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Role of Aluminide Coating on Oxidation Resistance of Ni-Based Single Crystal Superalloy at 900 °C

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In the present study, the role of aluminide coating on oxidation resistance of Ni-based single crystal superalloy was studied at 900 °C. The oxidation kinetics curves obey the parabolic law in both conditions. However, the significant difference was found after 100 h oxidation in both conditions. The coated specimens showed a better oxidation resistance than the uncoated ones. This is due to the phase transformation occurred from θ-Al_2O_3 to α-Al_2O_3 in the coated specimens with increasing oxidation time but not in the uncoated ones. The production of more α-Al_2O_3 during oxidation is expected since α-Al_2O_3 acts as a protective layer against oxidation due to its stability at high temperatures. It could be also recognized from the surface morphology of the oxidized coated specimen after 500 h oxidation.

Keywords: Ni-base superalloy, aluminide coatings, oxidation, microstructure, X-ray diffraction

1. INTRODUCTION

Ni-based single crystal (SC) superalloys are usually used as components in the hot section of the engine in the most advanced gas turbine engines [1,2]. These superalloys are unique since they have complex chemical compositions consisting of more than nine different elements. Variation in chemical composition delivers superior properties for the superalloys specifically in mechanical strength at high temperature applications [3]. Although the design of the superalloys in terms of alloying elements addition has always been attempted by the need to improve their high temperature mechanical properties, however, the enhancement of their oxidation/hot corrosion resistance is also important to take into consideration [4]. Recently, the surface operating temperature of the gas turbine engines has increased up to 1200°C and even more. High operating temperature has a big potential to degrade the surface of the components resulting in oxidation or corrosion process which can shorten the lifetime of the components [5,6].

Many efforts have been undertaken to overcome this severe problem, one of them is by applying the aluminide coating to prevent the oxidation process on the surface of the components [7]. Aluminide diffusion coatings are widely used for high temperature oxidation and hot corrosion protection of turbine blades used in engine hot sections [8]. Aluminide coatings can be applied on Ni-based single crystal superalloys by several methods such as pack cementation or sometimes also called as pack alumnizing [9], out of pack vapor phase aluminizing [10], and chemical vapor deposition (CVD) [11]. In the present study, the pack cementation was selected to prepare the aluminide coating on Ni-based SC superalloy.

The pack aluminizing method is used for deposition of protective coatings on the metallic surface to ensure the protection against oxidation, corrosion and damage [12]. At high temperatures, Al in the coating is oxidized and forms a thin Al_2O_3 scale, which works as the diffusion barrier and reduces the oxidizing speed of the base material. The coated elements are placed in the closed or half-closed containers and covered with mixture of powder, which consist of metals used for deposition (Al and Cr), the halide activating agent (NH_4Cl) and inactive filler (usually Al_2O_3). The coating is fabricated through the reduction of metal-halide vapors on the surface of the base material followed by diffusion in the solid state between the introduced metal and the substrate. The good repeatability of manufacturing process and low costs are the main advantages of the pack cementation method [13]. Generally, the pack cementation process can be classified into two types depending on its process temperature and the activity of Al available in pack. They are high-temperature low-activity (HTLA) and low-temperature high-activity (LTHA) as reported by Das et al. [14]. Therefore, this work aims to investigate the role of aluminide coating on oxidation resistance of Ni-based SC superalloy at 900 °C.

2. EXPERIMENTAL DETAILS

A Ni-based SC superalloy with a chemical composition of 5.74 Al, 0.73 Ti, 6 Cr, 9.3 Co, 1.4 Hf, 3.4 Ta, 8.3 W, 0.005 Zr, 0.016 B, 0.019 Fe, 0.07 C and balance Ni (in mass%) was used as an experimental material. SC superalloy with a rod shape was produced by casting and directionally solidified in [001] direction. The rod was solution-treated at 1274 °C for 8 h and continued with a two-steps aging at 1080 °C for 4 h and 871 °C for 20 h. Both heat-treatments were cooled down to room temperature in air. Laue X-ray diffraction (XRD) method was used to identify the principal oxidation surfaces of the SC specimens, and it was found to be within 3° of the desired orientations. The specimens were then cut from the rod with the dimension of 10 mm in length, 4 mm in width and 3.5 mm in thickness along [001] direction by electro discharge machine (EDM). The specimens were mechanically polished down to 1200-grit SiC paper, degreased in acetone, ultrasonically cleaned in alcohol and dried in air prior to aluminizing treatment.

