

Effect of the Electrodeposition Temperature on the Cyclic-Oxidation Resistance of Ni Aluminide Containing Zr Formed by Molten-Salt Electrodeposition

Michihisa Fukumoto¹, Takashi Suzuki^{1,*}, Motoi Hara¹ and Toshio Narita²

¹Department of Materials Science and Engineering, Faculty of Engineering and Resource Science, Akita University, Akita 010-8502, Japan

²Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

The effect of the Al electrodeposition temperature on the cyclic oxidation resistance of Ni aluminide containing Zr formed by molten salt electrodeposition was investigated. Zr and Al were deposited by molten salt electrolysis. For the sample treated with the Al deposition at 1073 K, a layer consisting of Ni₂Al₃ was uniformly formed. On the other hand, for the sample treated by Zr deposition, followed by Al deposition at 1073 K, a layer consisting of Ni₂Al₃ and a Ni aluminide layer containing Zr on the Ni₂Al₃ layer were formed. Furthermore, when the Al electrodeposition temperature was changed, the concentration of Zr in the Ni aluminide layer containing Zr changed. When the Al electrodeposition was carried out at 1153 and 1173 K, the Zr was scarcely observed in the surface region of the Ni aluminide layer. The cyclic oxidation test showed that for the sample treated with only the Al deposition and the sample treated with the Zr deposition, followed by Al deposition at 1073 K, a mass reduction due to scale exfoliation took place, whereas for the samples treated with the Zr deposition, followed by Al deposition at 1153 and 1173 K, no mass reduction was observed. For these samples, after the cyclic oxidation test, a scale consisting of α -Al₂O₃ adhering to the substrate was formed. Consequently, it was found that the cyclic oxidation resistance of Ni was improved by Zr deposition, followed by Al deposition at 1153 and 1173 K. [doi:10.2320/matertrans.MRA2008293]

(Received August 26, 2008; Accepted November 10, 2008; Published December 25, 2008)

Keywords: electrodeposition, molten salt, zirconium, aluminum, cyclic oxidation, nickel aluminide, coating

1. Introduction

In order to increase the thermal efficiency of the gas turbine for power generation, the temperature of the combustion gases at the turbine entrance has been increased. As the bond coat of the TBC system for the gas turbine blade, the MCrAlY coating prepared by a thermal spraying technique has been used. The increase in the turbine entrance temperature promotes the inner diffusion of Al for the MCrAlY coating to the substrate alloy. Consequently, the Al concentration in the coating decreases, preventing the maintenance of a high oxidation resistance by the coating for a long time. To solve this problem, a diffusion barrier type-bond coat was proposed as a new bond coat.¹⁾ The diffusion barrier type-bond coat consists of a diffusion barrier layer and an Al reservoir layer which contributes to the formation of Al₂O₃ scale and the maintenance of the scale.

It is requested for the Al reservoir layer to have a high melting point and to form a stable Al₂O₃ scale for a long time. As such a material, we have paid attention to a Ni aluminide, and tried to coat this aluminide using an electroplating technique.

For the Ni aluminide, a high oxidation resistance was maintained by the formation of the Al₂O₃ scale. However, for the Al₂O₃ scale on the Ni aluminide, spallation occurred during thermal cycling, and the oxidation resistance for the Ni aluminides was poor.²⁾ It was reported that the addition of a small amount of reactive elements as Zr and Hf is effective for improving the spallation of the Al₂O₃ scale on the Ni aluminide.³⁻⁷⁾

In the present study, we tried to form the Ni aluminide containing of a small amount of Zr by the electrodeposition of Al and Zr. Al and Zr cannot be electrodeposited from an

aqueous solution, however, they can be electrodeposited from a molten salt.⁸⁻¹¹⁾ The authors attempted the formation of a Ni aluminide containing Zr by the Zr deposition on Ni, followed by the Al deposition in the molten salt at 1023 K. As a result, it was determined that the cyclic oxidation resistance of the Ni aluminide was not good, because during the Al deposition, the mutual diffusion of Al and Ni only occurred without the mutual diffusion of Zr and Ni and the Zr-rich layer was formed in the surface region of the Ni aluminide.¹²⁾ On the other hand, we might expect that the Ni aluminide layer uniformly containing a small amount of Zr can be formed by Al electrodeposition at higher temperature, being caused by the mutual diffusion of Zr and Ni.

