



Phase transformation behavior of alumina grown on FeAl alloys with reactive element dopants at 1273 K



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ABSTRACT

The short-term isothermal oxidation behavior of B2 FeAl alloys doped with different reactive elements (REs) at 1273 K was investigated. All the RE-doped alloys showed retarded phase transformation from θ - to α -Al₂O₃ as compared to the RE-free alloy. The Y- and La-doping even led to much lower transformation rate than the Hf-, Zr- and Ce-doping. The effect mechanism associated with RE ion size and valence on the phase transformation of alumina was discussed. The additions of RE ions which have large size and matched valence with Al ions could be anticipated to inhibit the transformation more effectively and the combined effects of retarding θ - α phase transformation, promoting α phase nucleation and suppressing Al outward diffusion produced by RE doping might provide FeAl with improved oxidation property.

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1. Introduction

Iron aluminides have been widely documented as one important part of structural materials for commercial applications at temperatures up to 1073 K over the past few decades [1–3]. Recently, B2 FeAl intermetallic compound containing 35–50 at.% Al has attracted increasing attentions mainly due to its excellent isothermal oxidation resistance at temperatures up to 1473 K, low density with respect to steels or Ni-based alloys and relatively low cost, and these combined advantages have led to potential applications as oxidation-resistant coatings at higher temperatures than 1073 K in various industrial fields such as electric power generating and aero-engine manufacturing [2–7]. It is recognized that the satisfying oxidation performance of FeAl is attributed to its ability to form a dense and continuous alumina scale above 1173 K which benefits from high Al concentration [8,9]. However, the oxide scale grown on FeAl spalls readily during thermal cycling probably due to its weak adhesion to the underlying alloy caused by the growth of voids beneath the scale and rumpling of the scale, which is an obstacle to its widescale application [10,11].

To improve oxide scale adhesion of FeAl alloys, REs such as Hf, Zr, Y, La, and Ce which have stronger oxygen affinity than Al were

doped in FeAl and cyclic oxidation testing results indicated that minor RE doping not only improved the oxide scale adhesion but also reduced the scale growth rate [12,13]. Attempts have also been made to clarify this beneficial RE effect (REE) on the cyclic oxidation resistance of FeAl and a standard list of proposed mechanisms includes (1) a suppression of scale/alloy interfacial void growth by weakening the “sulfur effect” [12,14,15], (2) an alleviation of scale rumpling by “softening” the alloy and dissipating strain energy in the scale through alloy deformation [13,16], (3) a mechanical interlocking of the scale by “pegs” formed at the scale/alloy interface [12,17,18], and (4) a modification of cation transport process by the “blocking effect” [10,19]. Based on the above analysis, most attentions have been focused on the mechanism exploration of REE on the spallation resistance and growth rate of alumina in the last few decades. However, no single proposed mechanism can essentially explain all of experimental observations. Recently, phase transformation behavior of alumina was mentioned in several studies and results revealed that different types of alumina had distinct crystal structures and growth rates during oxidation [20–24], thus the effect of REs on the phase transformation behavior of alumina might directly affect the oxidation performance of FeAl.

Transient oxidation of alumina-forming alloys typically occurs at the temperature range of 1173–1373 K [21,25]. In the early stage of oxidation, the metastable θ -Al₂O₃ is formed on the alloy surface, and then transforms into α -Al₂O₃ which is the only

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thermodynamically stable phase of alumina. Previous studies showed that the phase transformation behavior of alumina was significantly influenced by RE additions. For instance, RE-doping such as Zr, Y and La was believed to slow down the transformation, but contradictory results associated with Y and Ce-doping were also reported as they accelerated the transformation due to the promotion of α -Al₂O₃ nucleation [9,26]. Since cubic θ -Al₂O₃ has substantially higher growth rate than α -Al₂O₃ with a hexagonal structure, promoting the transformation could be beneficial to the reduction in oxide scale growth rate [22,23,27,28]. However, the evolution of crystal structure during transformation is usually accompanied with 13.4% volume contraction, and accelerated transformation might induce the formation of cracks in the scale which is detrimental to the protection of the underlying alloy [29]. The existence of the above puzzling dilemma reflects that the effect mechanism of REs on θ - α phase transformation is not yet clarified. Besides, no efforts are made to compare the capabilities of affecting θ - α phase transformation between different REs as quantifying the REE is rather difficult.

In the present work, FeAl alloys doped with different REs including Hf, Zr, Y, La, and Ce were produced by arc-melting. The isothermal oxidation test at 1273 K was performed, aiming to investigate the roles of different REs in affecting the phase transformation behavior of alumina and to establish some fundamental understanding of those factors affecting the strength of REE.

