High temperature oxidation behavior of aluminide on a Ni-based single crystal superalloy in different surface orientations

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Received 18 November 2013; accepted 26 January 2014
Available online 19 April 2014

Abstract
An investigation on oxidation behavior of coated Ni-based single crystal superalloy in different surface orientations has been carried out at 1100 °C. It has been found that the {100} surface shows a better oxidation resistance than the {110} one, which is attributed that the {110} surface had a slightly higher oxidation rate when compared to the {100} surface. The experimental results also indicated that the anisotropic oxidation behavior took place even with a very small difference in the oxidation rates that was found between the two surfaces. The differences of the topologically close packed phase amount and its penetration depth between the two surfaces, including the ratio of α-Al2O3 after 500 h oxidation, were responsible for the oxidation anisotropy.

Keywords: Ni-based superalloy; Oxidation behavior; Microstructure; Aluminide coating; Crystallographic orientation

1. Introduction
Ni-based single crystal superalloys have been widely used in the industrial gas turbines and jet engines. The materials with superior properties such as mechanical strength and oxidation resistance are required for high temperature applications [1–3]. Recently, the surface operating temperatures of gas-turbine blades could reach 1200 °C or even higher. It has been reported [4,5] that high operating temperature motivates the degradation of superalloys during service with respect to oxidation or corrosion. More importantly, the oxidation behavior of materials becomes one of the predominant life-limiting factors for high temperature applications.

Aluminide coatings have been applied on the surface of Ni-based superalloys by the pack aluminizing process [6]. Many investigators have reported [6–11] that there are two types of aluminizing treatments, known as (1) high-temperature low-activity (HTLA) [6–9] and (2) low-temperature high-activity (LTHA) [6,7,10,11] processes. The difference between the two types depends upon the temperature of aluminizing and the activity of the pack used. However, the interdiffusion of elements between the superalloy substrate and the coating layer takes place when coated specimens are thermally exposed at high temperatures, resulting in a change in the microstructure of the substrates such as the formation of topologically close packed (TCP) [12]. Furthermore, the crystallographic orientation effect is one of the interesting subjects in Ni-based single crystal superalloys. It is well known that the mechanical properties of Ni-based single crystal superalloys are influenced by the crystallographic orientation of the surface of the specimen [13]. To date, the investigators have not paid much attention to the effect of crystal orientation on the oxidation behavior of alloys. From this point of view, the objective of the present work was to investigate the oxidation behavior of coated Ni-based single crystal superalloy in different surface orientations.
behavior characteristics of a coated Ni-based single crystal superalloy at high temperature with different surface orientations by using a variety of orientation and characterization tools such as the Laue technique, isothermal oxidation kinetics, optical and scanning electron microscopy (SEM).

2. Experimental procedures

A Ni-based single crystal superalloy, CM186LC was employed as an experimental material for the present study. The chemical composition of the superalloy in mass% was 5.74 Al, 0.73 Ti, 6.0 Cr, 9.3 Co, 0.5 Mo, 1.4 Hf, 3.4 Ta, 2.9 Re, 8.3 W, 0.07 C and balance Ni. A cylindrical rod of CM186LC was directionally solidified in the [001]-direction. The rod was solution heat-treated at 1274 °C for 8 h followed by gas fan cooling. A two-step aging treatment was then carried out at 1080 °C for 4 h and at 871 °C for 20 h before finally cooled down by an air cooling. The principal oxidation surfaces of single-crystal samples were identified to be within 4° of the desired orientations using the Laue technique. The specimens were cut from the rod along the {100} and {110} surfaces with the dimension of 10 mm in length, 5 mm in width and 3.5 mm in thickness using an electrodischarge machine (EDM). Prior to aluminizing treatment, the specimens were mechanically polished down to 1200-grit SiC paper, degreased in alcohol, ultrasonically cleaned in alcohol and finally dried in air.

In the present study, the specimens were coated by the pack aluminizing process. The HTLA process was used in preparing the aluminide coating. The specimens were then embedded in an Al2O3 retort containing a mixture of 24.5 Al, 24.5 Cr, 49.0 Al2O3 and 2.0 NH4Cl powders (all in mass%) and heated at 1000 °C for 5 h in argon atmosphere. All the coated specimens were subjected to isothermal oxidation in air at 1100 °C for 500 h. The specimens were then detached and weighed after varied oxidizing periods of 25, 50, 100, 200 and 500 h. The oxidation kinetics was determined through the relationship between mass gain and oxidation time. The mass gains were measured using an electrobalance that had a precision of 0.1 mg after the specimens were air cooled to room temperature.

