Preparation of Cyclic Oxidation Resistant Coating Consisting of Ni Aluminide and Ni-Hf Alloy Layers on Ni-Cr-Al Alloy by Electrodeposition

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The preparation of a coating consisting of a Ni aluminide layer and Ni-Hf alloy layer on a Ni-Cr-Al alloy was attempted by the four-step electrodeposition of Ni, Hf, Ni and Al. In this study, the Ni electrodeposition was carried out using an aqueous solution, while the Hf and Al electrodepositions were carried out using a molten salt at 1023 K. The cyclic oxidation resistance for the alloy covered with the coating was then evaluated in air at 1373 K. This estimation was carried out by comparison of the alloy covered with a single Ni aluminide layer. For the alloy covered with the single Ni aluminide layer, a decrease in the mass gain of the alloy due to scale spalling was observed, while for the alloy covered with the bilayer coating, such a decrease was not observed. It was found from the observation of a cross-section of the alloy covered with the single Ni aluminide layer that the Al concentration in the surface region of the Ni aluminide layer decreased due to the diffusion of Al from the Ni aluminide layer to the substrate alloy. On the other hand, for the alloy covered with the bilayer coating, the diffusion of Al from the Ni aluminide layer to the substrate alloy was inhibited by the diffusion barrier effect of the Ni-Hf alloy layer. After the 10-cycle oxidation, the decomposition of the Ni-Hf alloy layer proceeded, and as a result, Hf in the Ni-Hf alloy layer diffused into the surface region of the Ni aluminide layer. The Hf in the surface region of the Ni aluminide layer led to the formation of an adhesive scale having a spiked shape.

Keywords : Electrodeposition, Molten salt, Coating, Oxidation resistance, Nickel aluminide, Nickel-hafnium alloy

1 INTRODUCTION

Ni aluminides represented by β-NiAl are promising materials for a high-oxidation resistant coating because of forming a protective scale consisting of Al₂O₃. However, when the Ni aluminides are used as the high temperature coatings, the diffusion of Al from the Ni aluminides to the alloy substrate occurs due to a difference in the concentration of Al between the Ni aluminides and the alloy substrate. This fact leads to a decrease in the concentration of Al in the Ni aluminides, complicating the maintenance of the Al₂O₃ scale. For a solution to this phenomenon, it is effective to form a diffusion barrier of Al between the coating consisting of Ni aluminide and the alloy substrate. Narita et al. [1-3] reported that the Re alloy was effective as a diffusion barrier of Al and that the coating consisting of a Ni aluminide layer and a diffusion barrier layer consisting of the Re alloy produced a high-oxidation resistance to the alloy substrate. On the other hand, Haynes et al. [4] showed the possibility that a Ni-Hf alloy will act as the diffusion barrier of Al. Several of the authors [5] carried out studies of the diffusion couple of Ni-Al and Ni-Hf, and showed that the Al diffusion from Ni-Al to Ni-Hf only slightly occurred.

In the present study, we tried to prepare a high-oxidation resistant coating consisting of a Ni aluminide layer as the surface layer and a Ni-Hf alloy layer as the diffusion barrier layer on the Ni-20mass%Cr-2mass%Al alloy by the electrodeposition of Ni using an aqueous solution and those of Hf and Al using a molten salt as the reaction medium. The reason which the electrodepositions of Hf and Al were carried out using the molten salt is that Hf and Al cannot be electrodeposited from aqueous solution because both metals have electrodeposition potentials lower than the reduction potential of water.

