

Effect of rare earth Y on oxidation behavior of NiAl–Al₂O₃

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Abstract: In-situ NiAl–Al₂O₃ and Y-doped NiAl–Al₂O₃ were fabricated by mechanical alloying (MA) and pulse current auxiliary sintering (PCAS). The isothermal and cyclic oxidations were carried out at 1 000 °C in order to investigate the influence of Y on the oxidation behaviors of NiAl–Al₂O₃. The results indicate that the addition of Y does not change the oxidation product of NiAl–Al₂O₃ and the α -Al₂O₃ scale is detected on the surface of NiAl–Al₂O₃ and NiAl–Al₂O₃–Y after isothermal oxidation. The addition of Y changes the morphologies of the scale during isothermal oxidation and leads to the disappearance of the ridge structures. Meanwhile, the mass gain of NiAl–Al₂O₃–Y is much lower than that of NiAl–Al₂O₃. During cyclic oxidation, the cracking and spallation, which were observed in the scale of NiAl–Al₂O₃, are eliminated with the addition of Y because the θ – α transformation of Al₂O₃ is retarded and the formation of voids and cracking are reduced.

Key words: NiAl; oxidation resistance; rare earth Y

1 Introduction

Due to its high melting point, low density and good oxidation resistance, β -NiAl is thought as the promising candidates for high-temperature structural applications [1–2]. Nevertheless, its practical applications are limited due to the inherent low creep resistance and poor ambient temperature ductility [1–2]. Considerable attempts have been carried out to address these problems, such as grain refinement [3–4] and micro- or macro-alloying by adding Fe, Nb, Mo, etc [3]. Another feasible approach is to prepare oxide-dispersion strengthened (ODS) NiAl composite through mechanical alloying (MA) [5–7]. These ODS NiAl exhibits a significant improvement in mechanical properties, including room-temperature compressive ductility and high-temperature strength [8–9]. Among these dispersoids, the Al₂O₃ dispersoid is thought to be a suitable reinforcement because of its combination of low density, high specific strength, high modulus and excellent chemical stability [10].

For high-temperature materials, oxidation resistance is another important factor that determines the practical application. However, some researchers recently reported that the oxide scale of NiAl–Al₂O₃ suffered from serious cracking and spallation, which were harmful to the

oxidation resistance. It is well-known that grain refinement is conducive to improve the oxidation resistance of alloys because it can improve the adhesion of the oxide scale by relieving the growth stress and thermal stress [11]. For NiAl-based materials, however, it is difficult to reduce the grain size by conventional mechanical deformation or heat treatment [12]. Additionally, some researchers suggested that alloying is an effective way to improve the anti-oxidation property of NiAl-based materials. These reactive elements such as Y, Ce and Hf could eliminate or relieve the cracking and spallation during oxidation because it could affect the growth mechanisms of Al₂O₃ [13].

In this study, in order to improve the practical application of NiAl–Al₂O₃, NiAl–Al₂O₃ and NiAl–Al₂O₃–Y were fabricated by mechanical alloying and subsequent consolidation. Their oxidation resistances were evaluated through isothermal and cyclic oxidation, with a particular emphasis on the influence of Y on their oxidation resistance of NiAl–Al₂O₃.

2 Experimental

The bulk materials were fabricated through a powder metallurgy route consisting of mechanical alloying and subsequent consolidation. Ni (99.9% of mole fraction, 20 μ m) and Al (99.9%, mole fraction,

25 μm) were used as raw materials. Powders were mixed according to the nominal composition of NiAl-10%Al₂O₃ (volume fraction) and milled at a rotation speed of 300 r/min with a ball-to-powder mass ratio of 10:1. Reactant powders were milled under argon atmosphere for 2 h, followed by 20 h milling in air. After milling, part of the milled powders were mixed with 0.2% Y (mass fraction) (95.7% of mole fraction, 20 μm) and then the mixed powders were milled at a rotation speed of 100 r/min for 24 h under argon atmosphere. Sintering was conducted in a ZLY-60 pulse current auxiliary sintering furnace under a load of 50 MPa. The powders were heated to 1 200 °C with a heating rate of 120 °C/min in vacuum ($\sim 1.3 \times 10^{-2}$ Pa). The temperature and pressure were held constant for 5 min, followed by furnace cooling.

