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Effect of Al content on the high-temperature oxidation of Co-20Cr-(5, 10)Al oxide dispersion strengthened superalloys

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Abstract

The high-temperature oxidation of Co-based oxide dispersion strengthened (ODS) Co-20Cr-(5, 10) Al-2.4Hf-1.5Y₂O₃ (wt %) superalloys was investigated at 900 °C and 1000 °C. The 10Al (wt %) superalloys possess better oxidation resistance with the formation of alumina scale than the 5Al (wt %) with a duplex scale of CoCr₂O₄ / Cr₂O₃ and internal Al₂O₃. The alumina on the 10Al superalloy is composed of θ - and α -alumina at 900 °C but dominated by α -alumina at 1000 °C. The lower weight gain of 10Al superalloys at 1000 °C than at 900 °C was associated with different growth mechanisms of the Al₂O₃ scales.

Keywords

A. Cobalt; A. Alumina; B. SEM; C. Oxidation

1. Introduction

Oxide dispersion strengthening is widely used to develop high-temperature superalloys, such as Fe- and Ni-based ODS superalloys [1-5]. Besides their superior creep resistance and favorable high-temperature strength, ODS superalloys show better oxidation resistance than the ODS-free alloys with the same basic composition, which has been frequently proved with a large number of reports about oxidation behavior of Fe- and Ni based ODS superalloys [6-8].

However, a comparable attention on the development of Fe-based and Ni-based ODS superalloys has not been paid for Co-based ODS superalloys, and even no literature could be referred about the high-temperature oxidation of Co-based ODS superalloys. Co-based alloys are utilized in aggressive environments for their outstanding corrosion resistance and high-temperature strength [9], in which the carbides precipitation works as the main strengthening approach [10, 11]. However, the application of those conventional Co-based alloys is limited up to 800 °C because of the carbides coarsening or dissolution above this temperature [12-14]. Even though a γ' -Co₃(Al, W) precipitate has been later explored and considered to be more effective, the γ' -strengthening is stable only at a narrow temperature-composition range [15-19]. Such conventional carbides strengthened or the γ' -strengthened Co-based alloys are restricted in the alloying composition. Alumina has been considered more protective scale than other conventional metal oxide scale due to its lower growth rate and nonvolatility at elevated temperature, but the production of alumina-forming in the superalloys demands a high aluminum concentration or an adjustable composition with other elemental addition.

Based on an extremely high thermodynamic stability of dispersed oxide particles and a controllable composition of matrix, the oxide dispersion strengthening (ODS) is expected to be an advanced approach to increase service temperature of Co-based alloys [20]. In accordance with the achievements [21, 22] that Hf is effective to reduce the Y₂O₃ oxide particles size by forming fine Y₂Hf₂O₇ particles, Takezawa et al. [23] discovered Co-3Al-1.5Y₂O₃-1.2Hf (wt %) ODS superalloy with a significant

improvement of high temperature strength at 1000 °C compared to the non-ODS Co-based alloys with the same basic composition. Subsequently, a stable high-temperature microstructure of this Co-based ODS superalloy has also been verified by Sasaki et al. [24] through annealing at 1000 °C for 240 h.

Aimed at developing alumina-forming Co-based superalloys, 5 wt % and 10 wt % aluminum were added into the designed Co-based superalloys. In addition, 20 (wt %) chromium was also introduced, since the report that the alumina scale formation could be accelerated by Cr addition [25, 26]. The microstructure of the newly developed Co-20Cr-(5, 10) Al (wt %) ODS superalloys has been reported in the reference [27], which reveals that the Co-20Cr-(5, 10) (wt %) Al ODS superalloys are composed of two different phases, i.e. the Co solid solution of face-centered-cubic (fcc) structure, and the CoAl phase of B2 structure. Fine Y-Hf oxides particles are densely distributed inside the fcc solid solution and in the B2 phase. The average size of the Y-Hf particles in the fcc matrix is 5 nm, and it is much smaller than that in the B2 phase (12 nm). Grain boundaries are decorated with the Y-Hf-O particles, which is beneficial to the stabilization of the ultrafine grains with a mean size of 500 nm in the 5 Al (wt %) superalloy and 800 nm in the 10 Al (wt %) at elevated temperature [27].

