THE MECHANISM OF OXIDATION OF SPUTTERED Ni-Cr-Al NANOCRYSTALLINE COATINGS

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ABSTRACT

Complex layered oxide scales composed of a complete inner layer of α-Al_2O_3 were formed on the formerly Cr2O3-forming alloy Ni-8Cr-3.5Al (wt%) and the NiO-forming alloy Ni-5Cr-5Al (at%) through nanocrystallization. Due to the formation of the inner layer of α-Al_2O_3, Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) alloys with nano-sized grain were all Al_2O_3-formers. The results indicated that the oxide types of Ni-Cr-Al alloys could be altered through nanocrystallization. In this paper, the mechanism of oxidation for two Al_2O_3-forming sputtered Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) nanocrystalline coatings on the substrates of the same alloys was proposed based upon the interaction of Cr and Al during oxidation process.

KEYWORDS

Nanocrystalline coatings; Sputtering; Ni-Cr-Al; Oxidation

INTRODUCTION

The oxidation of Ni-Cr-Al alloys has received considerable attention during the past several decades and the formation mechanism of different types of oxides were proposed based upon experimental results /1,2/. Recently, it was found that the oxide types of Ni-base superalloys K38G /3,4/, K17F /5/ and LDZ125 /6,7/ were altered through nanocrystallization. Experimental results indicated that a unitary layer of α-Al_2O_3 was formed on the sputtered K38G, K17F and LDZ125 nanocrystalline coatings on the substrates of the same superalloys, whereas complex oxides of Cr, Al, Ti were formed on these cast superalloys. Therefore, the oxidation of Ni-Cr-Al alloys with nano-sized grain has been investigated in detail. It was suggested that a unitary α-Al_2O_3 scale could be formed on the Ni-20Cr-2,3,5Al (wt%) nanocrystalline coating on the substrate of the same materials /8,9/. Multi-layered oxide scales composed of a continuous inner layer of α-Al_2O_3 could be formed on the Ni-5Cr-5Al (at%) /10,11/ and Ni-8Cr-3.5Al (wt%) /12/ nanocrystalline coatings on the substrates of the same materials. According to the classification of oxide types formed on Ni-Cr-Al alloy proposed by Giggins /1/, due to the formation of this complete α-Al_2O_3 layer, all these Ni-Cr-Al alloys with nano-sized grain were considered as Al_2O_3-former. However, cast Ni-20Cr-2,3,5Al and Ni-8Cr-3.5Al (wt%) alloys with normal grain size were Cr_2O_3-former, cast Ni-5Cr-5Al (at%) alloy was NiO-former. There was no systematic investigation on the oxidation mechanism of these Ni-Cr-Al alloys with nano-sized grain. In the present study, the formation mechanisms of oxide scales formed on Al_2O_3-forming Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) together with Ni-20Cr-2,3,5Al (wt%) alloys with nano-grain have been discussed.

EXPERIMENTAL

Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) alloys were melted in a vacuum-induction furnace and then cut into specimens for oxidation and target for sputtering. Magnetron sputter deposition was used to prepare nanocrystalline coatings on the substrates of the same materials. The sputter deposition has been described in detail elsewhere /10-12/. Oxidation tests were performed at 1000°C in ambient atmosphere. After different periods of oxidation time, the weight changes of the specimens were measured. The as-sputtered coatings were characterized by atomic force microscopy (AFM). After oxidation, the oxidized specimens were examined by X-ray diffraction

(XRD), scanning electron microscopy (SEM) and energy-dispersive spectrometer (EDS).

RESULTS

Figures 1 and 2 show the AFM top-view images of the as-sputtered Ni-5Cr-5Al (at%) and Ni-8Cr-3.5Al (wt%) coatings. The grain size of these coatings was found to be less than 100 nm.

The oxidation kinetics for the sputtered Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) coatings at 1000°C in air are illustrated in Figure 3. The curves were characterized by rapidly increasing mass gains in the initial oxidation period followed by slowly increasing mass gain, which indicated that protective oxide scales were formed on the Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) coatings.

Figure 4 shows the XRD patterns for the sputtered Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) coatings after 200-h oxidation. It can be seen that Cr_2O_3, α-Al_2O_3 and $NiCr_2O_4$, $NiAl_2O_4$ spinel were formed on the Ni-8Cr-3.5Al (wt%) coating, NiO, α-Al_2O_3 and $NiAl_2O_4$ spinel were formed on the Ni-5Cr-5Al (at%) coating.

