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Oxide formation on sputtered Ni-3Cr-10Al nanocrystalline coating①

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Abstract: The oxide formation on the sputtered Ni-3Cr-10Al nanocrystalline coating at 900 ℃ and 1 000 ℃ in air has been studied. The results indicated that an oxide scale composed of $NiAl_2O_4$ and Al_2O_3 was formed on the sputtered Ni-3Cr-10Al nanocrystalline coating whereas a unitary Al_2O_3 scale was not formed even when the Al content was high in the sputtered coating. The formation of $NiAl_2O_4$ was directly related to the precipitation of Ni_3Al in the coating during oxidation process. It was suggested that the precipitation of Ni_3Al contributed to the formation of NiO and therefore NiO could react with Al_2O_3 and form $NiAl_2O_4$. With increasing oxidation temperature, the effect of Ni_3Al precipitation on the formation of $NiAl_2O_4$ decreased.

Key words: Ni-3Cr-10Al; sputtering; nanocrystalline coating; oxidation **Document code:** A

1 INTRODUCTION

Nanocrystalline coatings could be produced by magnetron sputter technique on the substrates of the same materials and exhibited good oxidation resistance resulted from the promotion of the selective oxidation of Al and the formation of a unitary layer of Al_2O_3 even with low Al content[1~5]. However, a unitary Al_2O_3 scale could not be developed on the sputtered Ni_3Al nanocrystalline coating even with high content of Al in the coating[6]. The presence of Cr in Ni-Al alloys could promote the selective oxidation of Al, therefore, some Cr was added into Ni_3Al and the sputtered $Ni_3(AlCr)$ nanocrystalline coating was prepared[7]. However, a unitary layer of Al_2O_3 was still not formed. Therefore, it must be related to some other factors in addition to the Cr effect and nanocrystallization. Ni, Cr and Al are the most important compositions in Ni-base superalloys. The investigation of oxidation behavior of the Ni-Cr-Al alloys was beneficial to the understanding of oxide formation of the complex Ni-base superalloys. In the present study, an Al-rich Ni-3Cr-10Al alloy was developed and the sputtered Ni-3Cr-10Al nanocrystalline coating was produced on the substrates of the same materials. The oxide formation on this sputtered coating was studied in an effort to examine the effect of microstructural change on the oxide formation.

2 EXPERIMENTAL

The Ni-3Cr-10Al (mass fraction, %) alloy was melted in a vacuum-induction furnace. The ingot was cut into 18 mm × 15 mm × 2 mm specimens, which were ground down to 600-grit, peened and ultrasonically cleaned in ethanol. The target for sputtering was also cut from ingot with dimension of 380 mm × 127 mm × 6 mm. The sputtering parameters were as follows: working Ar gas pressure 0.2 Pa, power 2 kW, substrate temperature 250 ℃. The composition of the sputtered coating was the same as that of the substrate and the thickness of the sputtered coating was about 50 μm.

The as-sputtered Ni-3Cr-10Al coating was examined by atomic force microscopy (AFM). Oxidation tests were carried out at 900 ℃ and 1 000 ℃ in air. After oxidation, the specimens were examined by scanning electron microscopy (SEM) with energy dispersive analysis of X-ray (EDAX) and X-ray diffraction (XRD).

3 RESULTS

Fig.1 shows the AFM top-view image of the as-sputtered Ni-3Cr-10Al coating. Based upon AFM image, the grain size of the coating is found to be less than 100 nm.

Fig.2 shows the oxidation kinetics for the sputtered coating at 900 ℃ and 1 000 ℃ in air. The kinetic curves at 900 ℃ and 1 000 ℃ show slowly increasing mass gain after rapidly increasing mass gain at early stage of oxidation, indicating the establishment of the protective oxide scales. The XRD patterns for the sputtered Ni-3Cr-10Al coating after 200 h oxidation at 900 ℃ and 1 000 ℃ in air are shown in Fig.3. It can be seen that both $NiAl_2O_4$ and Al_2O_3 were formed on the sputtered nanocrystalline coating. Both α and θ-Al_2O_3 were presented on the oxide scale formed at 900 ℃ whereas only α-Al_2O_3 existed on the oxide scale formed at 1 000 ℃, which suggests that