Since the current development of the Co-based ODS superalloys is limited and very little research of its oxidation behavior has been conducted, there is a need to focus on the oxidation resistance of the Co-based ODS superalloys. In the case of conventional Co-based alloys, Irving et al. studied the amount of Al which must be present to form a continuous layer of Al_2O_3 in the temperature range 800-1000 °C, and claimed that the critical Al content is the 10-13 wt % at 900 °C and 13 wt % at 1000 °C [28]. Present work aims to characterize the effect of Al content on the high temperature oxidation properties of the novel Co-based ODS superalloys through an oxidation test at 900 °C and 1000 °C under air condition.

2. Experimental

The Co-20Cr-2.4Hf-1.5Y₂O₃ (wt %) ODS superalloys with different Al addition of 5 and 10 wt % (nominal composition) were prepared by mechanical alloying, spark

plasma sintering (SPS), hot rolling and final annealing at 1200 °C, which are referred to as 5Al and 10Al hereafter. The detailed manufacturing process of the Co-based ODS superalloys is described elsewhere [27]. The samples for oxidation test were cut into a cuboid shape, and all the surfaces of these samples were wet ground using SiC paper up to 2400-grit, and then polished with 3 μm and 1 μm -diamond paste. After confirming that no residual scratches can be observed in the surfaces by an optical microscopy, the samples were ultrasonically cleaned in alcohol, and dried in hot air. The investigated samples possess an approximate dimension of 15 mm $\times$ 8 mm $\times$ 1.5 mm. In order to hang the samples in alumina crucible, a hole of 1.3 mm diameter was made to hook the sample with an Al_2O_3 rod. Oxidation test at 900 °C and 1000 °C was carried out inside a muffle furnace in air. Oxidation weight gains at different exposure durations (1, 4, 16, 25, 49, 100, 225 h) were measured after cooling at room temperature via a Sartorius precision electronic balance (MC 5) with a resolution of 1 μg .

The crystalline structure of oxidized samples were detected using X-ray diffraction (XRD, Philips X' Pert PRO). The surface morphologies of oxide scales were investigated by scanning electron microscope (SEM, Carl Zeiss Cross Beam 1540 EsB), also the fractured surface observation was carried out by the SEM. The polished cross sections of oxidized samples were analyzed by the electron probe micro-analyzer (EPMA, JEOL JXA-8530F), in which the elemental mapping and quantitative point analysis by WDS were carried out, besides, the distribution of trace element (Y and Hf) inside oxide scales has been investigated with high magnification EPMA elemental mapping.

3. Results

3.1. Weight gain by oxidation

Fig. 1 shows the weight gain per unit surface area as a function of exposure time for all the observed 5Al and 10Al Co-based superalloys at 900 °C and 1000 °C in 225 h. It can be confirmed that all the Co-based ODS superalloys are capable to form protective oxide scales to inhibit a further oxidation at 900 °C and 1000 °C. With

increasing of Al content from 5 wt % to 10 wt %, the 10Al alloys exhibit better oxidation resistance with smaller weight gains at 900 °C and 1000 °C than the 5Al. Besides, in comparison with a noticeable mass gain of the 5Al at higher temperature of 1000 °C, the 10Al shows a smaller weight gain after 225 h at 1000 °C than 900 °C.

Fig. 2 shows the oxidation mass gains (Δm) as a function of square root of time ($t^{1/2}$), which is re-arranged from Fig. 1 in order to assess the oxidation mechanism of alloys. Based on the plot of $\Delta m / (t^{1/2})$, the oxidation mass gain of alloys at 900 °C linearly increased with $t^{1/2}$, which indicates that oxidation of alloys follows parabolic behavior defined as equation (1) up to 225h. The k_p values at 900 °C were calculated and presented in **Table 1**, and those for the 5 and 10Al alloys are very similar. Whereas oxidation of alloys at 1000 °C, the slope of the curves for both alloys decreased with exposure time. This result indicates that the oxidation of alloys at 1000 °C follows an altered mechanism along with the exposed time.

$$\Delta m = k_p^{1/2} \cdot t^{1/2} + C \quad (1)$$

where Δm is measured weight change and t is corresponding exposure time, C is a constant [29].