Some specimens were coated by pack aluminizing process and some of them were not coated. In this study, HTLA process was used to prepare the aluminide coating on the surface of SC superalloy. The specimens were put into a container made of alumina containing a mixture of 24.5 Al, 24.5 Cr, 49.0 Al_2O_3 and 2.0 NH_4Cl powders (all in mass %) and then vacuumed up to a pressure of 1 x 10^{-4} mPa followed by heating at 1000 °C for 5 h under flowing argon. Afterwards, all specimens were isothermally oxidized at 900 °C for 500 h in a tube furnace under air environment. The oxidation kinetics was determined as a function of weight gain against exposure time. The surface structure of the SC superalloy after oxidation was examined by X-ray diffraction using Cu Kα radiation. The initial microstructure, surface morphology and cross-section of SC superalloy after oxidation were analyzed by a scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDS).

3. RESULTS

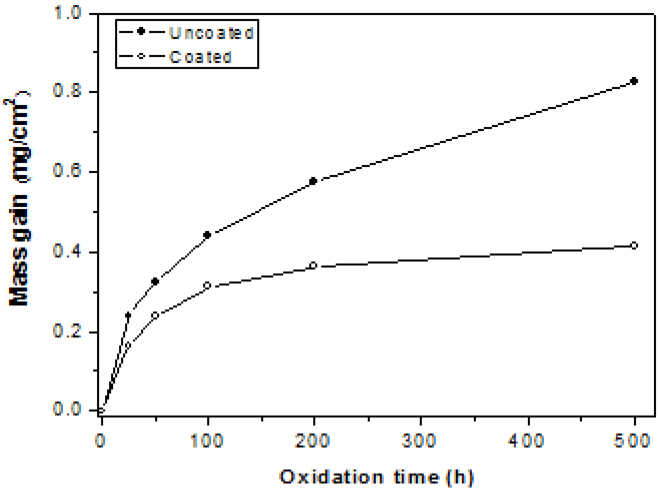

Figure 1. Oxidation kinetics curve of the SC superalloy after oxidation at 900 °C.

Figure 1 shows the mass-gain vs oxidation time curve for the isothermal oxidation experiment at 900 °C for 500 h. In the initial oxidation stage, the mass-gain of the uncoated and coated specimens was significantly increased. The mass-gain was then periodically increased in both specimens up to 100 h oxidation. However, after 100 h oxidation, both specimens showed different graph trend where the uncoated specimens revealed a gradual increase of the mass gain, whereas the coated ones seemed to have a nearly constant mass gain. In the other words, the mass-gain of the coated specimens was drastically decreased after 100 h oxidation. The parabolic oxidation rate, k_p during isothermal oxidation between the two specimens can be measured by a linear least-squares algorithm as previously reported by Wang et al. [15]. According to the measurements, the k_p values were 3.80 x 10^{-7} mg^2 cm^{-4} s^{-1} for the uncoated specimen and 5.05 x 10^{-8} mg^2 cm^{-4} s^{-1}. In brief, the application of aluminide coating on the surface of the SC superalloy showed better performance on oxidation resistance if compared with the uncoated specimens.