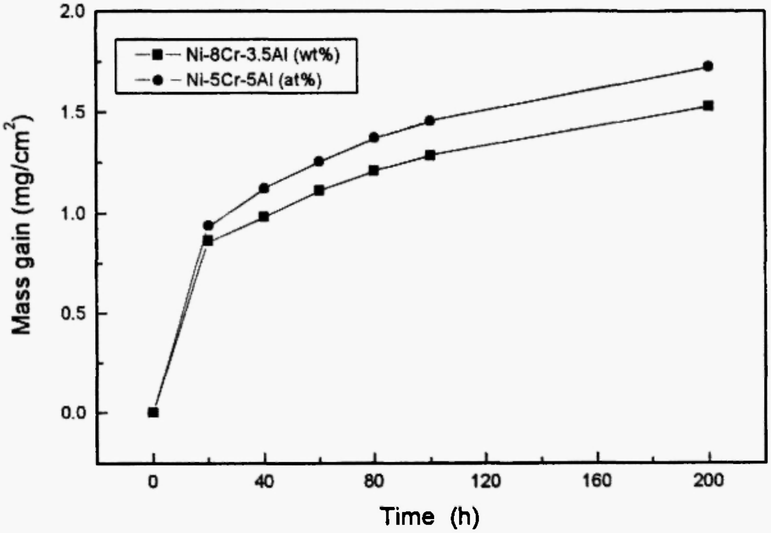

Fig. 1: AFM top-view image of the as-sputtered Ni-5Cr-5Al (at%) coating

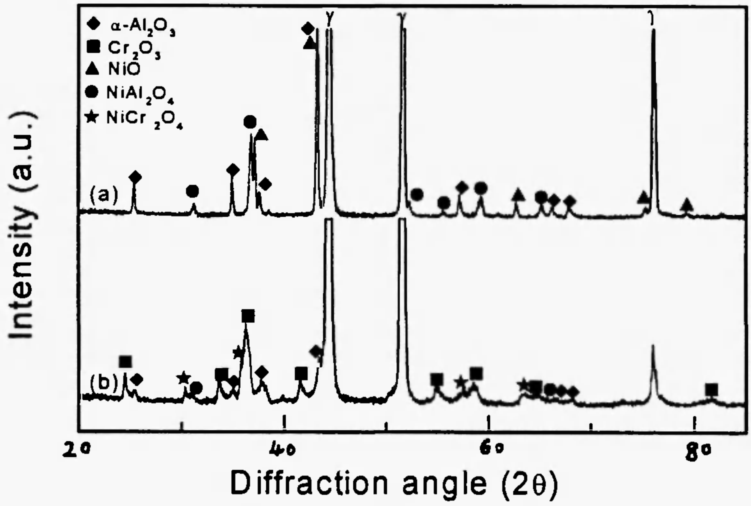

Fig. 2: AFM top-view image of the as-sputtered Ni-8Cr-3.5Al (wt%) coating

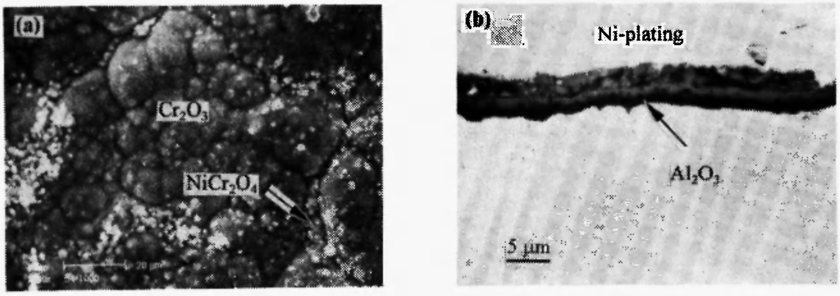

Fig. 3: Oxidation kinetics for the sputtered Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) coatings at 1000 in air

Figure 5 and 6 show the surface morphologies and cross-sectional microstructures of the sputtered Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) coatings after 200-h oxidation respectively. It can be seen that multi-layered oxide scales were formed on these coatings. For the Ni-8Cr-3.5Al (wt%) coating, the outer layer was composed of Cr_2O_3 and $NiCr_2O_4$, $NiAl_2O_4$ spinel and the inner layer was α-Al_2O_3. For the

