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Author(s)	Yu, Hao; Ukai, Shigeharu; Hayashi, Shigenari; Oono, Naoko Hori
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Effect of Cr and Y₂O₃ on the oxidation behavior of Co-based oxide dispersion strengthened superalloys at 900 °C

Hao Yu^{a*}, Shigeharu Ukai^b, Shigenari Hayashi^c and Naoko Hori Oono^b

^aGraduate school of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo 060-8268, Japan

^bFaculty of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo 060-8268, Japan

^cDepartment of Materials Engineering, Tokyo Institute of Technology, Japan

E-mail of the corresponding author: qqyu1111@163.com (Hao Yu)

Abstract

In order to study the effect of Cr and Y₂O₃ addition on the oxidation behavior of novel Co-20Cr-10Al (wt.%) oxide dispersion strengthened (ODS) superalloys, an isothermal oxidation test was carried out at 900 °C in air. The addition of Cr altered the oxide scale from the multilayered scale with an external Co oxide / CoAl₂O₄ and an inner Al₂O₃ to a single Al₂O₃ scale. Y₂O₃ addition increased oxidation mass gain slightly but improved spallation resistance of the external Al₂O₃ scale.

Keywords

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

1. Introduction

Although cobalt-based alloys show less strength than nickel-based alloys at higher temperatures, they are still the first choice for use in some critical components, such as gas turbines due to their outstanding hot corrosion resistance [1-3]. In order to make full use of this advantage and broaden application prospects, the advanced strengthening approaches for developing Co-based alloys are considered. Conventional Co-based alloys are strengthened by W, Mo, Ta and Cr carbide precipitates, but this strengthening method fails above 800 °C due to carbide coarsening or dissolution [4]. Lately, although a γ' -Co₃(Al, W) precipitate strengthened Co-Al-W system has been developed, this γ' -phase is stable below the temperature of around 900 °C [5-7]. Based on the superiority of oxide dispersion strengthening (ODS) with stable oxide particles up to 1200 °C [8-12], the development of Co-based ODS superalloys has recently been proposed [13-15].

As the operating temperature rises, the oxidation resistance approaches another critically important point which should be concerned, as well. In general, a superior high-temperature oxidation resistance can be achieved through developing an outer/single Al₂O₃ scale because of its higher stability and slow growth rate at elevated temperatures. The alumina-former requires alloys with a composition high in Al, which is unavailable in the conventional Co-based alloys due to their limited Al content [5, 6, 16, 17]. Even though Klein et al. reported that several additional elements like boron and silicon can improve the oxidation resistance of γ' strengthened Co-based alloys [18, 19], it is still impossible for the single alumina formation. However, in the case of Co-based ODS superalloys, there is no limitation on the alloys design and the composition can be controlled flexibly, which makes it possible to form the alumina scale.

In order to develop Co-base ODS superalloys with excellent mechanical properties and oxidation resistance at an elevated temperature, the Co-20Cr-10Al-2.4Hf-1.5Y₂O₃ (wt.%) ODS superalloys were proposed. The basic Co-20Cr-10Al (wt.%) system was designed based on a Co-Cr-Al phase diagram computed with the thermodynamic software Pandat [20]. The composition contains

the Co solid solution phase with fcc structure, and B2 phase with bcc structure. This offers the possibility of good ductility and favorable strength, respectively. It was expected that the 20 wt.% Cr addition would retain favorable corrosion resistance and enhance the formation of an external Al_2O_3 scale, by analogy to the Cr effect on Fe-(Cr, Al) and Ni-(Cr, Al) ODS superalloys [21-25]. The 10 wt.% Al addition guarantees the formation of appropriate B2 phase and an abundant Al supply for alumina-formation. The addition of 2.4Hf-1.5Y₂O₃ (wt.%) is necessary for the Y-Hf-O particles, which strengthened the alloys at elevated an temperature [15, 26].

It is well known that Cr and Y₂O₃ affect the oxidation resistance of conventional Co-based alloys and Fe-based ODS superalloys [25, 27, 28]. Irving et al. claimed that the addition of Cr to Co-Al base alloys markedly reduced the level of Al required in the ternary alloy below that required in the binary to form a continuous external scale of Al_2O_3 [28]. Klein et al. proved that the Cr in the γ' strengthened Co-based alloys possesses a deleterious influence on the γ' stability [18]. Quadakkers et al. reported that the presence of the Y₂O₃ decreased oxide growth rates by reducing cation diffusion in scales and causing the oxides on the Fe-based ODS alloys to grow mainly by oxygen grain boundary transport [25]. However, since the Co-based ODS system has received much less attention than the Ni-based ODS and Fe-based ODS superalloys, and the study of high-temperature oxidation in Co-based ODS superalloys has essentially not been conducted [29, 30], we have little information regarding the influence on the Co-based ODS superalloys.