Test specimens with the dimensions of 8 mm×6 mm×13 mm were cut by electro-discharge machining (EDM) for isothermal and cyclic oxidation. Prior to oxidation, all surfaces of the specimens were mechanically polished with 2.5 μm -diamond paste and then ultrasonically cleaned in ethanol. Isothermal and cyclic oxidation were conducted at 1 000 °C in the muffle furnace in air. During isothermal and cyclic oxidation, the specimens were given a total exposure for 24 h and 50 h (25 cycles), respectively. The test cycle involved exposing the specimens in furnace for 1 h, cooling quickly to room temperature, weighing and returning to the muffle furnace. Mass variations were evaluated before and after oxidation by using a Sartorius BS124S analysis balance. The data were normalized per unit area (square centimeter). Before and after oxidation, the test specimens were inspected by SEM (FEI QUANTA 200F) and X-ray diffraction (XRD).

3 Results and discussion

3.1 Microstructure and compositions of sintered compacts

After the initial 2 h of milling under argon atmosphere, subsequent milling was carried out in air and the ultra fine Al₂O₃ dispersoids were in-situ formed by the reaction of oxygen and residual Al. Figure 1 shows the XRD patterns of milled powders. It can be seen that the milled powders are composed of NiAl and Al₂O₃. The XRD results indicate that the diffraction peaks of Y are not detected. This is because the mass fraction of Y is only about 0.2%, which is much lower than the detection limit of XRD method. Figure 2 exhibits the BSE images of sintered compacts. The addition of Y is not found to have obvious effect on the microstructures of NiAl-Al₂O₃ composite. The EDS results reveal that, the bright area and dark area of Fig. 2(a) are composed of 50.22Ni-49.78Al and 30.24Ni-

49.72Al-21.04O (mole fraction, %), respectively, while the bright area and dark area of Fig. 2(b) are composed of 50.38Ni-49.62Al and 32.43Ni-50.54Al-17.03O (mole fraction, %) respectively. Thus, it can be deduced that the bright areas of Figs. 2(a) and (b) are both composed of