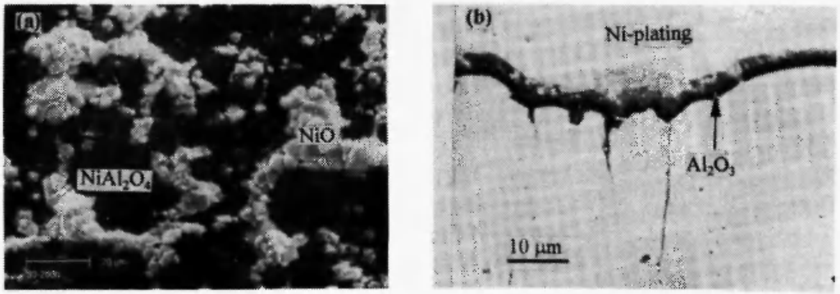

Fig. 4: XRD patterns for the sputtered (a) Ni-5Cr-5Al (at%) and (b) Ni-8Cr-3.5Al (wt%) coatings after 200-h oxidation

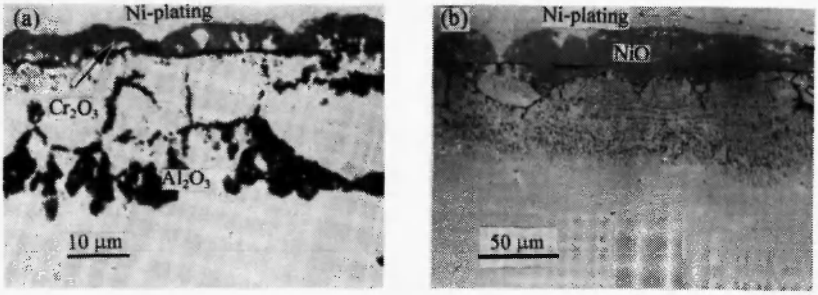

Fig. 5: Surface morphologies (a) and cross-sectional microstructures (b) of the sputtered Ni-8Cr-3.5Al (wt%) coatings after 200-h oxidation

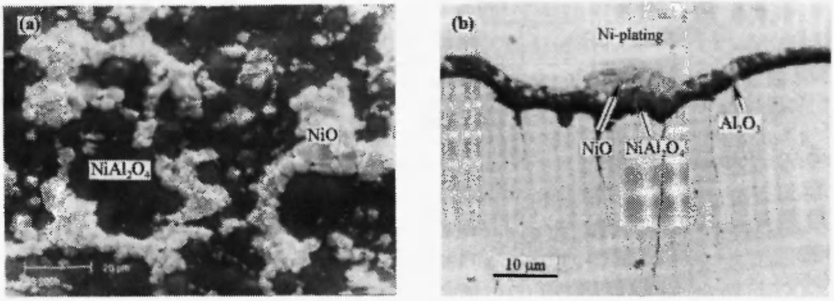

Fig. 6: Surface morphologies (a) and cross-sectional microstructures (b) of the sputtered Ni-5Cr-5Al (at%) coatings after 200-h oxidation

Ni-5Cr-5Al (at%) coating, the outer layer was composed of NiO and $NiAl_2O_4$ spinel and the inner layer was α-Al_2O_3. However, a Cr_2O_3 outer layer with internal oxide of Al was formed on the cast Ni-8Cr-3.5Al (wt%) alloy and a NiO outer layer with internal oxides of Cr and Al was formed on the cast Ni-5Cr-5Al (at%) alloy, which is shown in Figure 7.

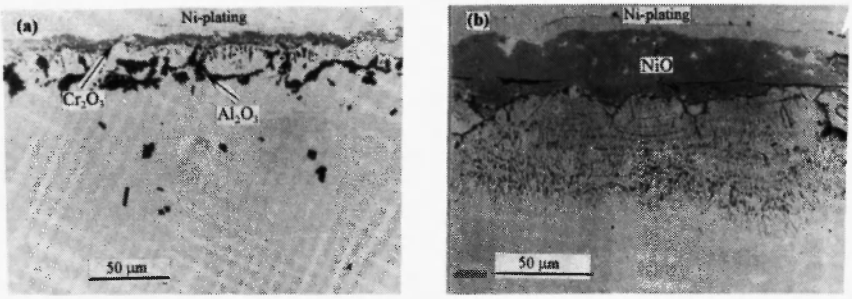

Fig. 7: Cross-sectional microstructures of cast (a) Ni-8Cr-3.5Al (wt%) and (b) Ni-5Cr-5Al (at%) alloys after 200-h oxidation