2 EXPERIMENTAL

The Ni-based alloy containing 20.1 mass%Cr and 2.02 mass%Al (denoted as Ni-20Cr-2Al alloy) was used as the substrate material. Figure 1 shows the preparation process which makes two layers consisting of Ni aluminide and Ni-Hf alloy on the alloy substrate. The preparation of the coating consisting of Ni aluminide and Ni-Hf alloy layers was carried out in two steps. First, the Ni-Hf alloy layer was prepared on the alloy substrate and the Ni aluminide layer was subsequently prepared on the Ni-Hf alloy layer. The preparation of the Ni-Hf alloy and Ni aluminide layers was conducted in two electrodeposition steps. For the preparation of the Ni-Hf alloy layer, Ni was electrodeposited on the alloy substrate, and Hf was subsequently electrodeposited on the Ni-deposited surface. For the preparation of the Ni aluminide layer, Ni was electrodeposited on the surface of the Ni-Hf alloy layer, and Al was subsequently electrodeposited on the Ni-deposited surface. The electrodeposition of Ni was carried out by galvanostatic electrolysis at 200 A m⁻² using Watt’s solution (323 K). The times of the Ni electrodeposition...
for the preparation of the Ni-Hf alloy layer and the Ni-aluminide layer were 1.8 ks and 7.2 ks, respectively. The electrodepositions of Hf and Al were carried out by potentiostatic electrolysis at the reduction potentials of the Hf and Al ions, -1.8 V and -1.4 V (vs. Ag/Ag+ (0.1)) [6] for 3.6 ks using equimolar NaCl-KCl melts (1023 K) containing 3.5 mol% AlF₃ and 3.5 mol% HfF₄, respectively. The reference electrode was an Ag wire immersed in an NaCl-KCl-AgCl (45:45:10 mol%) mixture held in a mullite tube. In order to evaluate the cyclic-oxidation resistance of the Ni-20Cr-2Al alloy covered with the coating consisting of the Ni aluminide and Ni-Hf alloy layers, a cyclic-oxidation test was carried out in air at 1373 K. For the experiment, each cycle consisted of heating for 3.6 ks. After the cyclic-oxidation, a cross-section of the specimen was observed by SEM and analyzed by EPMA.

3 RESULTS AND DISCUSSION

3.1 Morphology of Coating Consisting of Ni Aluminide and Ni-Hf Alloy Layers

Figures 2 (a) and (b) show scanning electron micrographs (back-scattered-electron image) and the concentration profiles of Ni, Al, Cr and Hf in the cross-sections near the surface of the Ni-20Cr-2Al alloys with the coating consisting of the Ni aluminide layer and with the coating consisting of the Ni aluminide and Ni-Hf alloy layers, respectively. For the alloy with the coating consisting of the Ni aluminide layer, the formation of the Ni aluminide layer of about 60 μm thickness was observed. The concentration profiles of the Al and Ni indicated that the layer consisted of a Ni₂Al₃ phase. Because the electrodeposition of Al proceeds on the Ni aluminide layer, it is presumed that the concentration gradient of Al where the concentration of Al decreases to the inside from surface of the Ni aluminide layer is formed. However, the concentration profiles of Al and Ni in the Ni aluminide layer shown in Figure 2 (a) showed that the concentration gradients of Al and Ni were not formed in the layer. It is thought that this result was attributable to the fact that the mutual diffusion rates of Al and Ni in the Ni aluminide layer were fast. Inside the Ni₂Al₃ layer, a Ni layer of about 20 μm thickness was observed. For the alloy with the coating consisting of the Ni aluminide and Ni-Hf alloy layers, the Ni aluminide layer consisting of the Ni₂Al₃ phase and the Ni layer was formed, as well as the sample shown in Figure 1 (a). Inside the Ni layer, the Ni-Hf alloy layer with about a 6μm thickness was formed.

Figure 3 shows an expanded micrograph of the region in the vicinity of the Ni-Hf alloy layer shown in the Figure 2 (b). The concentration profiles of Ni and Hf showed that the Hf concentration of this Ni-Hf alloy layer was about 25at% and this alloy layer was presumed to be α-Ni₃Hf phase.

3.2 Cyclic-Oxidation Behavior of Alloys with Coatings

Figure 4 shows the result of the cyclic-oxidation test in air at 1373 K of the Ni-20Cr-2Al alloys with the coatings shown in Figures 2 (a) and (b). This figure also contains the result of a non-treated Ni-20Cr-2Al alloy in the same atmosphere. It was found that increases in the mass of the alloys with the coatings were far lower than that of the non-treated alloy. For the Ni-20Cr-2Al alloy with the coating consisting of only Ni aluminide coating and (b) Ni aluminide/Ni-Hf alloy coating.
Preparation of Cyclic Oxidation Resistant Coating Consisting of Ni Aluminide and Ni-Hf Alloy Layers on Ni-Cr-Al Alloy by Electrodeposition

3.2 Morphology of Coating and Scale after Cyclic-Oxidation Test

The cyclic-oxidation resistance of the Ni-20Cr-2Al alloy was significantly improved by the coating consisting of the Ni aluminide and Ni-Hf alloy layers. These results indicated that the cyclic-oxidation resistance of the Ni-20Cr-2Al alloy was not reduced. These results indicated that the cyclic-oxidation resistance of the Ni-20Cr-2Al alloy was significantly improved by the coating consisting of the Ni aluminide and Ni-Hf alloy layers.