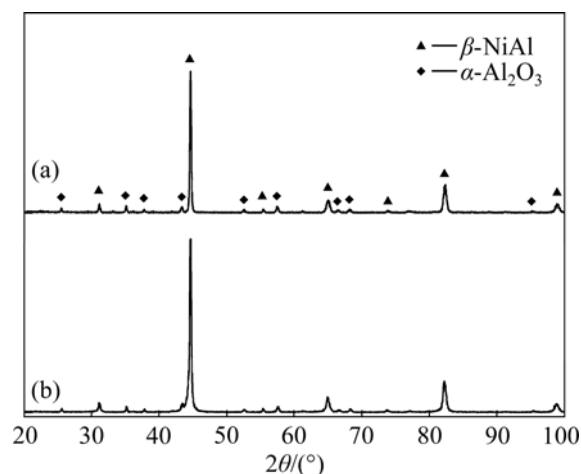


Fig. 1 XRD patterns of sintered compacts: (a) NiAl-Al₂O₃; (b) NiAl-Al₂O₃-Y

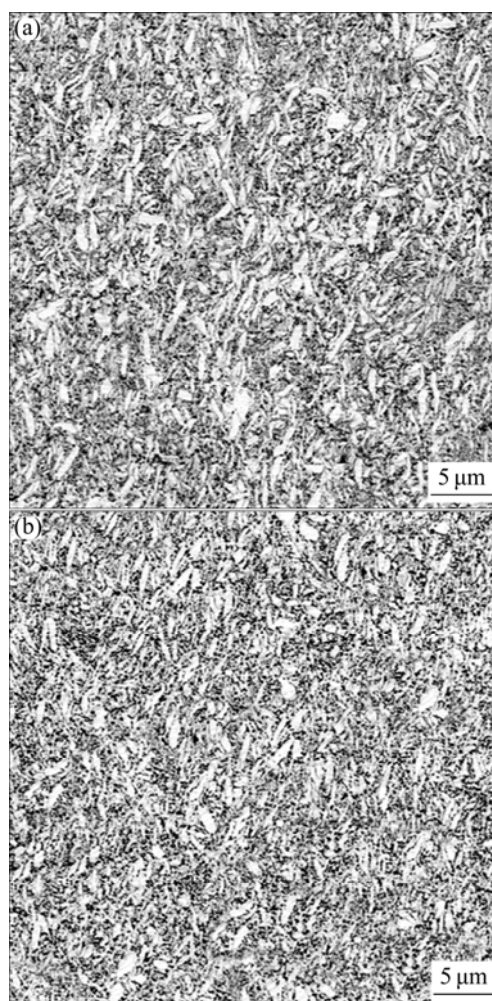


Fig. 2 BSE images of sintered compacts: (a) NiAl-Al₂O₃; (b) NiAl-Al₂O₃-Y

NiAl, while the dark areas are composed of NiAl and Al_2O_3 . Previous researches have revealed that Y is found to segregate along the grain or phase boundaries [14–17].

3.2 Isothermal oxidation

The relationship between mass gain and time of NiAl- Al_2O_3 and NiAl- Al_2O_3 -Y is described in Fig. 3. As the oxidation time increased, the mass of the test specimens increased monotonically during oxidation. In the initial few hours of oxidation, the mass of test specimens increased rapidly. In the later stage of oxidation, the oxidation rate slowed down and the mass gains were found to follow the familiar parabolic oxidation rate law. BRUMM et al [18] has reported that the higher oxidation rate of the initial stage of oxidation was caused by the formation of rapid-growing metastable aluminas. In the later stage of oxidation, these metastable aluminas were transformed to protective α - Al_2O_3 and consequently led to the decrease of oxidation rate [19]. Moreover, it could be noted that the mass gain of NiAl- Al_2O_3 -Y is much lower than that of NiAl- Al_2O_3 , which indicates that its scale formed is much more protective than NiAl- Al_2O_3 .

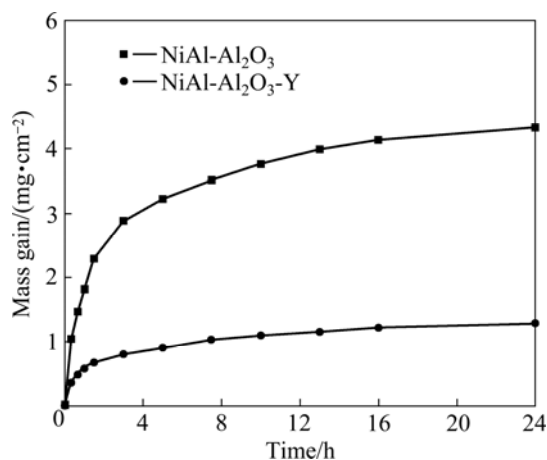


Fig. 3 Mass gain vs time curves during isothermal oxidation

Figure 4 shows the XRD patterns of the scales formed on NiAl- Al_2O_3 and NiAl- Al_2O_3 -Y after 24 h of isothermal oxidation at 1 000 °C. As can be seen, the oxide detected in the oxide scale is α - Al_2O_3 . Thus, the addition of Y does not change the oxidation products of NiAl- Al_2O_3 . Moreover, the diffraction peaks of NiAl are also observed in the XRD results since the X-ray can easily pass through the thin scale and be diffracted by the matrix. Furthermore, it can be noted that the NiAl- Al_2O_3 -Y has a higher intensity of NiAl diffraction peaks, which indicates that more matrix was detected. Thus, it can be deduced that the oxide scale of NiAl- Al_2O_3 -Y is much thinner than that of NiAl- Al_2O_3 , which is in accordance with mass gain curves.