In this research, the high temperature oxidation of the novel Co-based ODS superalloys in air was explored, along with the influence of Cr and Y₂O₃ addition. A temperature of 900 °C was chosen to be the target operating temperature. This temperature is above the critical temperature of the Co-based alloys strengthened by carbide, and close to the ultimate temperature of the one strengthened by γ' precipitates [4, 31].

2. Experimental procedure

The Co-based ODS superalloys were designed and fabricated by mechanical

alloying (MA), spark plasma sintering (SPS), hot rolling and final annealing at 1200 °C. The detailed microstructure and the phases formed in the Co-based ODS superalloys were investigated and interpreted elsewhere [14]. In order to evaluate the effect of Cr and Y₂O₃ on oxidation behavior at 900 °C, three kinds of compositions were prepared, as shown in **Table 1**, in which abbreviations are used to define each alloy. The detailed fabrication process was exhibited in our previous work [29]. Prior to oxidation testing, all the surfaces of the samples were wet ground and polished using 1 μm diamond paste and then ultrasonically cleaned in ethanol. An isothermal oxidation test was carried out at 900 °C in a muffle furnace in air, and the oxidation weight gains for different exposure times were measured by a Sartorius precision electronic balance (1 μg).

The crystalline structures of oxide layers were characterized using X-ray diffraction (XRD, Philips X' Pert PRO), with a 3 ° incident angle in order to obtain the diffracted signals from thin oxide scales. The microstructures of the surface in oxide scales were observed with a scanning electron microscope (SEM, Carl Zeiss Cross Beam 1540 EsB). The elements distribution across an oxide scale was analyzed with an electron probe micro-analyzer (EPMA, JEOL JXA-8530F). The distribution of nano-sized oxide particles in oxide scales was analyzed using transmission electron microscopy (TEM, JEM-2010), in which the cross-sections of a thickness near 100 nm were prepared by focused ion beam milling and FE-SEM imaging (FIB-SEM, JEOL JIB-4600F/HKD).

3. Results

3.1 Effect of Cr-addition

Fig. 1 shows the Co-Cr-Al phase diagram computed by the thermodynamic software Pandat [20], where the composition of Co-10Al (wt.%) and Co-20Cr-10Al (wt.%) are marked with round and triangular symbols, respectively. The volume fraction of B2 CoAl is almost equal to that in the fcc Co solid solution for Co-20Cr-10Al (wt.%), but less for Co-10Al (wt.%). **Fig. 2** shows the back scattered electron (BSE) images of the fabricated 10AlCrY and 10AlY alloys, where the grey

and dark areas correspond to the fcc matrix and the B2 phase, respectively. The 10AlCrY sample contains an almost equivalent volume fraction of the fcc phase and B2 phase, whereas the 10AlY possesses only 39% B2 phase. This result is consistent with the computed phase diagram shown in **Fig. 1**.

The measured weight changes for the 10AlY and 10AlCrY as a function of exposure time at 900 °C in air are shown in **Fig. 3 (a)**. Both Co-based ODS superalloys with and without Cr addition presented a low oxidation rate and a good spalling resistance up to 225 h. However, the oxidation kinetics was affected significantly by the Cr addition. Initially, the oxidation rate of 10AlY sample in the incipient stage up to 1 h was much faster than the 10AlCrY sample, resulting in a mass gain of up to 0.34 mg/cm² in 1 h, which is more than half of the total mass gain in the entire experiment. Subsequently, the rate of mass gain in 10AlY alloy decreased much more quickly with time than the 10AlCrY alloy. When the growth of oxide scale is controlled by diffusion through the oxide scale, mass gain follows a parabolic law [32, 33]:

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

where ΔW is the weight gain of the sample taken for unit surface area, k_p is the parabolic rate constant, t is the time of exposure, and C is a constant which showed the deviations from the parabolic law during the initial stages of oxidation. **Fig. 3 (b)** shows the mass gains as a function of the square root of time, in which the solid line denotes the fitted results. According to the kinetic measurements, the oxidation of the 10AlCrY sample complies with the parabolic law defined as **Eq. (1)** in 225 h, where the values of k_p and C are corresponding to $6.5 \times 10^{-7} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$ and 0.01 mg/cm^2 , respectively. However, one straight line cannot be drawn throughout the whole oxidation of 225 h in 10AlY. The 10AlY seems to have gone through different oxidation stages, i.e. a rapid mass gain in the initial stage (0-1 h), followed by reduced oxidation rates in the subsequent oxidation (1-225 h).