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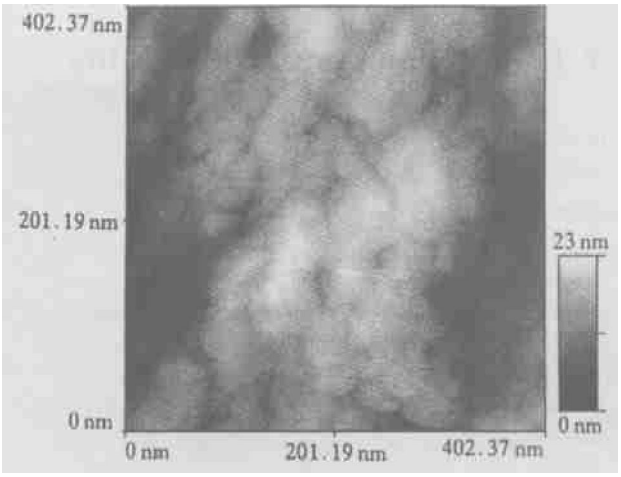

Fig.1 AFM top-view image of as-sputtered Ni-3Cr-10Al coating

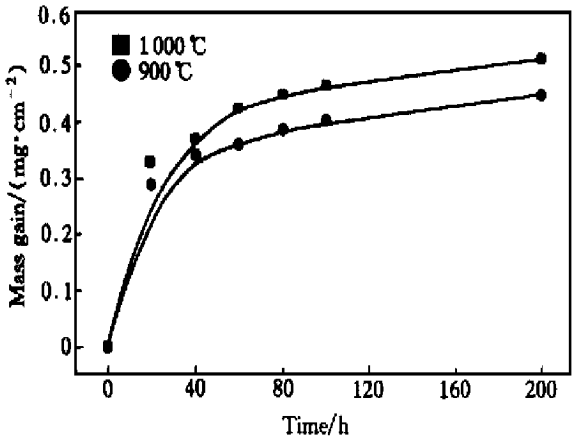

Fig.2 Oxidation kinetics for sputtered Ni-3Cr-10Al coating at 900 ℃ and 1 000 ℃ in air

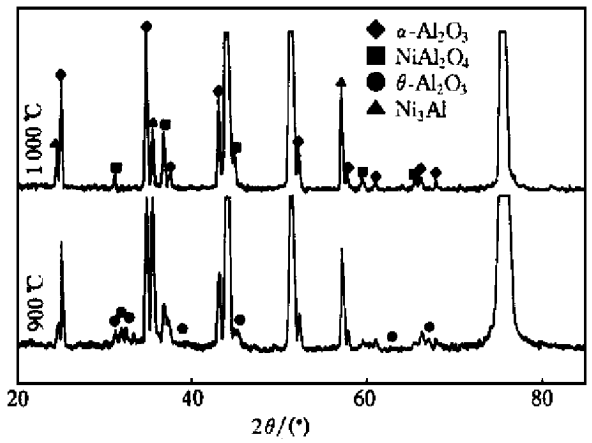

Fig.3 XRD results of sputtered Ni-3Cr-10Al coating after 200 h oxidation at 900 ℃ and 1 000 ℃

the transformation of θ-Al_2O_3 to α-Al_2O_3 was not complete at 900 ℃.

Fig.4 shows the morphology of the formed oxide scale after 200 h oxidation at 900 ℃. The white large particles of oxide can be observed. EDAX results indicated that it was the oxide of Ni and Al. Combined with the XRD results, we can confirm that this was

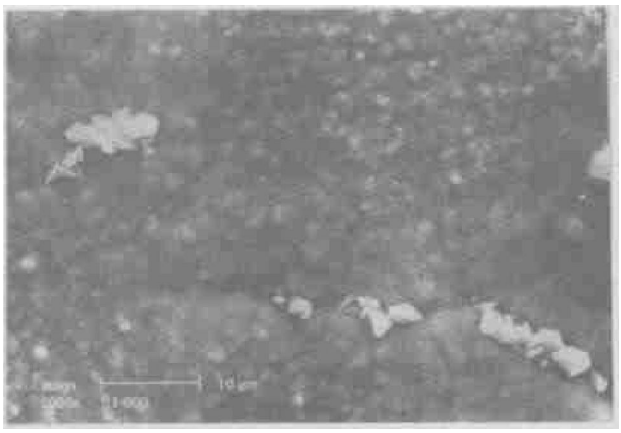

Fig.4 Morphology of formed oxide scale after 200 h oxidation at 900 ℃

$NiAl_2O_4$. The other oxides were α and θ-Al_2O_3.