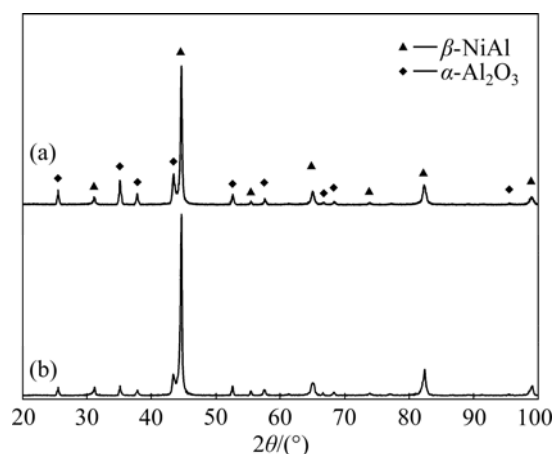


Fig. 4 XRD patterns of test specimens after 24 h of isothermal oxidation: (a) NiAl- Al_2O_3 ; (b) NiAl- Al_2O_3 -Y

Figure 5 presents the morphologies of the scales formed on NiAl- Al_2O_3 and NiAl- Al_2O_3 -Y during isothermal oxidation. In the initial stage of oxidation, some blade-like morphology appeared in the scales of both NiAl- Al_2O_3 and NiAl- Al_2O_3 -Y. Previous researches have demonstrated that these blade-like morphologies are metastable θ - Al_2O_3 [20]. With the increase of oxidation time, the θ - Al_2O_3 was transformed to α - Al_2O_3 and led to the disappearance of blade-like morphology. Moreover, it could be noticed that the characteristic ridge structure, which was usually observed in the NiAl alloys, appeared at the air/scale interface after a few hours of oxidation. According to Refs. [9, 21], these ridges are the intrinsic ridges which are formed as a result of the outward diffusion of Al. With the increase of oxidation time, the ridge structures of NiAl- Al_2O_3 became rough and close-packed, while the ridge structures of NiAl- Al_2O_3 -Y gradually disappeared through the lateral growth of these ridge structures. This is because the addition of Y changed the growth mechanism of α - Al_2O_3 scale. Previous research has revealed that the α - Al_2O_3 scale of NiAl was observed to grow by a mixed diffusion mode involving simultaneous Al and O transport, while the α - Al_2O_3 scale of Y-doped NiAl was observed to grow mainly by the inward diffusion of O [22]. With the addition of Y, the outward diffusion of Al was reduced and the growth of ridge structure was suppressed.

Figure 6 shows the photos of test specimens after 24 h of oxidation at 1 000 °C. Dense scales are observed on the surface of test specimens. Some serious crackings are observed in the scale of NiAl- Al_2O_3 (Fig. 6(a)). The oxide scale of NiAl- Al_2O_3 is detached from the matrix by these cracks and consequently leads to a higher mass gain. However, with the addition of Y, the cracks and detachment are not observed in the scales of NiAl- Al_2O_3 -Y.