The initial microstructure of the Ni-based single crystal superalloy was observed by optical microscopy (OM). The formed oxide phase on the surface of the superalloy after oxidation was identified by X-ray diffraction (XRD) using Cu Kα radiation. The outer surfaces and cross sections through the oxidized specimens were observed using SEM investigations. The chemical composition of the oxide scale-to-substrate regions after oxidation was determined by the energy-dispersive X-ray analyzer (EDX), which was attached to the SEM machine.

3. Results

3.1. Initial microstructure investigations

Fig. 1 shows (a) the optical (OM) and (b) SEM micrographs taken from the Ni-based single crystal superalloy surface before the aluminizing process. From Fig. 1a the γ'/γ two-phase structure can be easily observed, which has been usually found in the standard Ni-based single crystal superalloys. And Fig. 1b indicates that cuboidal γ' precipitates are regularly aligned along {001} during the aging treatment as a result of the elastic interaction between precipitates [14]. The SEM micrograph also confirms that the Ni-based single crystal superalloy contains about 70 vol% cuboidal γ' precipitates.

3.2. Microstructures of as-coated specimens

The microstructure of the as-coated surface of (a) {100} and (b) {110} specimens are shown in Fig. 2. It can be seen from Fig. 2 that the as-aluminized specimens consisted of the coating layer, a diffusion zone which is called as “interdiffusion zone (IDZ)”, and the substrate on both orientations. The formation of coating layer in a HTLA process is mainly due to the outward diffusion of Ni from the substrate and its reaction with aluminum available from the pack [15]. The formation of coating leads to the growth of a β-NiAl layer outward with regard to the initial substrate surface. Finally, the region under the initial surface of the substrate, which sustains the lack of Ni due to its outward diffusion, develops as the interdiffusion zone (IDZ) [10]. The IDZ thickness was circa 4.4 μm on {100} surface and about 4.7 μm on {110} surface.
3.3. Isothermal oxidation kinetics

Fig. 3 shows the isothermal oxidation kinetics curves of \{100\} and \{110\} coated specimens at 1100 °C. The change of mass gain with time indicated that the mass gain for both \{100\} and \{110\} coated surfaces increases significantly in the initial stages up to 100 h oxidation. Increasing the oxidation time (400 h and up to 500 h) at 1100 °C slightly increased the mass gain of the aluminized specimens in both \{100\} and \{110\} orientations. The recorded curves also indicate that the oxidation kinetics for the specimens at 1100 °C approximately followed a parabolic oxidation law. The parabolic rate constant, $K_p$, of the superalloy can be estimated by a linear least-squares algorithm from the following equation [16]:

$$\left(\frac{\Delta m}{A}\right)^2 = K_p t$$

where, $K_p$ is the parabolic rate constant and can be directly obtained by plotting the square of the mass gain (mg^2/cm^4) over exposure time. The $K_p$ values of the coated specimens recorded $1.11 \times 10^{-7}$ mg^2 cm^-4 s^-1 for \{100\} side-surface and $1.19 \times 10^{-7}$ mg^2 cm^-4 s^-1 for \{110\} side-surface. It is also noted that the oxidation rate of \{110\} surface was slightly higher than that of the \{100\} one, giving a strong indication on the occurrence of anisotropic oxidation behavior in the coated Ni-based single crystal superalloy.

3.4. X-ray diffraction (XRD) pattern

The XRD results of the surface of aluminized specimens after 25, 100, and 500 h oxidations at 1100 °C with different surface orientations are shown in Figs. 4–6, respectively. The oxide products formed on the aluminized specimens after oxidation for 25 h exhibited that the phases were mainly composed of \(\beta\)-NiAl accompanied with \(\theta\)-Al$_2$O$_3$ and \(\alpha\)-Al$_2$O$_3$ in both orientations (Fig. 4). After oxidation for 100 h, the diffraction peaks of \(\alpha\)-Al$_2$O$_3$ became stronger, whereas the peaks intensity of \(\theta\)-Al$_2$O$_3$ and \(\beta\)-NiAl were being weakened in both orientations (Fig. 5). Moreover after oxidation for 500 h, the diffraction peaks of \(\alpha\)-Al$_2$O$_3$ were further stronger than that obtained after 100 h. On the other hand, oxidation for 500 h led almost to the disappearance of the \(\theta\)-Al$_2$O$_3$ peaks, but
The β-NiAl phase was still detected on the coated specimen in both orientations as shown in Fig. 6.