Fig. 4 and **Fig. 5** show the XRD patterns and surface morphologies of two

specimens oxidized at 900 °C. Based on the detected characteristic peaks in the X-ray diffraction pattern, Co oxide (Co_3O_4 / CoO) in the 10AlY oxide scales and Al_2O_3 in the 10AlCrY oxide scales were determined, which correspond to the unique granule-like shape of Co oxide and the typical blade-like structure of alumina in **Fig. 5 (a)** and **(b)**, respectively.

The cross-sections of oxide scale formed on 10AlY and 10AlCrY after different exposure times (1h, 4h, 25h and 100h) at 900 °C were observed. **Fig. 6** shows the results of 1 h, in which the EPMA elemental mapping was conducted to investigate the initial scales. **Fig. 6 (a)** shows an obvious grey oxide film (Co oxide) on the surface of the 10AlY sample, which is much thicker than the scale formed in the 10AlCrY sample. Additionally, Al_2O_3 was confirmed as forming below the outer cobalt oxide. In contrast, a thin oxide scale was found in the 10AlCrY sample, as shown in the **Fig. 6 (b)**, an Al-containing scale developed near the dark area (B2) and a Cr-containing scale formed on the grey area (fcc). **Fig. 7** shows the cross-sections of 4h, 25h and 100h, based on a different contrast in the oxide layers with the BSE images, the formation of a multilayered oxide scale on the 10AlY alloys and a single scale on 10AlCrY samples can be confirmed along with the oxidation time. In order to make certain of the element distribution in each oxide scale, EPMA elemental mappings of the cross-sections were conducted and the results are presented in **Fig. 8**. **Fig. 8 (a)** proves that the oxide scales in the 10AlY alloy are composed of three layers, i.e. in addition to an external scale containing Co and an inner scale including Al, there is another intermediate layer of enriched Co and Al. **Fig. 8 (b)** shows that the homogeneous oxide layer in the 10AlCrY contains aluminum and oxygen elements, which can be easily defined as alumina according to the results of XRD. Chromia was not observed at 25 h oxidation. EPMA wavelength dispersive spectrometer (WDS) point analysis was carried out to more accurately determine the complex scales in the 10AlY alloy after 225 h oxidation, as shown in **Fig. 9**. Results suggest that the atomic percentages of all layers are correspondingly approximate to external Co oxide, inner Al_2O_3 and intermediate layer of CoAl_2O_4 . Additionally, the outer Co oxide was found to be uneven with a different thickness as well as the inner Al_2O_3 , which was

decorated with amounts of white particles, as shown in the **Fig. 10** of the fractured cross-sections.

3.2 Effect of Y_2O_3 -addition

Fig. 11 (a) shows the oxidation kinetics of 10AlCr alloys without Y_2O_3 addition at 900 °C, in which the result of 10AlCrY is also inserted to highlight the effect of Y_2O_3 addition. In contrast to the 10AlCrY ODS superalloy, the 10AlCr without yttria addition seems to maintain a better oxidation resistance, characterized by a smaller weight gain and a slower oxidation rate. The oxidation kinetics of 10AlCr does not conform to parabolic behavior, showing a continuous decrease in the parabolic rate with exposure time, as shown in **Fig. 11 (b)**.

Based on the XRD and EPMA characterization, as shown in **Fig. 12** and **Fig. 13**, the scale formed in the 10AlCr alloys was also determined as alumina. However, voids along the matrix/scale interface in the 10AlCr were found from the SEM image in **Fig. 14 (a)**. This is evidence of an inferior adherence of oxide scale in 10AlCr than that in 10AlCrY, which contains no noticeable voids, as shown in **Fig. 14(b)**.

In order to distinguish the difference between the two alumina scales formed on 10AlCr and 10AlCrY at 900 °C, TEM observation was performed, and the results are shown in **Fig. 15**. This clearly indicates that the Al_2O_3 scale in 10AlCrY has been decorated with a mass of particles through comparing the TEM bright-field images of **Fig. 15 (a)** and **(b)**. Additionally, the alumina grains in the 10AlCrY sample are smaller than those in the 10AlCr, as shown in the TEM dark-field images of **Fig. 15 (c)** and **(d)**. Based on the EPMA elemental mappings of Y and Hf in the alumina-scale (**Fig. 16**), the particles were determined as being Y-Hf oxides in accordance with the oxide characterization in reference [14].