Figure 2 shows the oxide scale product on the surface of the SC superalloy both in the uncoated and coated specimens after 500 h oxidation at 900 °C. The XRD patterns between the two specimens were totally different. The oxide scale product formed uncoated specimen exhibited several peaks consisting of various phases where the oxide scale was primarily composed of α-Al_2O_3 and followed by (Ni,Co)O. It was also seen the small amounts of spinels such as $(Ni,Co)Al_2O_4$ and $NiCr_2O_4$, and a complex structure of $CrTaO_4$. Moreover, a very small amount of HfO_2 and $W_{20}O_{58}$ was found in the uncoated specimen (Fig. 2a).

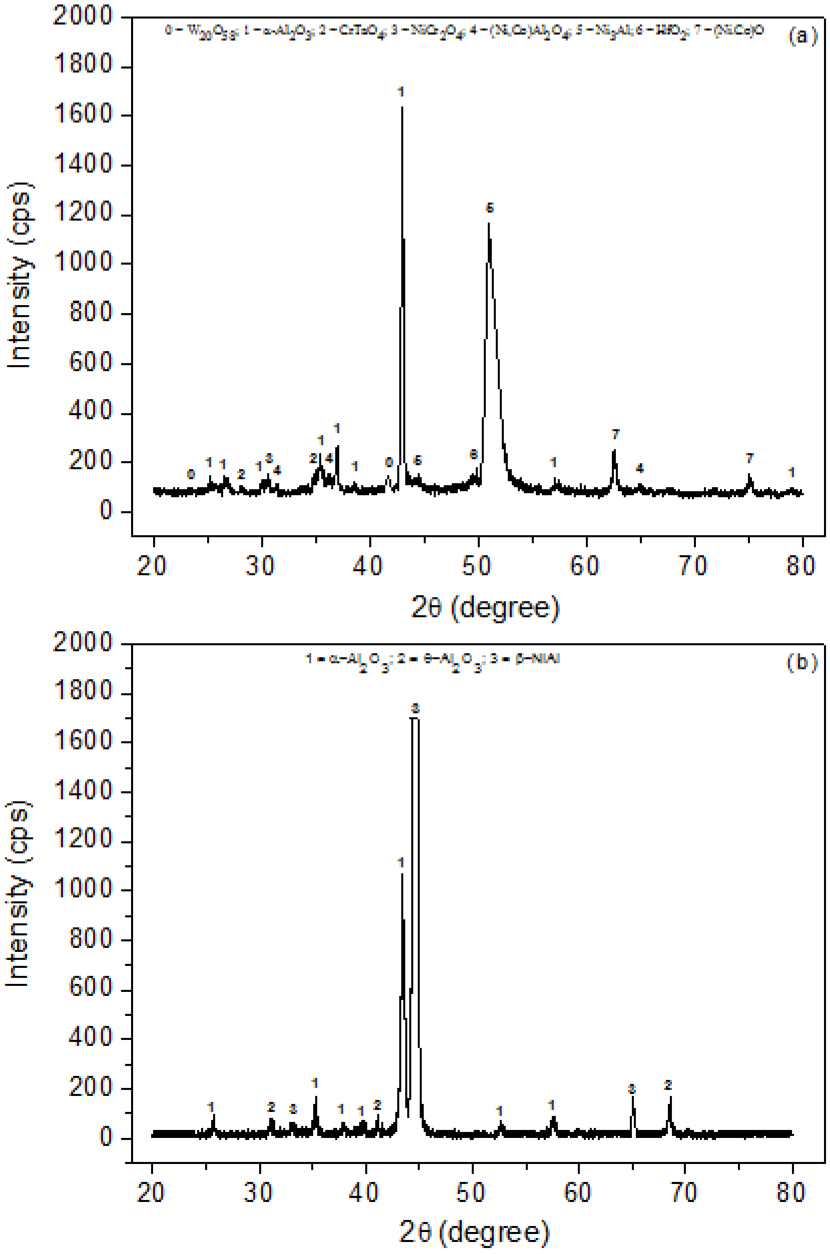

Figure 2. XRD patterns of the specimens after oxidation at 900 °C for 500 h.