3.2. XRD measurement of the oxide scales

Fig. 3 shows the XRD patterns for the Co-based ODS superalloys oxidized at 900 °C and 1000 °C with the exposure time of 225 h, in which (a) and (b) represents the results of 5Al and 10Al, respectively. In addition to the characteristic peaks coming from matrix, the obvious diffraction peaks of oxide products were detected. In the case of 5Al, the CoCr_2O_3 and Cr_2O_3 are dominated no matter at 900 °C or at 1000 °C, and several $\alpha\text{-Al}_2\text{O}_3$ peaks could be found in the samples oxidized at 1000 °C. On the other hand, for the 10Al samples, only the $\alpha\text{-Al}_2\text{O}_3$ has been detected at both the 900 °C and 1000 °C, and some faint peaks of $\theta\text{-Al}_2\text{O}_3$ have been demonstrated in the samples oxidized at 900 °C.

In order to obtain more information about the crystalline structure of alumina, a low incidence angle (3° incident angle) in XRD testing was conducted for the 10Al

alloys. It was proved through a number of short-term oxidation shown in **Fig. 4(a)** and **(b)** that the change during the θ - to α -alumina transformation significantly depends on temperature and exposure time. In contrast with the co-existing of θ and α -alumina throughout the oxidation at 900 °C in 225 h, the α -alumina predominates with a transient period of the θ - and α -alumina co-existing in the initial stage at 1000 °C.

3.3 Morphology and chemical composition of the oxide scales

Fig. 5 shows the surface morphologies of the 5Al and the 10Al samples oxidized at 900 °C and 1000 °C in 225 h. In the case of the 5Al alloys, a smooth and unbroken scale was observed at 900 °C. However, with the increasing of temperature to 1000 °C, a large amount of pores were observed in the surface, as shown in the **Fig. 5 (b)**. The 10Al possesses an intact scale at both the 900 °C and 1000 °C, as shown in the **Fig. 5 (c)** and **(d)**, in which the surface morphologies is so different, i.e., a noticeable blade-like morphology appeared at 900 °C and it was clarified to be the intrinsic structure of metastable θ -alumina by research [30, 31], whereas a stable α -alumina with equiaxed grains was observed at 1000 °C.

The cross sections of samples oxidized at 900 °C and 1000 °C for 225 h were examined with the backscattered electron pattern (BSE), as shown in **Fig. 6**, in which **(a)**-**(b)** belong to the 5Al samples as well as **(c)**-**(d)** belong to the 10Al samples. **Fig. 6 (a)** shows the oxide scales at 900 °C for the 5Al, which is composed of a gray layer at the outer surface and internal precipitates in the subsurface region with a dark contrast. With increasing temperature to 1000 °C, as shown in **Fig. 6 (b)**, the outer scale becomes porous with many visible voids, and the internal oxide precipitates become a continuous layer. In contrast, 10Al contains a duplex layer with outer homogeneous dark contrast layer and inner with white particles. It is to be emphasized that the thickness of this oxide scale is significantly decreased through comparing **Fig. 6 (c)** and **(d)**, when the temperature increases from the 900 °C to the 1000 °C.

In order to further identify the distribution of elements in the oxide scale, the EPMA elemental mapping was carried out for the specimens oxidized at 900 °C and 1000 °C in 225 h, and the results of the 5Al samples and the 10Al samples are

displayed in **Fig. 7(a, b)** and **Fig. 8 (a, b)**, respectively. Based on the **Fig. 7 (a)** at 900 °C, the gray scale of the 5Al is mainly composed of chromium and oxygen elements, and above this scale, a thin layer enriched cobalt, chromium and oxygen could be found. According to the XRD diffraction pattern in **Fig. 3 (a)**, those two scales were considered to be Cr_2O_3 and CoCr_2O_4 , respectively. However, with increasing temperature to 1000 °C shown in **Fig. 7 (b)**, the Cr_2O_3 scale becomes thinner and the CoCr_2O_4 region changes to be thicker. Besides, the internal oxides with dark contrast in 5Al is consider to be Al_2O_3 due to being enriched both aluminum and oxygen elements. The Al_2O_3 has grown from the discontinuous alumina oxides at 900 °C to a continuous alumina scale at 1000 °C, which is quite consistent with the appearance of the obvious alumina diffraction peaks in the 5Al oxidized at 1000 °C. On the other hand for the 10Al, based on the enrichment of aluminum and oxygen elements at the outer layer, as shown in the **Fig. 8 (a, b)**, and the alumina diffraction peaks obtained from the XRD results in **Fig. 3 (b)**, the oxide scales of the 10Al alloys at 900 °C and 1000 °C are defined as alumina.