DISCUSSION

1 Oxidation products

The mechanism of oxidation for the Ni-Cr-Al alloys with normal grain size has been described in detail and an oxidation products diagram showing the relationship between oxides and Ni, Cr, Al contents in Ni-Cr-Al ternary system with coarse-grain at 1000°Cwas established /1,2/. The cast Ni-8Cr-3.5Al (wt% i.e. Ni-8.6Cr-7.24Al at%) alloy was in the Cr_2O_3-forming zone; the cast Ni-5Cr-5Al (at%) alloy was in the NiO-forming zone. The present work indicated that good agreement with the results of Wallwork /2/ was obtained.

It was suggested that nanocrystallization exhibited a beneficial effect on oxidation resistance of alloys such as K38G (with 16 wt% Cr and 4 wt% Al) /3,4/, K17F (with 12.5 wt% Cr and 4 wt% Al) /5/, LDZ125 (with 9.5 wt% Cr and 5.2 wt% Al) /6,7/ and Ni-20Cr-2Al (wt%) /8,9/ by developing a unitary α-Al_2O_3 scale. Nanocrystallization could reduce the critical Al content for the formation of α-Al_2O_3 scale by increasing the diffusion rate of Al. However, besides the effect of nanocrystallization, the effect of a high content of Cr in these alloys should not be neglected. The presence of Cr in Ni-Al alloys can promote the establishment of α-Al_2O_3 scale in alloys of lower Al concentration, which can be called the third-element effect /13/. Therefore, the formation of a unitary α-Al_2O_3 scale on these coatings was attributed to the co-effect of Cr effect and nanocrystallization. With a decrease in Cr content, such a unitary α-Al_2O_3 scale would not be formed, just as the sputtered Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at% i.e. Ni-4.6Cr-2.4Al wt%) nanocrystalline coatings on which layered oxide scales were formed. However, due to the formation of the complete inner layer of α-Al_2O_3, Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) alloys with nano-sized grain were Al_2O_3-formers.

2 Oxidation mechanism

Considering the oxidation results that have been obtained in the present study, the following model can be constructed to described the oxidation of Al_2O_3-former Ni-Cr-Al alloys with nano-grained. In the initial oxidation stage, the rapid uptake of oxygen converts the bare surface of alloys to a thin oxide film. It was expected that all the oxides of Ni, Cr and Al were formed resulted from the high formation nuclei for oxide and the high grain boundaries existed in the nanocrystalline alloys. If the Cr content in Ni-Cr-Al alloys were high enough, just as Ni-20Cr-2,3,5Al (wt%), a complete thin Cr_2O_3 layer would be easily expected on the surface preceded by the formation of the film composed of oxides of Ni, Cr and Al. With the rapid establishment of this thin layer, the oxygen partial pressure at the metal-oxide interface decreased greatly. According to Wagner's theory /14/, the minimum Al concentration, N_{Al}, in the alloy to form an external oxide scale can be estimated by

$$N_{Al} = \left(\frac{\pi g N_O D_O V_m}{3 D_{Al} V_{OX}}\right)^{\frac{1}{2}} \qquad (1)$$

where g is a constant; $N_O D_O$ is the oxygen permeability in the alloy; V_m

is the molar volume of alloy; D_{Al} is the diffusion coefficient of Al; V_{OX} is the molar volume of the oxide.

Due to the rapid formation of a thin oxide film on the nanocrystalline materials, it is reasonable to consider that a new environment meet the requirement of the Wagner' theory was established at the interface between the thin oxide film and the base metal. Therefore, with the establishment of the thin Cr_2O_3 layer, N_OD_O would be very small; in addition, D_{Al} was enhanced due to the shot-circuit diffusion for the outward diffusion of Al in the nanocrystalline alloys. Both of them contributed to the formation of a complete Al_2O_3 layer below the thin Cr_2O_3 layer. Cr_2O_3 and Al_2O_3 can form a continuous solid solution over the entire composition range /15/. Therefore, the previously formed Cr_2O_3 can dissolve into Al_2O_3 and then a unitary external α-Al_2O_3 would be formed on Ni-20Cr-2,3,5Al (wt%) nano-grained alloys.