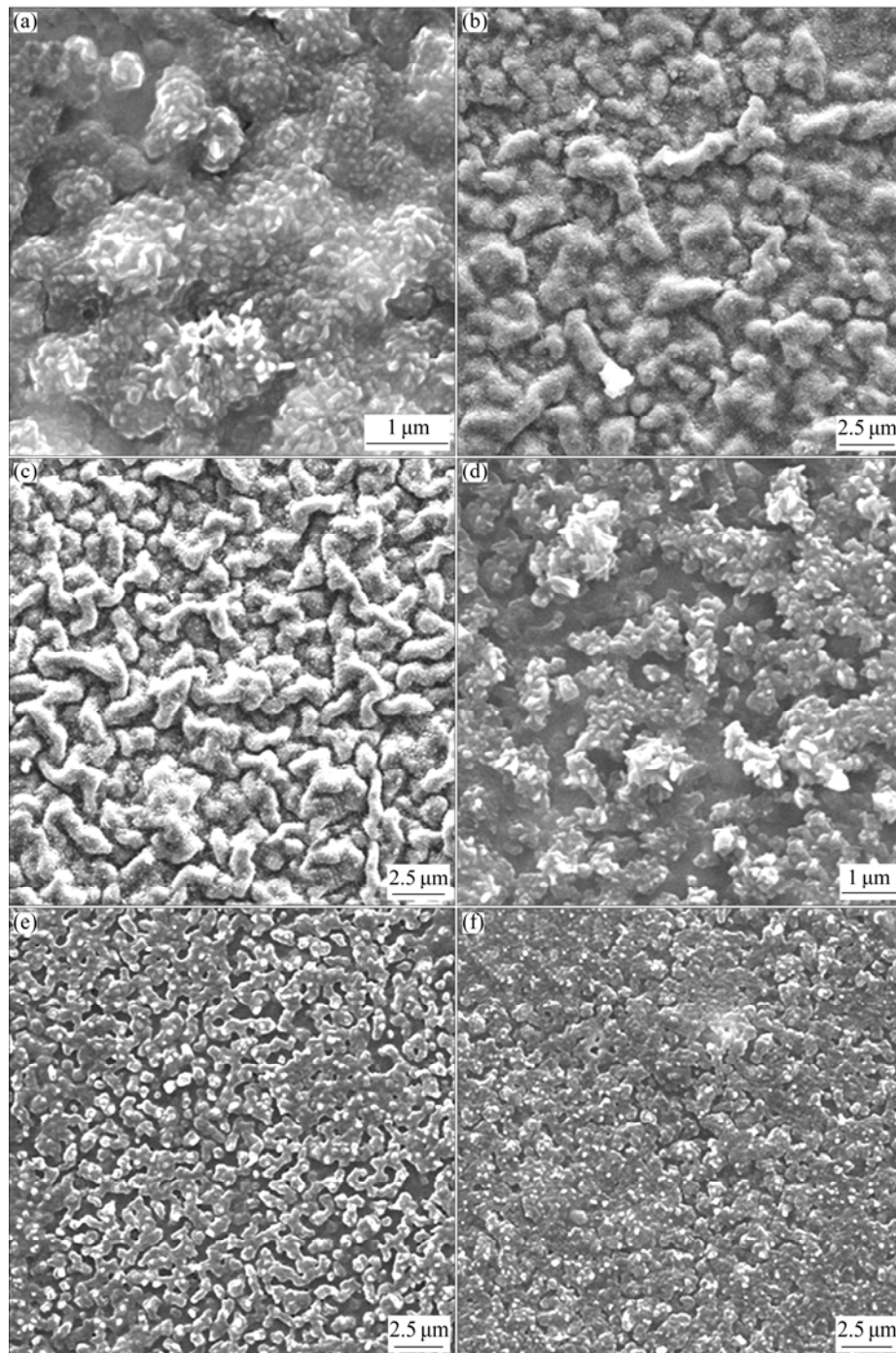


Fig. 5 Top view of scale morphologies of test specimens after isothermal oxidation at 1 000 °C: (a) NiAl-Al₂O₃, 1 h of oxidation; (b) NiAl-Al₂O₃, 5 h of oxidation; (c) NiAl-Al₂O₃, 24 h of oxidation; (d) NiAl-Al₂O₃-Y, 1 h of oxidation; (e) NiAl-Al₂O₃-Y, 5 h of oxidation; (f) NiAl-Al₂O₃-Y, 24 h of oxidation

3.3 Cyclic oxidation

Figure 7 presents the mass gain vs time curves of the NiAl-Al₂O₃ and NiAl-Al₂O₃-Y during cyclic oxidation. For the NiAl-Al₂O₃, mass loss was observed after several cycles of oxidation, with clear evidence of serious scale spallation. However, such a mass loss was not observed in the test specimens of NiAl-Al₂O₃-Y, which indicates that the addition of Y significantly

improved the anti-spallation property of the scale of NiAl-Al₂O₃.