3.5. Surface morphology

Fig. 7 shows the SEM micrographs for (a) {100} and (b) {110} surfaces of the coated specimens that were taken after 25 h oxidation at 1100 °C. Similar SEM micrographs were also imaged for (a) {100} and (b) {110} surfaces of the coated specimens after 100 h and 500 h oxidation at the same temperature of 1100 °C, as depicted in Figs. 8 and 9. All images show that the surface morphologies of the oxide scales grown on the coated specimens after the different oxidation periods. It is worth to mention that the initial stage of oxidation played an important role during overall oxidation process. It is seen from Fig. 7 that the platelet θ-Al₂O₃, which is named as metastable phase, was observed on the whole surface of the aluminized specimens with some amounts of equiaxed α-Al₂O₃ after oxidation for 25 h on both {100} and {110} surfaces. It is also seen from Fig. 8 that the θ-Al₂O₃ platelet was still found on the surface of the aluminized specimens, and the amount of equiaxed α-Al₂O₃ increased with increasing the exposure time of oxidation to 100 h. The increment of the amounts of α-Al₂O₃ revealed that the transformation from θ-Al₂O₃ to α-Al₂O₃ took place during the oxidation process. Further increasing the oxidation time to 500 h the scale morphology was primarily dominated by dense α-Al₂O₃ and remnant θ-Al₂O₃ locally existed in both {100} and {110} surfaces, as shown in Fig. 9. However, the {100} surface contained a higher percentage of α-Al₂O₃ than on {110} surface after all oxidation conditions. The high amount of α-Al₂O₃ is necessary to generate a better oxidation behavior of the superalloy. The details of α-Al₂O₃ percentage between the two surfaces are presented in Table 1.

3.6. Microstructures of oxidized specimens

The cross-sectional SEM images taken from the surface of (a) {100} and (b) {110} aluminized specimens after 25 h oxidation at 1100 °C are presented in Fig. 10. The same SEM micrographs were also collected of the surface of (a) {100} and (b) {110} aluminized specimens after 100 h and 500 h oxidation at the same temperature and the images are shown in Figs. 11 and 12, respectively. It is obvious from Fig. 10 that the diffusion zone formed during aluminizing treatment was
being extended on both \{100\} and \{110\} surfaces and a small amount of TCP phase as well as the presence of carbides were observed in the substrate. The microstructures after increasing the oxidation temperature to 100 h (Fig. 11) were found similar to those obtained after oxidation 25 h (Fig. 10). Meanwhile, the amount of TCP phases and carbides further increased with increasing oxidation time on \{100\} and \{110\} surfaces shown in Fig. 11. The TCP phases presented a typical preferable growth because it grew in a shape of cross-mark in \{100\} surface and in a shape of plus-mark in \{110\} surface. After 500 h oxidation, the amount of needle-like TCP precipitates was increased and its size became more lengthened compared to the previous ones obtained after shorter oxidation periods, as shown in Fig. 12. The chemical compositions of the scale-to-substrate regions in the coated specimens after oxidation for 500 h at 1100 °C on \{100\} and \{110\} surfaces were obtained and listed in Table 2.

4. Discussion

4.1. Oxidation kinetics

The results indicated that the kinetics curves of the coated specimens nearly followed the parabolic law. During the initial oxidation stage, the rates of the mass gains rapidly increased due to the formation of metastable $\theta$-$\text{Al}_2\text{O}_3$, which grew fast on the surface. The rates of the mass gain then decreased drastically when the phase transformation to thermodynamically stable and slowly growing $\alpha$-$\text{Al}_2\text{O}_3$ after oxidation for 100 h [17]. It was found that the phase transformation depends upon the temperature and the oxidation time. It was also observed during the transient stage that the oxidation rate was rapidly increased owing to the formation of $\theta$-$\text{Al}_2\text{O}_3$ [18]. Nevertheless, when the transformation from $\theta$-$\text{Al}_2\text{O}_3$ to $\alpha$-$\text{Al}_2\text{O}_3$ took place, the mass gain rates of the specimens obviously decreased. With increasing oxidation time, transient alumina such as $\theta$-$\text{Al}_2\text{O}_3$ transformed to $\alpha$-$\text{Al}_2\text{O}_3$, which
formed a continuous, stable, and protective oxide layer. When the protective alumina scale formed, the transport of Al to scale-gas interface can be precluded and resulted in hindering the formation of metastable $\theta$-Al$_2$O$_3$. As a consequence, the rate of mass gain rate was decreased due to the formation of protective alumina ($\alpha$-Al$_2$O$_3$). It also revealed that the mass gain rate was basically controlled by the growth of alumina scale.