3.3 Morphology of Coating and Scale after Cyclic-Oxidation Test

Figure 5 shows scanning electron micrographs and the concentration profiles of Ni, Al, Cr, Hf and O in the cross-sections near the surface of the Ni-20Cr-2Al alloy with the coating consisting of Ni aluminide layer and Ni-Hf alloy layer after 3- and 200-cycle oxidations. For the 3-cycle oxidation, a Ni aluminide layer containing about 40 at% aluminum was formed due to the mutual diffusion of the Ni2Al3 layer and Ni layer. Inside this layer, the Ni-Hf alloy layer of about 10 μm thickness was observed. The concentration of Hf in this layer was about 20 at%, suggesting that this layer consisted of a Ni7Hf2 phase. This concentration of Hf hardly changed with that before the oxidation test. This indicates that the Ni-Hf alloy layer diffused mutually with the Ni layers which the Ni-Hf alloy layer touched.

The morphology of the coating after the 10-cycle oxidation was similar to that after the 3-cycle oxidation. In the alloy substrate, no increase in the concentration of Al was observed. This suggests that the Ni-Hf alloy layer acted as a diffusion barrier of Al. On the coating, a scale consisting of Al2O3, whose morphology was characteristic, was formed. This scale entered locally into the metal below the outer scale. It is presumed that such a morphology of the scale resulted from the effect of Hf which slightly dissolved from the Ni-Hf alloy layer into the Ni aluminide layer and diffused to the Ni aluminide below the outer scale. In the Ni-Hf alloy layer, many voids were observed. It is presumed that

Figure 5 Cross-sectional micrographs and concentrations of Ni, Al, Cr and O across Ni-20Cr-2Al alloys with Ni aluminide coating after 3- and 200-cycle oxidation tests in air at 1373 K.

Figure 3 Cross-sectional micrograph and concentration of Ni and Hf across region in the vicinity of Ni-Hf alloy layer for Ni-20Cr-2Al alloy with Ni aluminide/Ni-Hf alloy coating.

Figure 4 Mass change-time curves of Ni-20Cr-2Al alloys with Ni aluminide coating and Ni aluminide/Ni-Hf alloy coating during cyclic oxidation test in air at 1373 K. For comparison, this figure contains the mass change-time curve of a non-treated Ni-20Cr-2Al alloy.

Ni2Al3 layer and Ni layer. It is presumed from the Ni-Al phase diagram that this Ni aluminide consisted of a β-NiAl phase. The formation of a thin Al2O3 scale was observed on the Ni aluminide layer. During an initial stage of oxidation, thus, the Ni3Al1 layer, which was formed after the electrodeposition of Al, mutually diffused with the Ni layer inside it, and changed to the NiAl layer. However, because the protective Al2O3 scale was formed on the NiAl layer, it is presumed that the coating consisting of the NiAl layer had a high oxidation resistance during the oxidation test. For the 200-cycle oxidation, the concentration of Al in the coating layer decreased to about 20 at%. It is presumed from the Ni-Al phase diagram that this coating consisted of a γ’-Ni3Al and γ-Ni solid solution. The concentration of Al in the alloy substrate increased to 10 at%. This indicated that the aluminum diffusion from the coating to the alloy substrate occurred.

The morphology of the coating after the 10-cycle oxidation was similar to that after the 3-cycle oxidation. In the alloy substrate, no increase in the concentration of Al was observed. This suggests that the Ni-Hf alloy layer acted as a diffusion barrier of Al. On the coating, a scale consisting of Al2O3, whose morphology was characteristic, was formed. Thus, the outer scale entered locally into the metal below the outer scale. It is presumed that such a morphology of the scale resulted from the effect of Hf which slightly dissolved from the Ni-Hf alloy layer into the Ni aluminide layer and diffused to the Ni aluminide below the outer scale. In the Ni-Hf alloy layer, many voids were observed. It is presumed that

aluminide and Ni-Hf alloy layers was not reduced. These results indicated that the cyclic-oxidation resistance of the Ni-20Cr-2Al alloy was significantly improved by the coating consisting of the Ni aluminide and Ni-Hf alloy layers.
the formation of these voids was caused by getting out of Hf from the Ni-Hf alloy layer with the decomposition of the alloy layer.