The substrate peak (referring to point 5 in Fig. 2a) was still detected after 500 h oxidation, it means the oxide scale was not perfectly covered the specimen surface even after 500 h oxidation. It may affect the structure of the oxide scale formed on the surface of the uncoated specimen. On the other hand, the oxide scale product formed on the surface of coated specimen was primarily comprised of α-Al_2O_3 and followed by θ-Al_2O_3. The coating layer (β-NiAl) peak was still existed after 500 h oxidation at 900 °C (Fig. 2b).

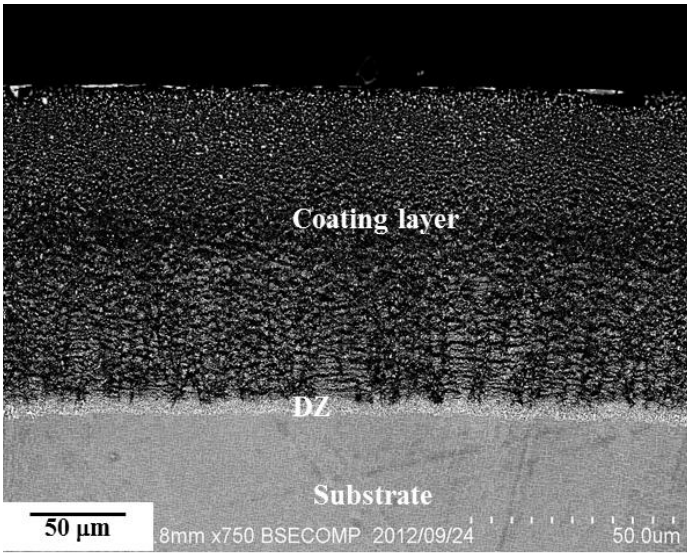

Figure 3. SEM micrograph of the as-coated specimen.

Figure 3 shows SEM micrograph of the as-coated specimen. The coated specimens presented an obvious characteristic structure of an outer layer and a diffusion zone (DZ) located between the coating layer and the substrate. The phenomenon that high-atomic-weight elements of the original substrate precipitate in the DZ presents that the formation of the coating layer is primarily through the outward diffusion of Ni [16]. The interface between the coating layer as outer layer and the DZ corresponds to the initial surface of the substrate.

Figure 4 shows surface morphologies of the uncoated and coated specimens after 500 h oxidation at 900 °C. With respect to the uncoated specimen, NiO particles were randomly distributed on the top of the oxide scale products. However, NiO particles were not fully covered the surface of the uncoated specimen after 500 h oxidation at 900 °C. Some areas revealed the oxide scale with finer grain size were also observed (Fig. 4a). NiO particles formed on the surface of the specimen have typically block morphology and porous structure with varied grain size between 0.2 - 3.8 µm. In case of the coated specimen, two oxide phases consisting of α-Al_2O_3 and θ-Al_2O_3 were observed on the surface of the coated specimen after 500 h oxidation at 900 °C (Fig. 4b). Both phases can be distinguished from their shapes where the α-Al_2O_3 has an equiaxed structure and θ-Al_2O_3 has a platelet-like [17]. This result is consistent with the XRD pattern as presented in Figure 2b.