Particles with white contrast observed in the alumina scales of the 10Al specimen, as shown in **Fig. 9(a)** and **(b)** are considered to be Y / Hf oxides in accordance with the reference [27]. The particle distribution is different at the 900 °C and 1000 °C, i.e. the particles located in the inner layer of alumina scale at 900 °C but the outer part of inner layer at 1000 °C. According to the corresponding WDS point analysis, the concentration of Y and Hf is fit with the heterogeneous arrangement of the oxide particles inside alumina scales. Furthermore, the high magnification of EPMA observation focused on the alumina scales in the 10Al samples at 1000 °C was carried out, as shown in **Fig. 10**, in which the element distribution of yttrium and hafnium were detected to be consistent with the distribution of the white particles. **Fig. 11 (a)** and **(b)** shows the fractured surfaces of 10Al samples oxidized at 900 °C and 1000 °C, respectively. An obvious stratification of Y / Hf oxides happens in the alumina scale generated at 900 °C; in contrast with the dense particles close to substrate, outer layer possesses few white particles. Due to the exclusive blade-like structure located at the outer part of alumina scale, the outer layer with sparse oxide particles was confirmed

to be θ -alumina. Besides, the inner area with dense particles was supposed to be mainly composed of α -alumina since its strong diffraction peaks detected in the XRD pattern. However, even though the alumina scale has been proved to be dominated with α -alumina at 1000 °C for 225 h and no blade-like structure could be found at the surface, a layered distribution of particles still exists, i.e. outer part of the inner layer contains large number of particles whereas an extremely thin outer layer and the inner region show few particles. Moreover, the coarsened alumina grains could be observed at the inner area, as shown in the **Fig. 11 (b)**, where the obvious outline of grain boundaries could be observed.

4. Discussion

The oxide scales formed on the 5 and 10 Al Co-based ODS superalloys seem to fit with the conventional Co-Cr-Al oxide map [25] even the oxide particles had been implanted during alloy manufacturing, as shown in **Fig. 12**, in which the 10Al (20 at %) sample exhibits “single layer” alumina former as well as 5Al (10 at %) shows duplex scale with chromia and internal alumina. The only difference is the existence of CoCr_2O_4 scale in 5Al samples, which is thin at 900 °C but thicker at 1000 °C. In the case of Cr-containing Co-based alloys, the cobalt is oxidized to CoO and could in turn react with Cr_2O_3 to form the protective CoCr_2O_4 compound oxide with a spinel structure [32-34]. At 900 °C, the 5Al shows internal alumina precipitates and an intact CoCr_2O_4 / Cr_2O_3 scale. The outer CoCr_2O_4 / Cr_2O_3 is protective for the 5Al at 900 °C, as proved with the less weight gain in the **Fig. 1**. With the temperature increasing to 1000 °C, it is widely reported that the loss of Cr_2O_3 as the volatile CrO_3 would occur [28], which could be associated with the pores in the surface (**Fig. 5**) and cross-section (**Fig. 6**). Kofstad et al. [33] claimed that the pores increase the oxidation, since gaseous oxygen can be transported across the pores. However, the internal alumina precipitates of the 5Al at 900 °C is able to evolve into a continuous alumina layer at 1000 °C, as shown in the **Fig. 7 (b)**. The internal alumina layer at 1000 °C should be α -alumina, since noticeable α -alumina peaks in the XRD pattern of the 5Al (**Fig. 3**) were detected at 1000 °C, which is consistent with the growth of this internal