Figure 7 shows scanning electron micrograph of the surface region of this coating (the region inside the white rim shown in Figure 6). It was found that in the scale which entered locally into the metal below the outer scale, there were some small particles having a light color. The point analysis using EPMA showed that the particles were HfO₂. It is postulated that such a formation of HfO₂ particles resulted from the fact that Hf diffused to the surface region of Ni aluminide layer from Ni-Hf alloy layer and oxidized. It is thought that the HfO₂ particles led to the formation of the wedge-shaped scale that locally penetrated into the substrate. The reason for the formation of the wedge-shaped scale on the alloy containing small amounts of reactive element was thought to as follows: standard Gibbs energy change for oxidation formation of a reactive element is largely a negative value. Therefore, reactive element is preferentially oxidized in the metal below the outer scale, forming internal oxide particles. Such particles become a nucleation site for the formation of Al₂O₃ because oxygen pressure at the metal near the particles becomes high due to the fact that the reactive element oxide could cause a short circuit for oxygen diffusion [7, 8]. As a result, the Al₂O₃ scale likely grows to surround the reactive element oxide. Consequently, the wedge-shaped scale is formed.

The morphology of the coating consisting of Ni aluminide after the 100-cycle oxidation was similar to that after the 10-cycle oxidation. On the contrary, the morphology of the Ni-Hf alloy layer after the 100-cyclic oxidation was different from that after the 10-cycle oxidation. Thus, the Ni-Hf alloy layer after the 100-cycle oxidation decomposed. The morphology of the scale formed on the coating after the 100-cycle oxidation was similar to that after the 10-cycle oxidation. After the 100-cycle oxidation, the amount of the scale, which entered locally into the metal below the outer scale, became high. It is presumed that this results from the fact that the concentration of Hf in the Ni aluminide below the scale increased after the 100-cycle oxidation.

Figure 8 shows changes in the concentration of Al in the Ni aluminide layer below the outer scale (a site of 10-µm depth from the bottom of the outer scale) of the Ni-20Cr-2Al alloys with the Ni
aluminide coating and Ni aluminide/Ni-Hf alloy coating, with the number of cycles during the cyclic oxidation test in air at 1373 K. For the alloy with the Ni aluminide coating, the concentration of Al decreased with an increase in the number of cycles, and became about 20 at% after the 200-cyclic oxidation test. On the contrary, for the alloy with the Ni aluminide/Ni-Hf alloy coating, the concentration of Al did not change after 3 cycles, and even if the number of cycles reached 200, the concentration of Al remained at about 40 at%. It was observed that the Ni-Hf alloy layer, which seems to act as the diffusion barrier of Al, decomposed after 100-cycle oxidation. Therefore, the fact that the concentration of Al remained at a high value during the period from 100- to 200-oxidation cycles is not attributed to the diffusion barrier effect of the Ni-Hf alloy layer but is attributed to the improvement in adherence of the Al2O3 scale. It is presumed that Hf supplied to the Ni aluminide below the outer scale by the decomposition of the Ni-Hf alloy layer led to the formation of a wedge-shaped scale, and improved the close adherence of the scale. It was found from the result of 100-cyclic oxidation test shown in Figure 6 that in the region of about 50 ~ 100 μm depth from the surface of the Ni aluminide layer, the diffusion of Al from the Ni aluminide layer to the alloy substrate with the decomposition of the Ni-Hf alloy layer occurred, and as a result, the concentration of Al in the region decreased to about 30 at%.

4 CONCLUSION

In this work, the preparation of a cyclic oxidation resistant coating consisting of a Ni aluminide layer and Ni-Hf alloy layer on a Ni-Cr-Al alloy was carried out by the electrodeposition of Ni using an aqueous solution and those of Hf and Al using a molten salt. The cyclic oxidation resistance of the alloy with the coating was evaluated in air at 1373 K. The following conclusions can be drawn.

(1) The formation of a coating consisting of Ni aluminide and Ni-Hf alloy layers on the alloy was carried out by the electrodedeposition of Ni on the alloy substrate, followed by the electrodeposition of Hf, and subsequently, the electrodeposition of Ni on the Hf-Ni alloy followed by the electrodedeposition of Al.

(2) The cyclic oxidation resistance of the alloy with a coating consisting of Ni aluminide and Ni-Hf alloy layers was far higher than that of the alloy without the coating. Furthermore, the cyclic oxidation resistance of the alloy with this coating was higher than that with a coating consisting only of the Ni aluminide layer.

(3) During the initial stage of the oxidation test, the metallurgical structure of the Ni-Hf alloy layer was stable. This alloy layer acted as a barrier to the Al diffusion from the Ni aluminide layer to the alloy substrate.

(4) After the 100-cycle oxidation, the Ni-Hf alloy layer decomposed. Hf, which dissolved into the Ni aluminide layer by the decomposition of the Ni-Hf alloy, diffused to the surface of the Ni aluminide layer and increased the adherence of the Al2O3 scale, improving the cyclic oxidation resistance of the coating sample.

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