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The influence of $CrTaO_4$ layer on the oxidation behavior of a directionally-solidified nickel-based superalloy at 850–900 °C

Weili Ren [a], [*], Fenfen Ouyang [a], Biao Ding [a], Yunbo Zhong [a], Jianbo Yu [a], [**], Zhongming Ren [a], Lanzhang Zhou [b]

[a] *State Key Laboratory of Advanced Special Steel, College of Materials Science and Engineering, Shanghai University, Shanghai 200072, PR China*
[b] *Metal Research Institute, Chinese Academy of Sciences, Shenyang 110015, PR China*

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ABSTRACT

The influence of $CrTaO_4$ on the oxidation behavior of a directionally solidified nickel-based alloy has been investigated at the temperatures between 850 °C and 900 °C for the different time intervals (the longest time is 300 h). The oxide scale consists of three layers. The outer layer is mainly composed of Cr_2O_3, TiO_2, and $NiCr_2O_4$, the middle layer is $CrTaO_4$, and the inner oxide layer mainly consists of Al_2O_3. The continuous $CrTaO_4$ layer is formed after oxidation for certain times. The formation time of continuous $CrTaO_4$ layer shortens with the temperature increase. Furthermore, the layer causes the transformation of the oxidation kinetics from the parabolic law to the cubic law. The control of oxidation process converts from the outward diffusion of Cr, Ti, and Ni to the inward diffusion of O when the continuous $CrTaO_4$ layer is established. The mechanism clarifies the influence of Ta on the oxidation behavior of Ni-based superalloys from the oxidation kinetics.

1. Introduction

Nickel-based superalloys have been widely applied in the hot-section components for the aerospace and power-generation engines, such as turbine disks and blades, due to their superior strength and adequate resistant-oxidation properties [1–3]. The excellent oxidation resistance of the alloys at elevated temperatures is associated with the formation of continuous Al_2O_3 and Cr_2O_3 oxide layers. Compared with other oxides, the oxide layer shows a dense structure, which can significantly decrease the element diffusion rate and consequently decrease the oxidation rate of the superalloys [4–6].

In order to ensure the strength and oxidation resistance of the Ni-based superalloys at elevated temperatures, the various alloying-elements are usually added, such as Al, Ti, Ta, Cr, Co, W, and Mo [7,8]. On the one hand, the addition of Ta in the Ni-based superalloys increases the contents of the strengthening phases through dissolving into the γ' (Ni_3Al) lattice and consequently enhances the superalloy strength [9,10]. On the other hand, it has a beneficial role in the oxidation resistance of the alloys with the appropriate configuration of the content and type of other elements and temperatures. Let us review briefly the investigations about the influence of Ta on the oxidation behavior of the Ni-based superalloys [11–17]. Firstly, the addition of appropriate amount of Ta in the alloy improves the oxidation resistance. Han et al. [11] found that the oxidation rate of Ni-based superalloys with 5.8 wt.% Ta is lower than that with 3.8 wt.% Ta. It was because the continuous dense $CrTaO_4$ formed in the high Ta-content superalloy. Kim et al. [12] studied the oxidation behavior of five types of Ni-based superalloys at 850 °C and 1000 °C and found that the superalloys containing higher Ta content were more oxidation-resistant than those with the lower addition levels of Ta. They also attributed the reason to the formation of $CrTaO_4$ and TaO layers in the superalloy with the high Ta content. By contrary, Yang [13] reported that an addition of Ta as small as 1 at.% (~3.0 wt.%) improved the oxidation resistance significantly by promoting early establishment of a protective Al_2O_3 layer. When 3 at.% (~8.8 wt.%) of Ta was added, complex oxides such as $NiMoO_4$, $NiTa_2O_6$, TaO_2, MAl_2O_4, and M_2CrO_4 were formed, causing degradation of the oxidation resistance. Secondly, the temperature affects the formation rate of Ta-containing oxides. Park et al. [14] found that the $CrTaO_4$ layer was more continuous at 1000 °C than that at 850 °C. The $CrTaO_4$ layer hinders the outward diffusion of the Al element,

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: wlren@staff.shu.edu.cn (W. Ren), jbyu@shu.edu.cn (J. Yu).

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resulting in a formation of a continuous dense Al_2O_3 inner layer and further a slower oxidation rate. Li et al. [15] reported that the X-ray diffraction peak of $CrTaO_4$ at 900 °C was stronger than that at 800 °C in the oxide scale. However, the $CrTaO_4$–rich oxide layer was very thin and discontinuous at 1000–1150 °C [16]. It could be attributed to the rapid establishment of a continuous Al_2O_3 inner layer at high temperatures, which retarded the outward diffusion of Ta element. Wang et al. [17] studied the form of Ta in the oxide film of the N5 Ni-based single-crystal superalloy oxidized at different temperatures. It was found that the continuous $CrTaO_4$ was not formed due to the low Cr content in the superalloy, while two types of Ta-containing oxides TaO_2 and Ta_2O_5 were formed. Thirdly, Ta segregation at the grain boundaries of Al_2O_3 scale increases the spallation resistance of oxide scales, which was confirmed through the structure observation of oxide scales under the transmission electron microscope by Wang [17]. Finally, the oxidation resistance and spallation resistance of Ta is related with the homogeneous extent of its distribution in the superalloy matrix. At the Ta-rich region, Ta was oxidized prior to Al, TaO_x was less protective than Al_2O_3, and the adhesion of the alloy substrate to TaO_x was inferior to Al_2O_3. The inhomogenous dispersion and the excessive TaO_x at some places upon superalloy substrate result in the formation of large cavities and the final spallation [17]. Moreover, a detrimental interspersed Ta-rich oxide particles developed in the top spinel scale on PWA-1484 superalloy [18]. Pedraza et al. found that the incorporation of Ta_xO_y in the oxidation scales clearly worsened their oxidation resistance in aluminide coatings on different superalloy substrates [19].