alumina. The evolution of this internal alumina is strongly related to the inward transport of oxygen and outward transport of Al in the Co substrate (fcc structure). If the outward supply of Al to the oxide / substrate interface is relatively higher than the inward oxygen diffusion flux, then Al_2O_3 layer can be developed in the alloy substrate. This is similar phenomenon that was known as “transition from internal to external oxidation” [35, 36]. Therefore, the transition from internal precipitates to the layered Al_2O_3 structure is attributed to a higher diffusivity coefficient of Al in the cobalt matrix (fcc structure) at 1000 °C. Cui et al. [37] studied the interdiffusion in the fcc Co-Al binary alloys at various temperature, and found that the interdiffusion coefficient at 1000 °C is one order of magnitude higher than that at 900 °C. Even though oxygen diffusivity possesses a stronger dependency on temperature, it is not enough to overpass aluminum diffusivity [38].

Furthermore, in comparison with a constant k_p value at 900 °C, the oxidation kinetics of the 5Al at 1000 °C deviated from the parabolic law, as shown in the **Fig. 2 (a)**. The decreased oxidation rate with exposure time at 1000 °C was proposed to derive from the internal α -alumina, which developed to be a continuous layer gradually and then dominated the oxidation process. Irving et al. [25] studied the Al-free Co-based alloys with the same basic compositions, namely, Co-20Cr (wt %) alloys, and found that this conventional one shows a much higher oxidation rate with only CoCr_2O_4 / Cr_2O_3 forming at 1000 °C. The oxidation resistance of the 5Al is far better than that one.

In the case of 10Al specimen, as predicted with the Co-Cr-Al oxide map (**Fig. 12**), a “single layer” of alumina could form with a higher Al supply. However, due to a different structure of the alumina, i.e., the co-existence of θ / α -alumina at 900 °C and the primary α -alumina at 1000 °C, the distribution of Y / Hf particles inside the alumina is much different, which is consistent with the fine white precipitates in the **Fig. 11**. In accordance with our previous work [27], we reported that a large number of Y-Hf oxide particles ($\text{Y}_2\text{Hf}_2\text{O}_7$ / $\text{Y}_2\text{Hf}_7\text{O}_{17}$) are distributed in substrate. The Y-Hf particles possess extremely high thermodynamic stability [20, 24] and serve as primary strengthening particles for the Co-based ODS superalloys at high temperature.

The Y-Hf particles were existed in the substrate before oxidation, and incorporated in the alumina scale due to the metal surface recession with the growth of alumina. Hence, the particles with white contrast in the alumina scale were considered to contain the Y-Hf-O dispersoids, which are a kind of the marker to indicate the original metal surface. The detailed chemical component of the white particles cannot be identified at present work. Y / Hf oxides are used to define it, since the **Figs 9 and 10** show that white particle-enriching area contains high Y and Hf element.

At 900 °C, the particles were observed in the middle part of alumina scale, which means the alumina containing the particles grew inward and the upper parts with free particles grew outward. According to the particles distribution, the alumina scale in 900 °C could be separated and defined to be the outer and inner part, as marked in the **Fig. 9** and **Fig. 11**, referring the layer determined by outward and inward growth, respectively. The growth process of θ -alumina has been certified to be dominated by outward aluminum diffusion [30], fitting the most outer layer in the 10Al samples at 900 °C, in which besides the unique blade-like structure, almost no particles could be detected. With the temperature increasing to 1000 °C, the outer layer with free particles was still formed, but it is much thinner than that formed at 900 °C, as show in the **Fig. 9** and **Fig. 11**. Since several faint θ -alumina peaks were detected with XRD patterns in 16 h, the θ -alumina should also exist in the early part of oxidation, which rapidly transformed to α -alumina during the initial stage at 1000 °C, resulting in the formation of the extremely thin outer layer. The particles were found to substantially decorate in the area beneath this extremely thin outer layer, suggesting the growth of the alumina scale was mainly toward the substrate. After formation of α -alumina, scale growth is controlled by the inward oxygen diffusion. However, a free-particle zone could be observed in the inner part of the α -alumina, as marked with “Inner / Few particles” in the **Fig. 11**. An accelerated intergranular diffusion of Y / Hf ions at high temperature had been considered to play a certain role on the shortage of Y / Hf oxide particles in this inner layer [39, 40]. Pint [41] verified that the RE ions use grain boundaries as pathways for diffusion from the metal substrate to the gas interface at high temperature, which leads to free-RE zone in the inner scale. The driving force for

this outward diffusion is the oxygen potential gradient across the scale. The oxidation processes of the 10Al samples oxidized at 900 °C and 1000 °C are summarized and shown schematically in **Fig. 13**.