Figure 8 presents the morphologies of the scales that formed on NiAl-Al₂O₃ and NiAl-Al₂O₃-Y after 50 h (25 cycles) of cyclic oxidation. Serious spallation and cracking were observed in the scale of NiAl-Al₂O₃ (Fig. 8(a)). Due to the spallation of scale, the substrate was totally exposed to the air and consequently led to the

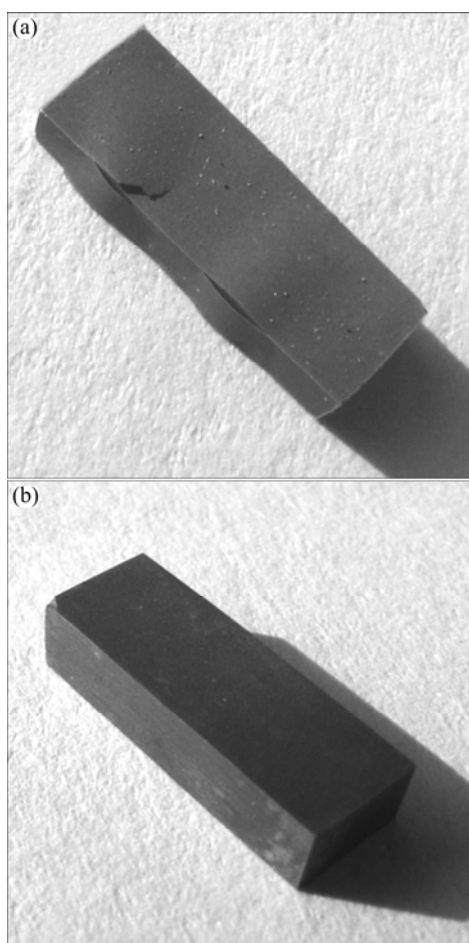


Fig. 6 Photos of test specimens after 24 h of isothermal oxidation at 1 000 °C: (a) NiAl-Al₂O₃; (b) NiAl-Al₂O₃-Y

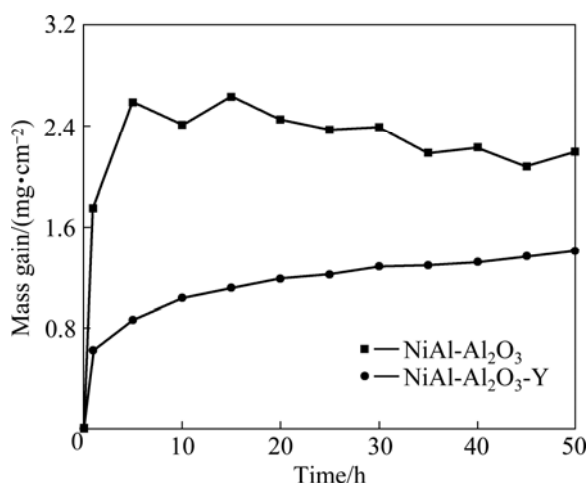


Fig. 7 Mass gain vs time curves during cyclic oxidation

secondary oxidation of the substrate. As seen in Fig. 8(c), the substrate beneath the scale was seriously oxidized and a lot of pores were observed. These pores reduced the contact between the oxide scale and matrix, and further weakened the oxidation resistance of NiAl-Al₂O₃.

Thus, the scale was found to spall from the matrix (Fig. 8(e)). As can be seen in Fig. 8(b), the oxide scale of NiAl-Al₂O₃-Y displayed superior adhesion during cyclic oxidation. Dense and continuous scale was formed after oxidation. Microstructure observation shows that equiaxed α -Al₂O₃ was the dominant oxide. Meanwhile, some blade-like θ -Al₂O₃ were also observed (Fig. 8(d)). Figure 8(f) shows the cross-section of the scale formed on NiAl-Al₂O₃-Y and it can be seen that the oxide scale is in good contact with the matrix and no void was observed along the matrix/scale interface.