The above investigation shows that the effects of Ta on the oxidation of the alloy exhibits the complex behaviors, and its beneficial role depends on whether it can form a continuous $CrTaO_4$ layer. The formation of the continuous dense $CrTaO_4$ could hinder the outward diffusion of other elements and decrease the oxidation rate of Ni-based superalloys. When the continuous dense $CrTaO_4$ could not form due to the small Ta and Cr content [11,12,17] or the low temperature [14,15] or the Al_2O_3 inner scale formation [13,17], the effect of Ta decreasing the oxidation rate is not exerted. However, the formation time of $CrTaO_4$ layer and its influence on the rate exponent of oxidation kinetics and on the activation energy of oxidation rate have not been reported up to now. The present paper studied that the influence of $CrTaO_4$ layer on the oxidation behavior of a directionally-solidified nickel-based superalloy with 5.0 wt.% Ta at temperatures between 850 °C and 900 °C. The formation time of the $CrTaO_4$ was determined at the different temperatures. The influence of $CrTaO_4$ layer on the rate exponent and the activation energy were studied. The oxidation mechanism was proposed after the formation of the $CrTaO_4$ layer. The investigation reflects the essentials of oxidation behavior, and clarifies the influence of Ta on the oxidation mechanism of Ni-based superalloys.

2. Experimental procedure

The nominal composition of the investigated alloy is shown in Table 1. The alloy with a diameter of 16 mm was directionally solidified at a withdrawal speed of 7 mm/min. The oxidation specimens with the dimensions of 10 mm × 10 mm × 3 mm were cut from the heat-treated ingots, ground, and polished. The heat-treatment procedure is 1210 °C × 2 h (AC) + 1080 °C × 3 h (AC) + 850 °C × 24 h (AC) (AC: air cooling).

Table 1
Nominal chemical composition of the superalloy.

Element	Co	Cr	Mo	W	Al	Ti	Ta	C	Zr	Ni
wt.%	10.00	14.00	1.50	4.00	4.00	3.00	5.00	0.08	0.03	Bal.

The isothermal oxidation was carried out in static air at 850 °C, 875 °C, and 900 °C. The corundum crucibles used in the oxidation were all heat-treated in the furnace at 1200 °C for enough time to ensure that their weight would not be changed. The oxidation kinetics curves of the alloys were determined by the static weight gain method. After appropriate time intervals, the specimens were taken out of the furnace, cooled in air, and then weighed with an electronic balance with a resolution of 0.1 mg. Three specimens were simultaneously tested at each temperature. The oxidation time is up to 300 h.

The phases formed on the oxidized specimens were determined by X-ray diffraction (XRD). The surface morphology of the oxidized samples was evaluated by the scanning electron microscope (SEM) equipped with an energy dispersive spectrometry (EDS) without any preparation. However, for evaluation of cross-sections, all specimens were initially covered with a thin layer of Ni, which aimed to prevent damage to the oxide layer during the specimen preparation for SEM observation. The chemical plating was used to cover the Ni layer. The samples were preprocessed in the solution of $SnCl_2$ (13 g/L) + HCl (40 ml/L)+ deionized water for 2 min, and further were put in the solution of $PbCl_2$ (0.2 g/L) + HCl (7 ml/L) + deionized water for 1 min at room temperature, which ensures the surface activation of the samples. Then, the plating process was carried out in the solution of $NiSO_4 \cdot 6H_2O$ (25 g/L) + $NaH_2PO_2 \cdot H_2O$ (30 g/L) + CH_3COONa (12 g/L) + $Na_3C_6H_5O_7 \cdot 2H_2O$ (14 g/L) + $C_3H_6O_3$ (13 g/L) + deionized water for 90 min at 90 °C.

3. Results

3.1. Phases in the oxide film

The phases forming during the oxidation were characterized by XRD. Fig. 1(a) shows the XRD patterns of the specimens oxidized at 850 °C, 875 °C, and 900 °C for 200 h. At each temperature, the diffraction peaks of the Cr_2O_3, TiO_2, $NiCr_2O_4$, Al_2O_3, $CrTaO_4$, and the matrix are observed. But the peak intensity of the $CrTaO_4$ phase is weak. With the increase of the oxidation temperature from 850 to 900 °C, the peak intensity of the matrix phases of Ni and Ni_3Al decreases. Fig. 1(b) shows the XRD patterns of the specimen oxidized at 900 °C for the different times in the range from 24 to 200 h. With the time increase, the peak intensity of the oxides increases, while that of the matrix phases decreases. No oxides of Co, W, and Mo were identified. The reason will be illustrated in the discussion part.

3.2. Surface morphology and composition

No oxide spallation was observed during the sample cooling. The surface morphology of the oxide scale formed on the alloy after exposure time of 300 h at the different temperatures is presented in Fig. 2. The oxides uniformly cover the scale surface. With increasing the temperature, the oxide grains gradually increase. The composition of the scale surface was analyzed by EDS, which are shown in Table 2. It can be seen that the compositions are rich in Cr, Ti, Ni, and O, which are in agreement with the results of XRD and the cross-section of oxidation scale. It should be stated that Al and Ta are hardly detected in the surface oxide with EDS due to the shallow penetration depth of the electron beam.

3.3. The cross-section morphology and structure of the oxide film

In order to further clarify the structure of the oxidation scale of the superalloy, the cross-sections were studied. Fig. 3(a–c) shows the morphology and structure of the cross-section of the samples