4. Discussion

4.1 Effect of Cr-addition

In comparison with a smooth mass gain of the 10AlCrY sample, the 10AlY sample without Cr addition showed a complex oxidation process, i.e. an extremely

rapid oxidation rate at the beginning of the oxidation in the first 1 h and a significantly reduced oxidation rate during the late period. At the initial stage of oxidation, the 10AlY sample formed Co oxides and resulted in a continuous Co-oxide scale in an external layer, as shown in the **Fig. 6 (a)**. An obvious grey oxide film (Co oxide) was found on the surface of the 10AlY sample at 1 h oxidation, which was much thicker than the scale formed in the 10AlCrY sample. Therefore, the rapid mass gain of the 10AlY sample during the initial oxidation stage (0-1 h) should be attributable to the formation of the outer Co-oxide which had much higher growth rate [34]. In the subsequent oxidation stage, growth of an inner scale with a darker contrast was observed, which was determined to be alumina by EPMA elemental mapping in as in the **Fig. 8 (a)**. Since the alumina is less defective than the Co oxide, the oxidation process would be slowed down by the inner alumina layer and resulted in a decrease in the oxidation rate of the 10AlY sample. Additionally, the growth of the inner alumina could be restricted with a limited oxygen supply due to the cover of outer Co oxide and CoAl_2O_4 spinel. With the prolongation of exposure time, a noticeable increase in the thickness of the intermediate CoAl_2O_4 layer was observed, as shown in **Fig. 7**. The spinel structure of the CoAl_2O_4 layer was confirmed with a significant blocking effect on the diffusion of cations and anions [35], which was responsible for the oxidation kinetics with a slower rate during the oxidation process. The overall oxidation was considered to be still controlled by oxygen and/or Al diffusion in the inner Al_2O_3 scale. However, multiple oxide scales formed in the 10AlY sample, and such changes in the thickness of each layer may have resulted in a deviation in the overall oxidation kinetics from the parabolic behavior, as shown in **Fig 3 (b)**.

With the addition of Cr, the formation of Co-oxides was suppressed and a thin oxide scale enriched Al and Cr was produced on the surface of the 10AlCrY sample at 1 h, as shown in **Fig. 6 (b)**. EPMA mapping indicated that an initial chromia (Cr_2O_3) scale formed on 10AlCrY particularly on the regions of the fcc matrix, which contained more Cr. Subsequently, chromia could be dissolved into the alumina because both phases underwent a complete solid solution at 900 °C. It is well known that the presence of Cr in Fe- and Ni-based alloys can reduce the Al level needed to

form a protective Al_2O_3 layer [36, 37], defined as the third-element effect (TEE) [38]. This indicates that the addition of a third-element B to binary A–C alloys can decrease the critical C concentration needed to establish an external scale of the C oxide, in which A is the most inert element and C is the most reactive one in the ternary system [36]. The TEE seems to work in the Co-based ODS superalloys, since the Cr possesses an oxygen affinity falling in between those of Co and Al, and also the addition of Cr reduces the concentration of Al required to establish an external alumina scale. This is shown in **Fig. 7**, where an exclusive alumina scale could be formed by adding Cr to the 10AlY sample. The mechanism of TEE is not yet completely clear, but based on the suggestion claimed by Wagner [38, 39], it is supposed that an initial external Cr_2O_3 scale promotes Al_2O_3 formation. In this study we did not observe Cr_2O_3 formation at the very early stages of oxidation. However, Cr_2O_3 formation was expected since a Cr-containing scale was observed after 1 h oxidation and Co-rich oxide scale formation was completely suppressed by Cr addition.

In addition, based on the phase diagram (**Fig. 1**), due to the addition of 20Cr (wt. %), the volume fraction of CoAl (B2) increased from 39% in the 10AlY to 50% in the 10AlCrY, which is consistent with the increase of the dark areas (B2) from **Fig. 2 (a)** to **Fig. 2 (b)**. As mentioned above, the B2 phase contained a higher Al content than the fcc phase, and so the alumina scale was more easily generated at the surface of the B2 phase than at the fcc phase in the initial stages of oxidation. Due to the higher volume fraction of CoAl in the 10AlCrY alloy, the Al content in the fcc matrix must have decreased. Although this decrease in Al content in the fcc matrix was not favorable for Al_2O_3 scale formation, the fcc matrix contained higher Cr, which promoted external Al_2O_3 scale formation by the TEE, as mentioned above. The 10AlY which does not contain Cr, formed Co oxides due to a high percentage of cobalt solid solution regions, resulting in a continuous Co-oxide scale in an external layer. Even though initially small amounts of alumina formed on the B2 phase region in 10AlY, it was insufficient to evolve into a complete outer alumina scale. However, the formation of Co oxide near the B2 phase was substantially suppressed, which lead to

the uneven morphology of the outer Co oxide scale, as shown in **Fig. 10**.