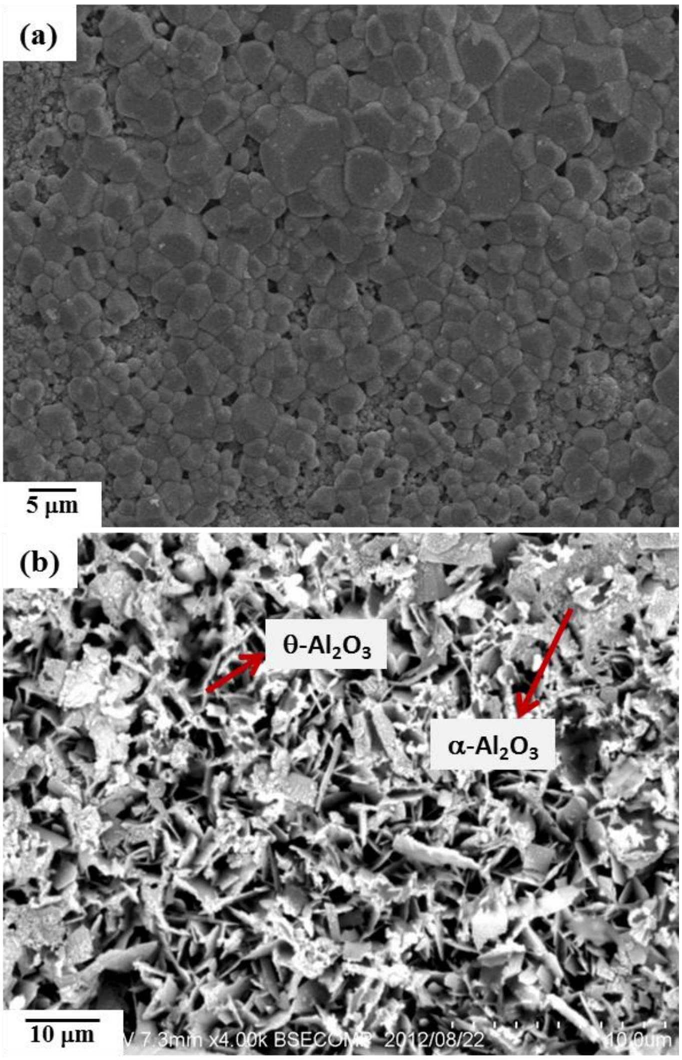

Figure 4. Surface morphologies of the oxidized specimens after oxidation for 500 h at 900 °C: (a) uncoated and (b) coated.

Figure 5 shows the microstructures of the as-oxidized specimens after oxidation for 500 h at 900 °C. After oxidation for 500 h, the uncoated and coated specimens presented different appearance. The uncoated specimen had a complex structure after 500 h oxidation (Fig. 5a). Based on the EDS observation, the microstructure of the oxidized uncoated specimen can be divided into three regions generally: (i) top layer, (indicated by point 1), composing of NiO particles together with a small content of CoO, (ii) intermediate layer (points 2 and 3), having a complex structure, since it contained some spinels (Ni,Co)Al_2O_4 and $NiCr_2O_4$), a bright phase of $CrTaO_4$ and a small amount of $W_{20}O_{58}$, and (iii) bottom layer (point 4), consisting of dark continuous α-Al_2O_3 layer with a small amount of HfO_2 precipitates distribution (Fig. 5a). For details, the EDS analysis result of the uncoated specimen after 500h oxidation is presented in Table 1.