Cracking and spallation are the main modes that weaken the protective properties of the scale because they can expose the sub-surface of the matrix to the atmosphere and lead to secondary oxidation. For NiAl-based materials, the cracking of scale is mainly caused by two factors, thermal stress and θ - α transformation of Al₂O₃. During cooling, due to the mismatch of the coefficients of thermal expansion, there is a large thermal stress between the scale and the matrix, which can induce cracking in cyclic oxidation. Moreover, during oxidation, the initially formed θ -Al₂O₃ is gradually transformed to stable α -Al₂O₃. The phase transformation of Al₂O₃ results in a volume reduction of 8.3% in the scale and consequently leads to emerge of cracking [23]. Spallation of scale is caused by the cracking and the formation of voids. During oxidation, the stable α -Al₂O₃ scale forms through a mixed diffusion mode involving simultaneous outward diffusion of Al and inward diffusion of O [24]. The consumption of Al near the matrix/scale interface causes Ni diffusion to the bulk to compensate for the Al depletion and consequently leads to the formation of voids along the matrix/scale interface [25]. These voids reduce the contact between the scale and matrix and weaken the adhesion of the scale [25].

In order to be protective, the scale formed on the high-temperature structural material should be dense, slow-growing and, above all, adherent [26]. Thus, it is so encouraging that the adhesion of the α -Al₂O₃ scale is found to be significantly improved by the addition of Y. The role of Y on the oxidation behavior of NiAl-based materials has been investigated [9]. It is reported that Y could stabilize the fast growth of metastable alumina and augment the transformation period of metastable alumina phase to α -Al₂O₃, which decreases the possibility of cracking in the scale. Moreover, with the addition of Y, the outward diffusion of Al is suppressed [14, 16]. The scale is observed to grow mainly by the inward diffusion of O and new oxides preferentially form at the scale/substrate interface [23]. Thus, the void, which is caused by the outward diffusion of Al, is reduced or even eliminated in the scale of NiAl-Al₂O₃-Y, as seen in Fig. 8(f).