Fig.5 shows the morphologies of $NiAl_2O_4$ after 1 h, 200 h oxidation at 1 000 ℃. It can be observed that the morphology of $NiAl_2O_4$ after 1 h oxidation was similar to that of $NiAl_2O_4$ formed after 200 h oxidation at 900 ℃. However, $NiAl_2O_4$ existed on the oxide scale in the form of small particle after 200 h oxidation. The results indicated that with increasing oxidation time, $NiAl_2O_4$ could be overlaid by the growth of Al_2O_3, whereas $NiAl_2O_4$ could not be overlaid completely.

4 DISCUSSION

According to the oxide map for Ni-Cr-Al alloys with normal grain size[8], Ni-3Cr-10Al alloy was in the Al_2O_3-forming zone and an external Al_2O_3 scale could be developed on Ni-3Cr-10Al alloy with normal grain size. Nanocrystallization could promote the selective oxidation of Al. The grain size of sputtered Ni-3Cr-10Al coating was less than 100 nm. Therefore, a unitary Al_2O_3 should be formed on the coating. However, $NiAl_2O_4$ and Al_2O_3 complex oxide scale were formed on the sputtered Ni-3Cr-10Al nanocrystalline coating.

Fig.6 and Fig.7 show the XRD patterns for the sputtered Ni-3Cr-10Al coating after different times of oxidation at 900 ℃ and 1 000 ℃ respectively. In order to emphasize the phase structure of the coating, the diffraction peaks of oxide formed on the coating were made not obvious. It can be seen that the as-sputtered Ni-3Cr-10Al coating was composed of only γ phase, as shown in Fig.6. According to the phase diagram of Ni-Cr-Al[9], Ni-3Cr-10Al alloy was composed of γ phase and Ni_3Al. Ni_3Al could be precipitated during oxidation process. It can be seen that the intensity of (022) plane of Ni_3Al became strong after 1 h oxidation, the strongest after 20 h oxidation and then decreased at 900 ℃. However, such phenomena appeared after 1 h oxidation at 1 000 ℃.