4.2 Effect of Y_2O_3 -addition

Although both the samples with and without Y_2O_3 maintained a single alumina scale, the growth mechanism of the alumina in 10AlCrY and 10AlCr changed because of the differences in oxidation kinetics and the microstructure. Namely, the 10AlCrY exhibited a larger weight gain and resulted in a thicker alumina scale than the 10AlCr alloy. The alumina scale in 10AlCrY is decorated with abundant particles, and its grain size is smaller than that of the 10AlCr.

Based on reports that the dispersed particles can effectively decrease the alumina grain size in Fe-ODS and Ni-ODS superalloys [40-42], the fine grain size of alumina in 10AlCrY alloys was attributed to the distribution of Y-Hf complex oxide particles in the Al_2O_3 scale. Even though the alumina scale is composed of θ - and α -alumina, the Al_2O_3 layer which contains Y-Hf oxide particles is presumed to be α -alumina since it grows inwards [29]. Due to the pinning effect of such dense oxide particles [43, 44], the grain enlargement of α -alumina scale can be effectively suppressed; many particles are located within the alumina grains and disperse along the grain boundaries, as shown in the TEM images (**Fig. 15**). Consequently, a high grain boundary density exists in the alumina-scale of 10AlCrY and it accelerates the transport of Al outward and oxygen inward, which was considered to be a reason for the enhanced oxidation rate in the 10AlCrY.

By contrast, unlike the shape of the alumina grain in the 10AlCrY which is more close to equiaxed morphology, a noticeable columnar grain was observed in the sample of 10AlCr, as evidenced by the dark field images shown in **Fig. 15**. Based on the reports regarding the alumina-forming scale on FeCrAl alloys [45, 46], the columnar grains with a lateral size which increased linearly with depth beneath the scale surface is responsible for the reduction of the k_p value given the decreased density of grain boundary along with the exposure time. Even an overall distribution of the alumina grains was not exhibited in the TEM images, the coarsening of the columnar grains with the direction towards the substrate was also supposed to occur

in the 10AlCr because of the restricted oxygen inward diffusion near the interface of scale/substrate.

However, as shown the fracture surfaces in **Fig. 14**, in comparison with a superior adherence of alumina scale in the 10AlCrY, some voids were detected along the alloy/scale interface of the 10AlCr after the exposure at 900 °C. In the case of conventional alloys, the voids can often be observed at the alloy/scale interface due to the Kirkendall effect [47, 48]. But according to the suggestion by Arun et al. [49], the interfaces between Y-Hf oxide particles in the 10AlCrY were considered to act as vacancy sinks at sites away from the alloy/oxide interface, hence significantly suppressing the void formation and improving the oxide-scale adherence. Additionally, the segregation of Y-Hf oxide particles along the grain boundary can play a role in the reduction of voids by decreasing the cation outward diffusion with a blocking effect [25, 40].

5. Conclusions

To investigate the effect of Cr and Y₂O₃ on the oxidation behavior of a novel Co-20Cr-10Al (wt.%) ODS superalloy, the isothermal oxidation test was carried out at 900 °C in air. The addition of Cr into Co-based ODS superalloys effectively improved high-temperature oxidation resistance by promoting the formation of an exclusive alumina scale instead of the multilayered scale with an external Co oxide /CoAl₂O₄ and an inner Al₂O₃. Although Y₂O₃ addition accelerated the oxidation rate by suppressing the grain growth of the alumina scale, the spallation resistance of this external Al₂O₃ scale could be significantly improved with the distribution of fine Y-Hf oxide particles. Based on the doping of Cr and Y₂O₃, a favorable single alumina scale was generated and the Co-20Cr-10Al (wt.%) ODS superalloy was expected to be available at an elevated temperature.