4.2. Formation of oxide scale

The metastable $\theta$-Al$_2$O$_3$, which is formed in coated specimen during transient oxidation stage, is sometimes named as a transition alumina. The formation of such a metastable $\theta$-Al$_2$O$_3$ leads to a fast oxidation rate in the transient stage [18]. It has been also reported [19] that Cr presumably accelerates the initial growth of metastable alumina phase leading to rapid mass gains that occurs during the initial oxidation. The metastable $\theta$-Al$_2$O$_3$ will then transform with further oxidation time to $\alpha$-Al$_2$O$_3$ which is the only stable structure in this system. It can be proved that the oxide scale primarily composed of metastable $\theta$-Al$_2$O$_3$ phase with a small amount of stable $\alpha$-Al$_2$O$_3$ phase after 25 h oxidation. The amount of $\alpha$-Al$_2$O$_3$ increased with increasing the oxidation time. After 500 h oxidation, the $\alpha$-Al$_2$O$_3$ dominated on the surface of the coated specimens (Fig. 12). Here, the {110} surface produced a slightly higher amount of $\alpha$-Al$_2$O$_3$ than the {100} surface did, and a small amount of $\theta$-Al$_2$O$_3$ was still observed in both orientations. This means that the transformation of alumina phase from $\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ on {110} surface was slightly faster than that on {100} one.

It was also found that the amount of TCP phases increases with increasing oxidation time as can be seen from Figs. 10–12. This may be attributed to that exposing the coated specimens to high temperature environments and stress leads to the occurrence of an interdiffusion of elements between the single crystal substrate and the coating layer [20]. The outward diffusion of Ni from the substrate results in an enrichment of refractory elements and promotes the formation of TCP phases. The refractory elements such as Re, W, and Mo promote the precipitation of TCP phase [20]. The high amount of TCP phase will deteriorate the properties of Ni-based single crystal superalloys, including its oxidation behavior [21].

4.3. Anisotropic oxidation behavior

The oxidation rate on {110} surface was slightly higher than on {100} side-surface. The difference in $K_p$ value between the two surfaces was very small, which is possibly due to the loss
of Al concentration in the coating layer. The diffusion of Al from the coating layer into the substrate occurred during the isothermal oxidation test. Consequently, it reduced the Al concentration in the coating layer that is available for the alumina scale formation and is an important degradation mode in the aluminized specimens [21]. The comparison of chemical composition of Al in the coating layer after 500 h oxidation in both orientations is listed in Table 1. It is visible that the Al concentration in the coating layer on [110] surface is slightly lower than on [100] surface.

At high temperature oxidation, the interdiffusion of elements between the single crystal substrate and the coating layer took place. The outward diffusion of Ni from the substrate leads to the enrichment of refractory elements (such as Re, W, Cr and Mo) and promotes the formation of TCP phases. As has been previously reported [22], the TCP phase had a deleterious effect that can reduce the mechanical properties of Ni-based single crystal superalloys. Wu et al. [23] have reported that the amount and penetration depth of TCP phase might affect the oxidation behavior of Ni-base single crystal superalloys. As seen from Fig. 12, the amount of TCP phase was larger on [110] side-surface than that on [100] side-surface. Nevertheless, the depth penetration of TCP phase was about 67 μm on [100] side-surface and 79 μm on [110] side-surface. Another possible reason that may be considered is the amount of metastable phase $\theta$-Al$_2$O$_3$ between the two orientations as seen in Fig. 12. The percentage of $\theta$-Al$_2$O$_3$ after 500 h oxidation at 1100°C was about 20% on [100] side-surface and 24% on [110]. In the other words, the [100] surface contained a little bit higher amount of $\alpha$-Al$_2$O$_3$ than that of [110] surface (Table 1), which confirms that the [100] surface showed a better oxidation resistance than that of [110] surface.

5. Conclusions

The current work reported the oxidation behavior of aluminide coating on a Ni-base single crystal superalloy at high temperature with different surface orientations. The oxidation rate on [110] surface was somewhat higher than that on [100] surface. The specimens with [100] surface had a

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Table 2: Chemical composition on the substrate and scales of coated specimens after oxidation at 1100°C for 500 h corresponding to Fig. 12.
better oxidation resistance than the specimens with \{110\} surface. Consequently, the occurrence of anisotropic oxidation behavior took place. The anisotropic oxidation behavior between the two surfaces was caused by the difference of the TCP phase amount and its penetration depth, as well as the percentage of $\alpha$-$\text{Al}_2\text{O}_3$ as a stable phase after 500 h oxidation.

**Acknowledgments**

The authors would like to gratefully acknowledge to Dr. Murakami of NIMS (National Institute for Materials Science), Tsukuba, for the support of pack aluminizing process.

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