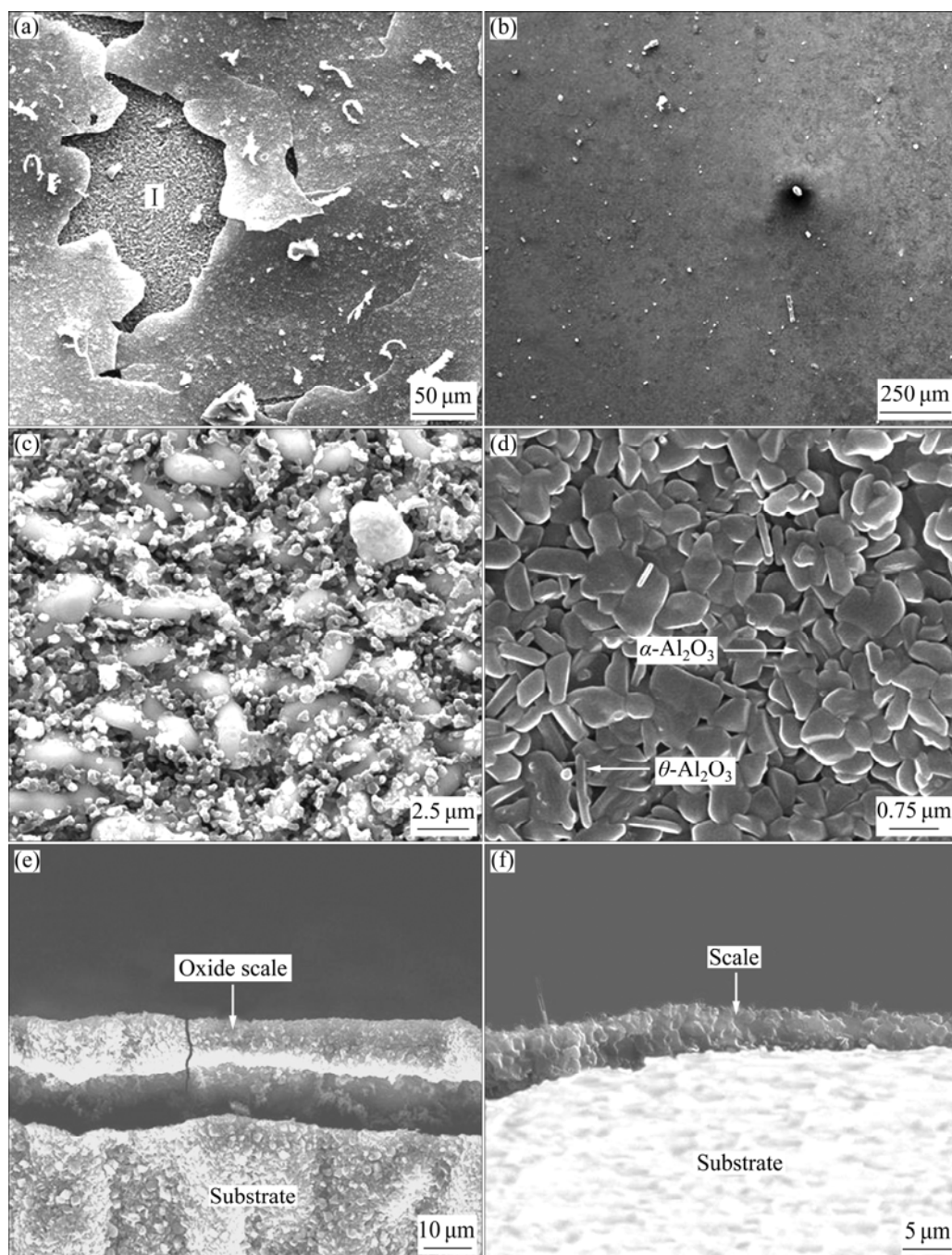


Fig. 8 Morphologies of oxide scale after 50 h (25 cycles) of cyclic oxidation: (a) Top view of scale formed on NiAl-Al₂O₃; (b) Top view of scale formed on NiAl-Al₂O₃-Y; (c) Magnification of site I in (a); (d) Magnification of (b); (e) Cross-section of scale formed on NiAl-Al₂O₃; (f) Cross-section of scale formed on NiAl-Al₂O₃-Y

4 Conclusions

1) α -Al₂O₃ scale is formed after isothermal oxidation at 1 000 °C and the addition of Y is not found to have influence on the oxidation product of NiAl-Al₂O₃. With the addition of Y, the mass gain during oxidation is greatly reduced.

2) Ridge structures appear after a few hours of

oxidation at 1 000 °C. During subsequent oxidation, the ridges become rough and close-packed in the scale of NiAl-Al₂O₃, while the ridges of NiAl-Al₂O₃-Y gradually disappear with the increase of oxidation time.

3) During cyclic oxidation, the scale of Y-doped NiAl-Al₂O₃ displays favorable adhesion. This is because Y can retard the θ - α transformation of Al₂O₃ and decrease the formation of voids and cracking.

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稀土元素 Y 对 NiAl- Al_2O_3 抗氧化性能的影响

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摘 要: 为考察稀土元素 Y 对 NiAl- Al_2O_3 抗氧化性能的影响, 通过脉冲电流辅助烧结(PCAS)制备了 NiAl- Al_2O_3 和 NiAl- Al_2O_3 -Y 块体材料, 并在 1 000 °C 下测试了材料的恒温氧化和循环氧化性能。结果表明, 稀土元素 Y 对 NiAl- Al_2O_3 的氧化产物没有影响。恒温氧化后, NiAl- Al_2O_3 和 NiAl- Al_2O_3 -Y 表面都形成一层 α - Al_2O_3 氧化膜。Y 的添加改变了氧化膜的形貌并造成了屋脊状形貌的消失。此外, NiAl- Al_2O_3 -Y 的质量增加也明显较少。在热循环测试中, NiAl- Al_2O_3 -Y 的氧化膜中没有观察到 NiAl- Al_2O_3 中常见的裂纹和剥离现象, 这是由于 Y 能够阻碍 Al_2O_3 的 θ - α 转化并减少空洞的形成所造成的。

关键词: NiAl; 抗氧化性能; 稀土元素 Y

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