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References

- [1] J.H. Bilbrey, Cobalt: A Materials Survey, U.S. Bureau of Mines, 1962 3–5.
- [2] D. Coutsouradis, A. Davin, M. Lamberigts, Cobalt-based superalloys for applications in gas turbines, *Mater. Sci. Eng.* 88 (1987) 11–19.
- [3] L.F. Liu, S.S. Wu, Y.B. Dong, S.L. Lu, Effect of alloyed Mn on oxidation behaviour of a Co-Ni-Cr-Fe alloy between 1050 and 1250 °C, *Corros. Sci.* 104 (2016) 236–247.
- [4] S.H. Zangeneh, H. Farhangi, Influence of service-induced microstructural changes on the failure of a cobalt-based superalloy first stage nozzle, *Mater. Des.* 31 (2010) 3504–3511.
- [5] J. Sato, T. Omori, K. Oikawa, I. Ohnuma, R. Kainuma, K. Ishida, Cobalt-base high-temperature alloys, *Science* 312 (2006) 90–91.
- [6] L. Klein, A. Bauer, S. Neumeier, M. Goken, S. Virtanen, High temperature oxidation of γ/γ' -strengthened Co-base superalloys, *Corros. Sci.* 53 (2011) 2027–2034.
- [7] N. Vermaak, A. Mottura, T.M. Pollock, Cyclic oxidation of high temperature coatings on new γ' -strengthened Co-based alloys, *Corros. Sci.* 75 (2013) 300–308.
- [8] S. Ukai, S. Ohtsuka, Nano-mesoscopic structure control in 9Cr–ODS ferritic steels, *Energy Mater.* 2(1) (2007) 26–35.
- [9] S. Ukai, T. Kaito, S. Ohtsuka, T. Narita, M. Fujiwara, T. Kobayashi, Production and properties of nano-scale oxide dispersion strengthened (ODS) 9Cr martensitic steel claddings, *ISIJ int.* 43 (2003) 2038–2045.
- [10] S. Ukai, M. Fujiwara, Perspective of ODS alloys application in nuclear environments, *J. Nucl. Mater.* 307–311 (2002) 749–757.
- [11] M. Yamamoto, S. Ukai, S. Hayashi, T. Kaito, S. Ohtsuka, Formation of residual ferrite in 9Cr-ODS ferritic steels, *Mater. Sci. Eng. A* 527 (2010) 4418–4423.
- [12] Q. Tang, T. Hoshino, S. Ukai, B. Leng, S. Hayashi, Y. Wang, Refinement of oxide particles by addition of Hf in Ni-0.5 mass%Al-1 mass%Y₂O₃ Alloys, *Mater. Trans.* 51 (11) (2010) 2019–2024.
- [13] L. Zhang, X.H. Qu, X.B. He, R.U. Din, H.S. Liu, M.L. Qin, H.M. Zhu, Microstructural characterization of Co-based ODS alloys, *J. Mater. Eng. Perform.* 21 (2012) 2487–2494.
- [14] H. Yu, S. Ukai, N. Oono, T. Sasaki, Microstructure characterization of Co-20Cr-(5, 10)Al oxide dispersion strengthened superalloys, *Mater. Charact.* 112(2016)188–196.
- [15] H. Yu, S. Ukai, N. Oono, Tensile properties of Co-based oxide dispersion strengthened superalloys, *J. Alloy and Comp.*, 714 (2017) 715–724.
- [16] G.N. Irving, J. Stringer, D.P. Whittle, The high-temperature oxidation resistance of Co-Al alloys, *Oxid. Met.* 9 (1975) 427–440.
- [17] P.S. Liu, K.M. Liang, High-temperature oxidation behavior of the Co-based superalloy DZ40M in air, *Oxid. Met.* 53 (2000) 351–360.
- [18] L. Klein, Y. Shen, M. Killian, S. Virtanen, Effect of B and Cr on the high

- temperature oxidation behavior of novel γ/γ' -strengthened Co-base superalloys, *Corros. Sci.* 53 (2011) 2713–2720.
- [19] L. Klein, M. Killian, S. Virtanen, The effect of nickel and silicon addition on some oxidation properties of novel Co-based high temperature alloys, *Corros. Sci.* 69 (2012) 43–49.
- [20] W. Cao, S.L. Chen, F. Zhang, K. Wu, Y. Yang, Y.A. Chang, R. Schmid-Fetzer, W.A. Oates, PANDAT software with PanEngine, PanOptimizer and PanPrecipitation for multi-component phase diagram calculation and materials property simulation, *Calphad* 33 (2009) 328–342.
- [21] L. Marechal, B. Lesage, A.M. Huntz, R. Molins, Oxidation behavior of ODS Fe–Cr–Al alloys: aluminum depletion and lifetime, *Oxid. Met.* 60 (2003) 1–28.
- [22] G.R. Wallwork, A.Z. Hed, Some limiting factors in the use of alloys at high temperatures, *Oxid. Met.* 3 (1971) 171–184.
- [23] T. Liu, C.X. Wang, H.L. Shen, W.S. Chou, N.Y. Iwata, A. Kimura, The effect of Cr and Al concentrations on the oxidation behavior of oxide dispersion strengthened ferritic alloys, *Corros. Sci.* 76 (2013) 310–316.
- [24] T. Liu, L.B. Wang, C.X. Wang, H.L. Shen, Effect of Al content on the oxidation behavior of $Y_2Ti_2O_7$ -dispersed Fe-14Cr ferritic alloys, *Corros. Sci.* 104 (2016) 17–25.
- [25] W.J. Quadakkers. Growth mechanisms of oxide scales on ODS alloys in the temperature range 1000–1100 °C, *Werkstoffe und Korrosion* 41 (1990) 659–668.
- [26] L. Zhang, S. Ukai, T. Hoshino, S. Hayashi, X. Qu, Y_2O_3 evolution and dispersion refinement in Co-base ODS alloys, *Acta Mater.* 57 (2009) 3671–3682.
- [27] F.B. Ismail, V.A. Vorontsov, T.C. Lindley, M.C. Hardy, D. Dye, B.A. Shollock, Alloying effects on oxidation mechanisms in polycrystalline Co-Ni base superalloys, *Corros. Sci.* 116 (2017) 44–52.
- [28] G.N. Irving, J. Stringer, D.P. Whittle, The oxidation behavior of Co-Cr-Al alloys at 1000 °C, *Corrosion-Nace* 33 (1977) 56–60.
- [29] H. Yu, S. Ukai, S. Hayashi, N. Oono, Effect of Al content on the high-temperature oxidation behavior of Co-20Cr-(5, 10)Al oxide dispersion strengthened superalloys, *Corros. Sci.* 118 (2017) 49–59.
- [30] H. Yu, S. Ukai, S. Hayashi, N. Oono, Effect of Cr on the Oxidation Resistance of Co-based Oxide Dispersion Strengthened Superalloys, *Mater. Trans.* (2017), <http://doi.org/10.2320/matertrans.MJ201603>.
- [31] L. Klein, B. von Bartenwerffer, M.S. Killian, P. Schmuki, S. Virtanen, The effect of grain boundaries on high temperature oxidation of new γ' strengthened Co-Al-W-B superalloys, *Corros. Sci.* 79 (2014) 29–33.
- [32] C. Wagner, Diffusion and high temperature oxidation of metals, *Atom Movements*, Ohio (1951) 153.
- [33] P. Kofstad, High-temperature oxidation of metals, John Wiley & Sons, Inc., New York 1966.
- [34] S. Mrowec, T. Walec and T. Werber, Oxidation of cobalt at high temperatures, *Corros. Sci.* 6 (1966) 287–297.
- [35] P.K. Kofstad, A.Z. Hed, High-temperature oxidation of Co-10 w/o Cr alloys, *J.*