In addition, it should be noted that the 10Al sample also exhibited an obvious deviation from classical parabolic kinetics at 1000 °C, as described in the **Fig. 2 (b)**. This characteristic scaling kinetics has often been found for the growth rates of α -alumina on reactive-element (RE)-containing alloys, which is frequently close to cubic time dependence [29, 42, 43]. It was explained by the assumption that oxygen inward diffusion dominates scale-growth process and the oxide grain size increases in the growth direction [30, 44]. In the present study, it is difficult to derive cubic scaling kinetics from the limited data of mass gains. However, the scale-growth for the 10Al at 1000 °C was dominated by oxygen inward diffusion, which has been proved by analyzing the Y / Hf particles distribution. In addition, coarsening alumina grains near the substrate were observed, as shown in the **Fig. 11 (b)**, which implies that the enlargement of the α -alumina grain occurs in the direction of the scale / substrate interface.

5. Conclusions

The high-temperature oxidation behavior of Co-based superalloys has been characterized through a study on the oxidation of the novel Co-20Cr-(5, 10) Al (wt %) ODS superalloys at 900 °C and 1000 °C in air. The following conclusions can be drawn:

(1) Even though the alloy is ODS with small substrate grain size which can enhance outward Al diffusion, 5Al is not sufficient to form Al_2O_3 . The 10Al specimens possess a better oxidation resistance with the formation of an exclusive alumina scale than the 5Al specimens with a duplex scale of CoCr_2O_4 / Cr_2O_3 and internal Al_2O_3 .

(2) A faster θ - to α -alumina transformation at higher temperature is responsible for the smaller weight gain at 1000 °C than at 900 °C for the 10Al specimens oxidized in 225 h, i.e., θ - and α -alumina coexist at 900 °C whilst α -alumina dominates at 1000

°C. Since the confirmation that the θ -alumina grows with cation outward diffusion and the α -alumina forms with oxygen inward diffusion, the alumina scale growth of 10Al is determined by bilateral diffusion of cation outward and oxygen inward at 900 °C and by oxygen grain boundary transport at 1000 °C.

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Fig. 1 Weight gain curves for the 5Al and the 10Al Co-based ODS superalloys oxidized at 900 °C and 1000 °C in air for 225 h.

Fig. 2 The fitted parabolic curves for the 5Al (a) and the 10Al (b) Co-based ODS superalloys oxidized at 900 °C and 1000 °C in air for 225 h.

Table 1

Parabolic rate constants obtained from the 5Al and the 10Al Co-based ODS superalloys oxidized at 900 °C. The listed values are the squares of the gradients in Fig. 2.

Superalloys	Parabolic rate constant, k_p ($\text{mg}^2 \text{cm}^{-4} \text{h}^{-1}$)
5Al	2.48×10^{-3}
10Al	2.34×10^{-3}

Fig. 3 XRD results for the 5Al (a) and the 10Al (b) Co-based ODS superalloys oxidized at 900 °C and 1000 °C in 225 h.

Fig. 4 Grazing incidence XRD results obtained from a number of short-term oxidation, (a) and (b) represents the results of the 10Al alloys obtained at 900 °C and 1000 °C, respectively.

Fig. 5 Surface morphologies obtained from the 5Al (a, b) and the 10Al (c, d) samples oxidized in 225 h, (a) and (c) for 900 °C as well as (b) and (d) for 1000 °C.

Fig. 6 Cross sections of the samples oxidized at 900 °C and 1000 °C in 225 h, (a) and (b) for the 5Al samples as well as (c) and (d) for the 10Al samples.

Fig. 7 EPMA elemental mappings obtained from the 5Al samples oxidized in 225 h, (a) and (b) represents the results at 900 °C and at 1000 °C, respectively.

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Fig. 10 Distribution of Y / Hf oxides in alumina scale of the 10Al sample oxidized at 1000 °C in 225 h, which was obtained from high magnification EPMA element mappings.

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