2. Experimental details

B2 FeAl alloys containing different REs were used as model alloys in this work. The nominal doping level was ascertained according to literature values to ensure that each RE had an appropriated concentration [8,10,16–19,21–31]. Since RE atoms entering the FeAl lattice preferentially occupy Al lattice sites [32], the chemical compositions of model alloys were designed as Fe-40Al, Fe-39.9Al-0.1Hf, Fe-39.9Al-0.1Zr, Fe-39.9Al-0.1Y, Fe-39.9Al-0.1La, and Fe-39.9Al-0.1Ce (in at.%), respectively. High purity iron, aluminum and reactive elements (Hf, Zr, Y, La, and Ce) were employed as starting materials. All the alloy ingots were produced by arc-melting and casting in argon atmosphere. Each ingot was melted four times to guarantee sufficient alloying and subsequently annealed at 1373 K for 24 h also in argon atmosphere to realize homogenization. Table 1 lists the actual chemical compositions of the as-annealed alloys. Specimens for isothermal oxidation testing were cut from the ingots into 15 × 10 × 3 mm³, ground to an 800-grit SiC finish and ultrasonically cleaned in alcohol and acetone, respectively.

Isothermal oxidation test at 1273 K was conducted in a tube-type air furnace equipped with an automation system to realize the specimens moving in and out of the furnace automatically. Each specimen was hung in a pre-annealed alumina crucible to avoid direct contact with furnace walls. After desired oxidation time, the specimens were taken out of the furnace and cooled in air for phase identification and morphology characterization.

The phases of the oxide scales were identified by luminescence spectra excited by a probing argon-ion laser (RM2000, Renishaw). It is reported that the spectrum peaks of θ -Al₂O₃ were at frequencies of 14575 and 14645 cm⁻¹, and those of α -Al₂O₃ were at frequencies of 14402 and 14432 cm⁻¹ [29]. During the measurement, the laser beam from the argon-ion laser was focused on the selected region of the oxide scale through objective lens. The luminescence arose from Cr ions which are inevitable impurities incorporated into the alumina scale during oxidation. Since the luminescence spectra from Cr ions in θ - and α -Al₂O₃ were distinct from each other, different polymorphs of Al₂O₃ can be distinguished by their respective spectra. After excited by the laser beam, the

Table 1

Actual chemical compositions of the as-annealed FeAl alloys determined by inductively coupled-plasma analysis (in at.%).

	Fe	Al	Hf	Zr	Y	La	Ce	Cr (ppm)
FeAl	Bal.	39.46	–	–	–	–	–	87
FeAl-Hf	Bal.	39.21	0.10	–	–	–	–	120
FeAl-Zr	Bal.	39.35	–	0.10	–	–	–	98
FeAl-Y	Bal.	39.74	–	–	0.09	–	–	73
FeAl-La	Bal.	38.80	–	–	–	0.09	–	76
FeAl-Ce	Bal.	39.41	–	–	–	–	0.09	62

luminescence spectra were gathered through the same lens and recorded. The surface morphologies of the oxide scales were characterized by a field emission-scanning electron microscopy (FE-SEM, S4800, Hitachi) equipped with an energy dispersive X-ray spectrum (EDXS).

3. Results and discussion

3.1. Oxide phase identification

After isothermal oxidation testing, phases of the oxide scales formed on the RE-doped and undoped FeAl samples were clearly identified. Fig. 1 shows the luminescence spectra obtained from the oxide scales after desired oxidation time. Since the corresponding frequencies of spectrum peaks of different aluminum oxides can be distinguished from each other, the appearance of unique spectrum peaks can directly corroborate the existence of corresponding aluminum oxide. It is obvious that both transient θ -Al₂O₃ and stable α -Al₂O₃ peaks appeared on all the samples after 2 h exposure, which indicates that the phase transformation from θ -to α -Al₂O₃ was just in progress. For the undoped sample, θ -Al₂O₃ peaks sharply decreased with increased oxidation time and only α -Al₂O₃ peaks were found after 10 h oxidation (Fig. 1a), revealing an accomplished transformation. Similar phenomenon was also observed on the 0.1 at.% Hf doped sample (Fig. 1b). However, it is believed that Hf doping substantially retarded the transformation as the fraction of θ -Al₂O₃ on the Hf-doped sample after 2 h exposure was higher than that on the undoped one which is inferred from higher peak intensity ratio of θ - and α -Al₂O₃ on the Hf-doped sample as shown in Fig. 1a–b.

Different from the above two samples, θ -Al₂O₃ peaks were still detected on the 0.1 at.% Zr doped sample after 10 h oxidation despite their much lower intensity as compared to α -Al₂O₃ peaks (Fig. 1c), which demonstrates that the addition of Zr produced a stronger effect on inhibiting the transformation than Hf addition. The additions of 0.1 at.% Y, 0.1 at.% La and 0.1 at.% Ce also led to pronounced peak position distribution similar to Zr addition did after 10 h exposure (Fig. 1d–f). However, it should be noted that the peak intensity ratios of θ - and α -Al₂O₃ on the Y- and La-doped samples were much higher than that on the Zr-doped one, especially the La-doped sample, on which the peaks of θ -Al₂O₃ still existed even after 20 h oxidation, representing the lowest transformation rate among the RE-doped alloys. With exposure time prolonging to 30 h, only α -Al₂O₃ peaks were observed and all the alloys had completed the transformation. From these results, it can be supposed that the phase transformation of alumina was intimately related to the alloy composition and the above REs played different roles in affecting the θ - α phase transformation rate.

3.2. Surface morphology characterization

To further investigate the development of oxide scales and analyze the difference in the phase transformation of alumina

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