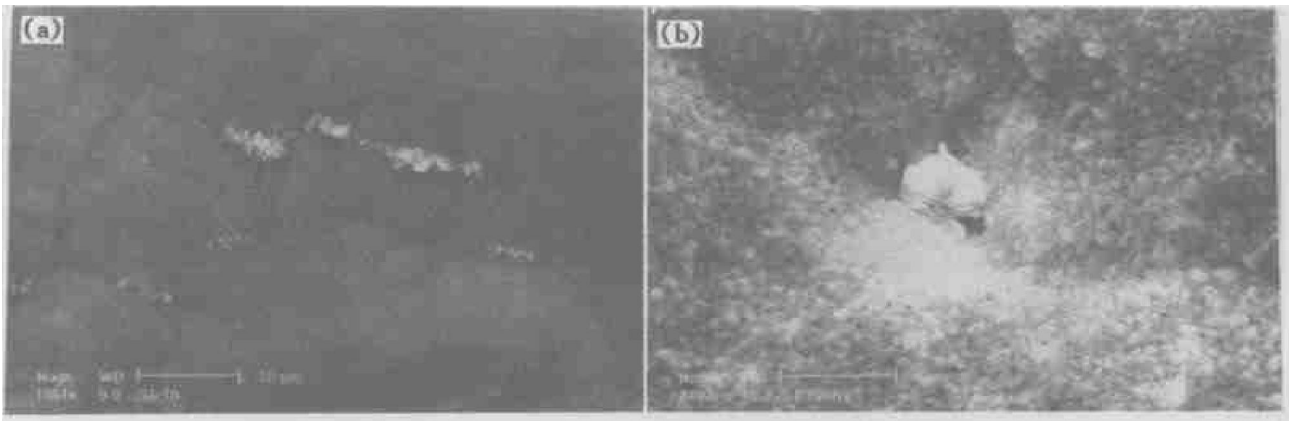

Fig .5 Morphologies of $NiAl_2O_4$ after (a) 1 h, (b) 200 h oxidation at 1 000 ℃

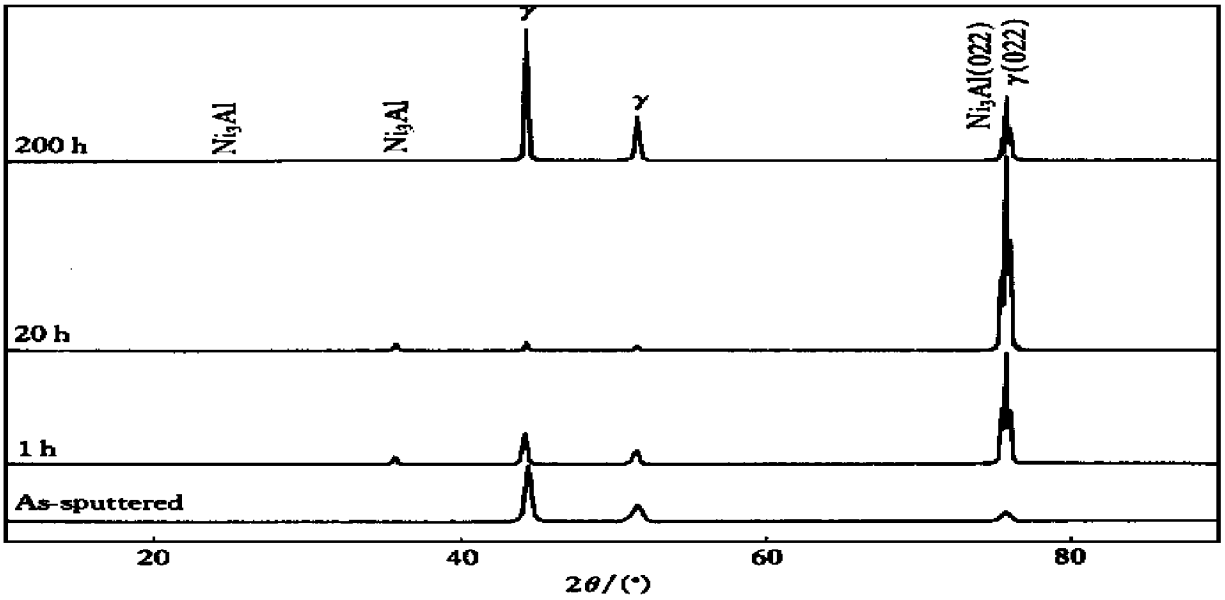

Fig .6 XRD spectra of sputtered Ni-3Cr-10Al coating after different times of oxidation at 900 ℃