- Electrochem. Soc. 116 (1969) 224-229.
- [36] Y. Niu, S. Wang, F. Gao, Z.G. Zhang, F. Gesmundo, The nature of the third-element effect in the oxidation of Fe-xCr-3 at.% Al alloys in 1 atm O₂ at 1000 °C, Corros. Sci. 50 (2008) 345–356.
 - [37] Y. Niu, X.J. Zhang, Y. Wu, F. Gesmundo, The third-element effect in the oxidation of Ni-xCr-7Al (x = 0, 5, 10, 15 at.%) alloys in 1 atm O₂ at 900–1000 °C, Corros. Sci. 48 (2006) 4020–4036.
 - [38] C. Wagner, Passivity and inhibition during the oxidation of metals at elevated temperatures, Corros. Sci. 5 (1965) 751–764.
 - [39] C. Wagner, Z. Elektrochem. 63 (1959) 772.
 - [40] W.J. Quadakkers, H. Holzbrecher, K.G. Briefs, H. Beske, Difference in growth mechanisms of oxide scales formed on ODS and conventional wrought alloys. Oxid. Met. 32 (1989) 67–88.
 - [41] T. Kaito, T. Narita, S. Ukai, Y. Matsuda, High temperature oxidation behavior of ODS steels, J. Nucl. Mater. 329-333 (2004) 1388–1392.
 - [42] H.J. KLAM, Temperature and oxidation resistance of the ODS materials MA 956 and PM 2000, J PHYS IV. 3 (1993) 731–734.
 - [43] V.C. Nardone, J.K. Tien, Pinning of dislocations on the departure side of strengthening dispersoids, Scr. Metall. 17 (1983) 467–470.
 - [44] S. Ukai, T. Okuda, M. Fujiwara, T. Kobayashi, S. Mizuta, H. Nakashima, Characterization of high temperature creep properties in recrystallized 12Cr-ODS ferritic steel claddings, J. Nucl. Sci. Technol. 39 (2002) 872–879.
 - [45] D. Naumenko, B. Gleeson, E. Wessel, L. Singheiser, W.J. Quadakkers, Correlation between the microstructure, growth mechanism, and growth kinetics of alumina scales on a FeCrAlY alloy, Metall. Mater. Trans. A, 38 (2007) 2974–2983.
 - [46] D.J. Young, D. Naumenko, L. Niewolak, E. Wessel, L. Singheiser, W.J. Quadakkers, Oxidation kinetics of Y-doped FeCrAl-alloys in low and high pO₂ gases, Materials and Corrosion 61 (2010) 838–844.
 - [47] M. Turker, T. A. Hughes, Oxidation behavior of three commercial ODS alloys at 1200 °C, Oxid. Met. 44 (1995) 505–525.
 - [48] J.K. Tien, F.S. Pettit, Mechanism of oxide adherence on Fe-25Cr-4Al (Y or Sc) Alloys, Metall. Trans. 3 (1972) 1587–1599.
 - [49] K. Arun, M. Nasrallah, D.L. Douglass, The effect of yttrium and thorium on the oxidation behavior of Ni-Cr-Al alloys, NASA CR-2422 (1974).