Due to the low content of Cr in the Ni-8Cr-3.5Al (wt%) and Ni-5Cr-5Al (at%) nanocrystalline coatings, such a Cr_2O_3 layer could not be expected. Therefore, more NiO would be expected on the surface of these coatings. It was suggested that the addition of Al to Ni-Cr alloys or Cr to Ni-Al alloys would reduce the amount of Cr or Al to form Cr_2O_3 or Al_2O_3 /16/. Therefore, compared with Ni-5Cr-5Al (at%) coating, the formation tendency of Cr_2O_3 and Al_2O_3 on the Ni-8Cr-3.5Al (wt%) coating was much higher due to the relatively high Cr, Al contents. However, the formed Cr_2O_3 and Al_2O_3 could not coalesce into a continuous layer, NiO would continue to grow laterally. More Cr_2O_3 could be formed than Al_2O_3 on the Ni-8Cr-3.5Al (wt%) coating and reacted with NiO to form $NiCr_2O_4$ at the early stage of oxidation. With increasing oxidation time, some Al_2O_3 would dissolve into Cr_2O_3 and the other would react with NiO to form $NiAl_2O_4$. When the complex oxide scales became dense, only Al_2O_3 could be formed at the metal-oxide interface and a continuous Al_2O_3 layer was formed due to the low oxygen partial pressure and the relatively increased Al concentration combining with the high Al diffusion.

For the Ni-5Cr-5Al (at%) coating, in the early stage of oxidation, a large number of oxide nuclei rapidly coalesced to form a thin oxide layer. This layer was primarily composed of NiO with some oxide of Cr and Al due to the high concentration of Ni in the alloy. After a closed oxide layer had formed, the oxygen partial pressure at oxide-coating interface decreased to the formation pressures of Cr_2O_3 and Al_2O_3, which are lower than that of NiO. Thus, more precipitates of Cr_2O_3 and Al_2O_3 were formed. The formation of the internal precipitates of Cr_2O_3 and Al_2O_3 would remove oxygen atoms from the coating matrix and reduce the ingress of oxygen atoms into the coating. Due to the activity of oxygen required to oxidize Al is smaller than that required to oxidize Cr, more Al_2O_3 precipitated and extended deeper into coating than Cr_2O_3. However, due to the low concentration of Al and Cr in the coating, the precipitates of Cr_2O_3 and Al_2O_3 could not form a continuous healing layer. Therefore, the formed NiO continued to out-grow. Simultaneously, NiO reacted with Cr_2O_3 and Al_2O_3 to form $NiCr_2O_4$ and $NiAl_2O_4$. Due to the very low Cr_2O_3 precipitation and then little formation of $NiCr_2O_4$, the formed $NiCr_2O_4$ could dissolve into $NiAl_2O_4$. With increasing oxidation time and the formation of $NiAl_2O_4$, the growth rate of NiO decreased and the oxygen partial pressure decreased more to the formation pressure of Al_2O_3, which is the lowest one. Furthermore, nanocrystalline structure can promote the diffusion of Al in the alloy and the diffusivity of Al would become large. This occurred as the concentration of Al approached that required for the formation of the continuous Al_2O_3 layer. Thus, an Al_2O_3 inner layer was established.

CONCLUSIONS

The oxide formation on Ni-Cr-Al alloys with nano-sized grain depended on the contents of Cr and Al. A unitary layer of Al_2O_3 could be formed on the Ni-Cr-Al nanocrystalline coatings with very high content of Cr and extremely low Al content. The formation of a unitary Al_2O_3 scale was attributed to the establishment of a Cr_2O_3 thin layer, which promoted the formation of Al_2O_3, and the dissolution of Cr_2O_3 into Al_2O_3. With the decrease of Cr content and the increase of Al content, due to the inter-promotion effect of Cr and Al to form Cr_2O_3 and Al_2O_3, complex oxide scales with inner layer of Al_2O_3 could be formed.

ACKNOWLEDGEMENTS

The NNSF of China under the research project No. 59671060 supported this work.

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