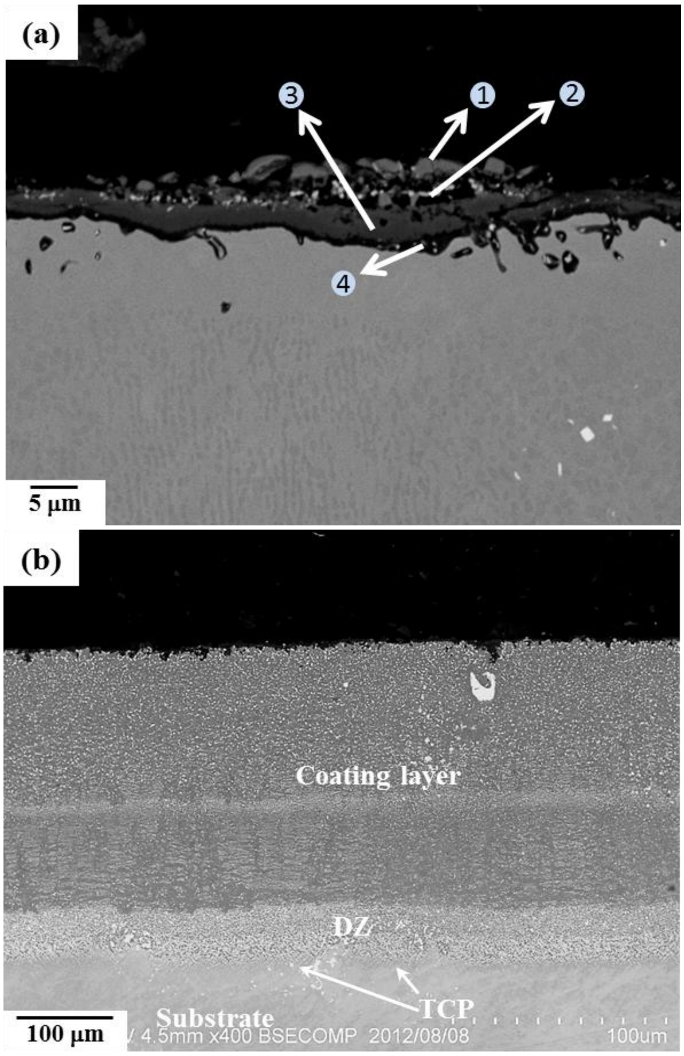

Figure 5. The as-oxidized microstructures of: (a) the uncoated, and (b) the coated specimens after 500 h oxidation at 900 °C.

Table 1. Chemical composition of the oxidized uncoated specimen (at.%) corresponding to Fig. 5a.

Points of no.	Element content (at.%)									Note
	O	Ni	Al	Cr	Ti	Co	Ta	W	Hf	
1	43.22	52.95	-	-	-	3.83	-	-	-	NiO+CoO
2	56.44	17.26	5.34	7.07	2.74	3.67	7.34	0.14	-	$(Ni,Co)Al_2O_4$+$NiCr_2O_4$+$CrTaO_4$+$W_{20}O_{58}$
3	47.10	15.42	23.47	7.89	0.79	5.05	0.27	-	-	$(Ni,Co)Al_2O_4$+$NiCr_2O_4$+$CrTaO_4$
4	54.82	1.49	37.20	-		-	-	-	6.50	α-Al_2O_3+HfO_2

In terms of the coated specimen after oxidation 500 h, the microstructure was dissimilar if compared with the uncoated one. The extension of diffusion zone (DZ) and small amounts of topologically close-packed (TCP) phase with a needle-like were found in the coated specimen after oxidation for 500 h (Fig. 5b). Both DZ and TCP phase are typical of the SC superalloy coated by aluminide coating after thermal exposure especially at elevated temperatures, and their presence in the microstructure will deteriorate the properties of the SC superalloy. In addition, the precipitation of TCP phase occurs at temperatures ranging from 800 °C to 1140 °C [18]. So that the presence of TCP phase in this study is consistent with the previous study.

4. DISCUSSION

Previous investigation that reported by An et al. [19] mentioned that the oxidation kinetics of the SC superalloys in the temperature range 800-1100°C in air obey the parabolic law. Moreover, it was also reported that the oxidation of the SC superalloy nearly follows the parabolic law in the temperature range 1000-1150°C, and they concluded that the oxidation kinetics were primarily controlled by the growth of the inner α-Al_2O_3 after the initial oxidation stage [5]. As for the present oxidation kinetics curve showed that both specimens, uncoated and coated, had a nearly parabolic shape during oxidation at 900 °C. It means the oxidation kinetics in both specimens follows the parabolic law. Hence, the present results are consistent with the previous studies.

