxygen analyzed by EDS (see Table 3) indicates the average in the oxides and the matrix in solid solution, although quantitative distinction is difficult at

Fig. 10 Element distribution maps in cross section observed by means of SEM-EPMA showing effectiveness of yttrium content in 0.6 at%Y-added TiAl alloy after isothermal exposure in air at 800°C for 350 h: (a) Ti, (b) Al, (c) Mn, (d) Mo and (e) Y. Each element shows the white contrast in the micrographs.

present. In this respect, the improvement in high temperature oxidation behavior by yttrium addition can be explained by Wagner's classical theory:³²⁾ the oxidation resistance of the alloy is in reverse proportion to the oxygen solubility. According to this interpretation, yttrium enhances the oxidation resistance by lowering the oxygen solubility in TiAl through the formation of Y_2O_3 phase. The results presented in Fig. 3 indicate that this effect is proportional to the yttrium content, not exceed 0.6 at%. Consequently, the decrease of oxygen concentration inside TiAl by addition of yttrium is undoubtedly useful for the oxidation resistance although the degree of the effect is limited. However, the most beneficial effect of yttrium lies in upgrading the chemical and morphological characteristics of the scale.

A schematic illustration of the oxide scale in Y-free and 0.6 at%Y-containing alloys is shown in Figs. 12(a) and (b), respectively, in which the scale structure and the role of

yttrium in the Y-containing alloy are explained compared with those in Y-free TiAl. The unique presence of an intermediate layer is illustrated, the thin Y-rich subscale layer and Al-rich mixed layer. Y-addition induces formation of the subscale layer that is significantly more resistant to atmospheric oxygen than TiO_2 is. As shown in the XRD phase analysis of the oxide scale, the Y-rich layer contained (Y, Al)O-type oxides except for other oxides. According to the equilibrium diagram,³³⁾ (Y, Al)O-type oxides form if aluminum reacts with oxygen in the Y_2O_3 scale. The reaction of alumina and yttria is as follows:²³⁾

Therefore, $\alpha-Al_2O_3$ and Y_2O_3 are precursors for the formation of the $Al_5Y_3O_{12}$. The latter phase is better for oxidation resistance than TiO_2 although it is also non-

Fig. 11 Distributions of each element found by EPMA of the cross-section of the oxide scale on the 0.6 at%Y-added alloy at 800°C for 350 h. Note: I-Y-rich layer, II-Ti₃Al layer with Mo-rich, III-Mixed layer, IV-Al-rich mixed layer, V-TiO₂ crystals layer, VI-plastic grinding mounts.

protective. In the Y-containing alloys, because of the lower solubility of yttrium in Al₂O₃,²³⁾ yttrium was apt to form the (Y, Al)O-type oxides in the Y-rich area in the transitional layer. Particularly, the addition of yttrium promoted the formation of Al₂O₃, which evidenced by a considerable amount of Al₂O₃ in the outer scale and the presence of (Y, Al)O-type oxides because the formation of the latter needed a large supply of Al₂O₃. In the Y-free alloy, however, the lack of protective Al-rich layer in the scale resulted in a fast oxidation with a thick scale, see Table 2 and Fig. 8. Therefore, the Y-rich subscale and Al-rich mixed layer may delay the diffusion of Ti and oxygen transport from the atmosphere, resulting in the improvement of TiAl-based alloys.

The improvement of cracking resistance with yttrium additions in TiAl-based alloys was closely related to the thinness of the scale. In this case, the thermal stress arising from the difference in the thermal expansion coefficient between the matrix and the oxide during the oxidation was easily removed. As for the Y-free alloy, the thickening of the scale resulted in scale spallation (Fig. 8(c)). In contrast, absence of any interface crack in the Y-containing alloy, see Fig. 9, manifests the effect of yttrium on resisting cracking and spalling of the scale.

5. Conclusions

The effect of Y-addition on the high temperature oxidation behavior of EPM TiAl-Mn-Mo-C alloys was examined and the following conclusions were drawn:

Fig. 12 Schematic of the cross-sectional microstructure of the oxide formed in (a) Y-free alloy and (b) 0.6 at%Y-added alloy after isothermal exposure in air at 800°C for 350 h. I-Y-rich layer, II-Ti₃Al layer enriched with Mo, III-Mixed layer, IV-Al-rich mixed layer, V-TiO₂ crystals layer.

- (1) Y-additions remarkably improved the oxidation resistance of EPM TiAl-1.4Mn-2Mo-0.3C alloys exposed at 800°C for 350 h. With increasing yttrium content from 0.1 at% to 0.6 at%, the mass gain and scale thickness as well as the parabolic rate constant of the experimental alloys decreased in sequence.
- (2) Due to the oxygen-scavenging effect of yttrium by the formation of Y₂O₃, the concentration of internal oxygen in the matrix of TiAl introduced during EPM processing was decreased, especially for the 0.6 at%Y-added alloy, and oxidation resistance of the alloys was improved.
- (3) The structures of the scales were modified by Y-additions. A transitional Y-rich subscale adjacent to the substrate and a mixed scale with a considerable amount of α-Al₂O₃ oxides in the intermediate layer underneath TiO₂ crystals were formed in the Y-added alloys. Mo was enriched in the Ti₃Al oxide layer. The formation of the (Y, Al)O-type oxides was correlated with improving the oxidation resistance of EPM TiAl-Mn-Mo-C alloys.

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