Table & Figure captions list

- Table 1** Nominal compositions of the investigated alloys and utilized abbreviations.
- Fig. 1** The ternary Co-Cr-Al phase diagram calculated with Pandat software at 1100 °C.
- Fig. 2** BSE images obtained from the samples prior to oxidation, (a) and (b) represent the 10AlY and the 10AlCrY alloys, respectively.
- Fig. 3** (a) shows the weight gain curves for the 10AlY and the 10AlCrY samples oxidized at 900 °C in air for 225 h, (b) is the fitted parabolic curves for the both samples.
- Fig. 4** Grazing incidence XRD results obtained from the 10AlY and the 10AlCrY alloys oxidized at 900 °C in air for 225 h.
- Fig. 5** Surface morphology of oxide scales oxidized at 900 °C for 25 h, (a) is 10AlY sample and (b) is 10AlCrY sample.
- Fig. 6** EPMA elemental mappings obtained from the oxidized 10AlY (a) and 10AlCrY (b) samples at 900 °C for 1 h.
- Fig. 7** Cross-sections of oxidized samples with different exposure time (4 h, 25 h, 100 h) at 900 °C, (a) is 10AlY sample and (b) is 10AlCrY sample.
- Fig. 8** EPMA elemental mappings obtained from 10AlY (a) and 10AlCrY sample (b) oxidized at 900 °C for 25 h.
- Fig. 9** EPMA WDS point analysis on the metal atomic percent of the 10AlY sample oxidized at 900 °C for 225 h.
- Fig. 10** SEM images of the fractured surface obtained from the 10AlY alloys oxidized at 900 °C for 100 h.
- Fig. 11** (a) shows the weight gain curves for the 10AlCr and the 10AlCrY alloys oxidized at 900 °C for 225 h in air, (b) is the fitted parabolic curves for the both samples.
- Fig. 12** Grazing incidence XRD results obtained from the 10AlCr sample oxidized at 900 °C for 225 h in air.
- Fig. 13** EPMA elemental mappings obtained from the 10AlCr sample oxidized at 900 °C for 4 h and 25 h.
- Fig. 14** SEM images of the fracture surface obtained from the oxidized 10AlCr (a) and 10AlCrY (b) alloys at 900 °C for 100 h.
- Fig. 15** (a) and (b) exhibit the alumina scales of the 10AlCr and the 10AlCrY at 900 °C for 225 h with TEM bright-field pattern, (c) and (d) show the morphology of the alumina grains of 10AlCr and 10AlCrY with TEM dark-field pattern.
- Fig. 16** Distribution of Y/Hf oxides in alumina scale of the 10AlCrY sample oxidized at 900 °C for 100 h.

Table 1 Nominal compositions of the investigated alloys and utilized abbreviations.

Alloys	Elements, wt. %				
	Co	Cr	Al	Hf	Y ₂ O ₃
10AlCrY	Bal.	20	10	2.4	1.5
10AlY	Bal.	0	10	2.4	1.5
10AlCr	Bal.	20	10	2.4	0

Fig. 1 The ternary Co-Cr-Al phase diagram calculated with Pandat software at 1100 °C [20].

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Fig. 8 EPMA elemental mappings obtained from 10AlY (a) and 10AlCrY sample (b) oxidized at 900 °C for 25 h.

Fig. 9 EPMA WDS point analysis on the metal atomic percent of the 10AlY sample oxidized at 900 °C for 225 h.

Fig. 10 SEM images of the fractured surface obtained from the 10AlY alloys oxidized at 900 °C for 100 h.

Fig. 11 (a) shows the weight gain curves for the 10AlCr and the 10AlCrY alloys oxidized at 900 °C for 225 h in air, (b) is the fitted parabolic curves for the both samples.

Fig. 12 Grazing incidence XRD results obtained from the 10AlCr sample oxidized at 900 °C for 225 h in air.

Fig. 13 EPMA elemental mappings obtained from the 10AlCr sample oxidized at 900 °C for 4 h (a) and 25 h (b).

Fig. 14 SEM images of the fracture surface obtained from the oxidized 10AlCr (a) and 10AlCrY (b) alloys at 900 °C for 100 h.

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Fig. 16 Distribution of Y/Hf oxides in alumina scale of the 10AlCrY sample oxidized at 900 °C for 100 h.