The most interesting thing, as can be seen in Figure 1, the oxidation kinetics curve contradicts between the two type specimens after 100 h oxidation where the mass-gain was gradually increased in the uncoated specimens, but it was dramatically decreased in the coated specimens. It indicates the mechanism of the oxidation process between the uncoated and coated specimens is different. In the uncoated specimens, the simple oxides were formed during the initial oxidation stage where it is also called as transient oxidation stage. This transient stage occurs in a short period and then followed by the rapid formation of the inner α-Al_2O_3 continuous layer at the bottom of the oxide scale. The inner α-Al_2O_3 continuous layer was derived from the outward diffusion of Al from the substrate to the interface of metal/oxide scale at relatively high temperature. After sometimes the chemical reaction among them occurred continuously. Finally, the phases such as $(Ni,Co)Al_2O_4$, $NiCr_2O_4$, $CrTaO_4$, and others were formed on the surface of the uncoated specimen. The oxide scale thickness became larger in accordance with increasing oxidation time. Turning to NiO formation on the top of the oxide scale, Ni diffusion outward also occurs from the substrate to the interface actually since Ni element is a major element in the SC superalloy. Nevertheless, the growth of NiO particles was impeded by the rapid growth of the inner α-Al_2O_3 continuous layer with increasing oxidation time, resulting in the detention of the NiO growth after 500 h oxidation. From this sense, it could be understood that the oxidation resistance of the uncoated specimens was controlled by the growth of the inner α-Al_2O_3 layer. The formation of inner α-Al_2O_3 continuous layer plays an important role to provide a good protection in the uncoated specimens [5].

Different from the uncoated specimens, the θ-Al_2O_3 called as metastable phase was rapidly formed during the initial/transient oxidation stage [20], whereas the α-Al_2O_3 is known as stable phase which provides a good protection from oxidation with the application of aluminide coating on the surface of the SC superalloy. By prolonging the exposure time, the phase transformation from θ-Al_2O_3 to α-Al_2O_3 were more effectively to occur after 100 h oxidation although the metastable phase was still detected after 500h oxidation (Fig. 2b). As shown in Figure 1, it can be realized that the rapid formation α-Al_2O_3 took place due to the phase transformation from metastable to stable one, leading to the decrease in mass-gain rate after 100 h oxidation [21]. Hence, the present results show that the phase transformation is influenced by the oxidation time as well as temperature. The surface morphology of the oxidized coated specimen after 500 h oxidation also presented that both phases were formed with the difference in shape (Fig. 4b). It is clear evidence for the phase transformation occurrence in the coated specimen. Note that aluminide diffusion coatings are generally adopted to guarantee long-term environmental stability against oxidation by the formation of a protective layer of α-Al_2O_3 scales [22]. More interestingly, the TCP phase was found in the coated specimen after 500 h oxidation [23] and it is undesirable due to its disadvantageous [24]. When aluminide coatings on the surface of the SC superalloys are exposed to high temperatures, the aluminium diffuses into the substrate to form the aluminium rich inter-metallics β-NiAl (coating layer) and γ'(Ni_3Al). Owing to the solubility of the refractory elements such as W, Re, Mo and Cr, is much lower in both of these phases than in γ [25], as a consequence, the refractory elements are locally precipitated nearby the DZ to promote the formation of TCP phases during outward diffusion of Ni from the substrate to the coating layer at high temperatures [26]. TCP phases became lengthened with increasing oxidation time, and they can intrude into the substrate to a considerable distance and finally destruct the γ/γ' structure in the substrate (Fig. 5b), which is the fundamental for the superior properties of the SC superalloys. At the end, the application of aluminide coating on the SC superalloy delivers better oxidation resistance by the formation of α-Al_2O_3 scale on the surface of the SC superalloys.

5. CONCLUSION

The oxidation resistance of the uncoated and coated specimens of Ni-base SC superalloy has been investigated at 900 °C for 500 h. The application of aluminide coating improved the oxidation resistance of the SC superalloy. This oxidation improvement occurred due to the phase transformation from θ-Al_2O_3 as a metastable phase to α-Al_2O_3 as stable phase. In case of the uncoated specimens, the presence of α-Al_2O_3 was less, and consequently the mass-gain rate was gradually increased from 100 h to 500 h oxidation. In addition, the formation of α-Al_2O_3 is expected to occur since it provides a good protection against oxidation due to harsh environment. Long-term exposure produces more protective layer of Al_2O_3 scale on the surface of the SC superalloys to prevent them from oxidation.

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