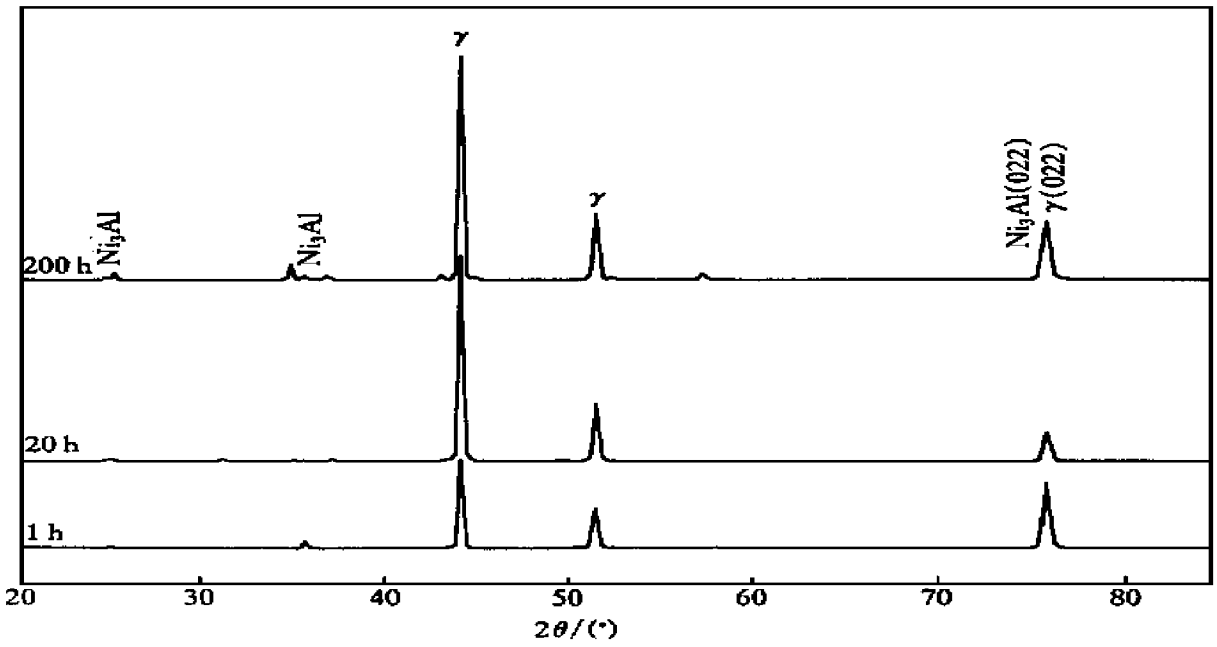

Fig .7 XRD spectra of sputtered Ni-3Cr-10Al coating after different times of oxidation at 1 000 ℃

It was suggested that Ni atoms occupied the (022) plane in Ni_3Al. Therefore, the precipitation of Ni_3Al could easily occur along the (022) plane of γ phase. XRD results proved that Ni_3Al precipitated along the (022) plane of γ phase. In a Monte Carlo simulation study, the diffusion of Al was found to be reduced markedly as the system becomes more ordered, while the diffusion of Ni does not show such a drastic effect. Numakura et al[10] proposed a model for the self-diffusion in Ni_3Al and suggested that the diffusion of Al is 10 ~ 25 times slower in Ni_3Al than that in Ni-base γ phase. Therefore, with the precipitation of γ' (Ni_3Al) phase, more Al would be ordered and then the diffusion of Al be remarkably decreased. NiO was easily formed in the precipitation region. In the oxidation of alumina forming alloys, Al_2O_3 occurs in different modifications. In the early stage of oxidation, the metastable oxides γ and θ-Al_2O_3 grow and finally the transformation to α-Al_2O_3 takes place. The presence of Cr in Ni-Al alloys can accelerate the $\gamma \rightarrow \theta \rightarrow \alpha$-$Al_2O_3$ transformation[11]. Due to the low content of Cr in the Ni-3Cr-10Al coating, the transformation of transient alumina to stable alumina was very slow. XRD results revealed the presence of transition alumina such as γ and θ-Al_2O_3, which can be evidenced by the presence of θ-Al_2O_3 on the coating after 200 h oxidation at 900 ℃. Schumann et al[12] reported that spinel $NiAl_2O_4$ could be easily formed by a solid state reaction between NiO and γ-Al_2O_3 resulted from the small nucleation barrier for such reaction in the two-phase region due to the cube-on-cube orientation in lattices of NiO and γ-Al_2O_3. It was acceptable that $NiAl_2O_4$ could be easily formed on the Ni-3Cr-10Al coating during initial oxidation period. The presence of $NiAl_2O_4$ on coating after 1 h oxidation at 1 000 ℃ confirmed this supposition. The precipitation time of Ni_3Al was longer at 900 ℃ than at 1 000 ℃, and then the effect of Ni_3Al on the formation of $NiAl_2O_4$ was also high. Therefore, more $NiAl_2O_4$ could be observed on the oxide scale formed at 900 ℃. The presence of $NiAl_2O_4$ on the oxide scale formed on the sputtered $Ni_3(AlCr)$[7] and Ni_3Al[6] nanocrystalline coatings was also probably directly related to the presence of Ni_3Al in the coatings.

Therefore, the microstructural change of sputtered nanocrystalline coating during oxidation process should be taken into consideration. The present study also suggests that the oxidation resistance is not influenced seriously by the formation of $NiAl_2O_4$.

5 CONCLUSIONS

$NiAl_2O_4$ and Al_2O_3 complex oxide scale was formed on the sputtered Ni-3Cr-10Al nanocrystalline coating after 200 h oxidation at 900 ℃ and 1 000 ℃. The formation of $NiAl_2O_4$ was directly related to the precipitation of Ni_3Al in the coating during oxidation process.

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