In the present study, we attempted to perform Al electrodeposition at higher temperature than that in a previous study.¹²⁾ The Al electrodeposition was carried out at 1023 K, 1073 K, 1153 K or 1173 K, and the change in the Zr content in the surface region of the Ni aluminide was examined. In addition, the cyclic oxidation resistance for the specimens with these Ni aluminide coatings was examined in air at 1423 K.

2. Experiment

A 10 × 10 × 1.5 mm test piece was cut out of the Ni to serve as the cathode substrate. The sample surface was polished with #800 SiC paper and then ultrasonically washed in acetone. A 1 mm diameter hole was drilled at the top of the electrode specimen and connected to a 0.5 mm Pt lead wire. A 6 × 50 mm graphite rod was employed as the anodic counter electrode. The electrolytic bath was an equimolar NaCl-KCl melts containing 3.5 mol%ZrF₄ or AlF₃ for the electrodepositions of Zr and Al, respectively. The NaCl, KCl, ZrF₄ and AlF₃ were prepared from reagent-grade chemicals. NaCl and KCl were vacuum-dried for 86.4 ks at 543 K prior to mixing.

*Graduate Student, Akita University

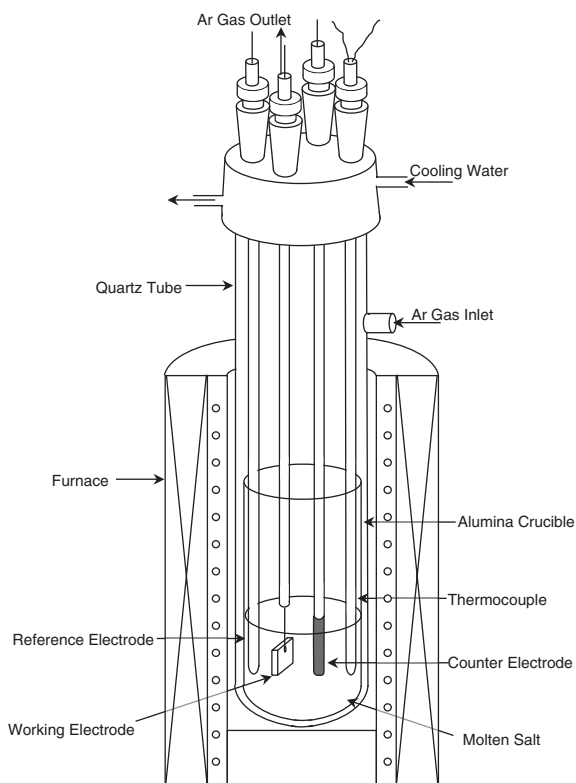


Fig. 1 Electrolytic cell for electrodeposition experiment.

Figure 1 is a schematic depiction of the electrolytic cell.⁸⁻¹²⁾ The cell container was an alumina crucible (internal diameter 35 mm, height 158 mm) held in a quartz tube (external diameter 63 mm, height 300 mm) set in a vertical electric furnace. The mixed salt was placed in the cell container installed with a reference electrode and a protective sheath for the thermocouple, and then it was heated in the furnace. When the salt melted and the temperature reached the prescribed temperature, the specimen electrode and counter electrode were immersed in the molten salt. Prior to the heating, high-purity Ar gas was introduced into the cell to make the environment inert. During the heating and

the electrodeposition experiment, Ar gas was fed into the cell at a flow rate of $3.3 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$. The reference electrode was an Ag wire immersed in an NaCl-KCl-AgCl (45 : 45 : 10 mol%) mixture held in a mullite tube (6 mm external diameter, 500 mm length).

The cathodic polarization curve was measured at 1023 K by a potential sweep at $1.7 \times 10^{-3} \text{ V} \cdot \text{s}^{-1}$ using the Ni specimen electrode. The Zr electrodeposition was done for 0.06 ks at the reduction potential of the Zr ion determined in this way in the equimolar NaCl-KCl melt with 3.5 mol%ZrF₄ at 1023 K. The Al electrodeposition was done for 3.6 ks at the reduction potential of the Al ion determined in this way in an equimolar NaCl-KCl melt with 3.5 mol%AlF₃. The temperature of the Al electrodeposition was at 1023 K, 1073 K, 1153 K or 1173 K.

After the electrodeposition, the specimen was removed from the cell and its surface was washed to remove the salt from the molten salt bath adhering to it. The specimen's cross-section was inspected by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA), and the deposited layer was identified by XRD (X-ray diffraction; CuK α radiation).

The cyclic oxidation resistance of the Ni specimen after the electrodeposition treatment was evaluated by measuring the oxidation weight gain curve in air at 1423 K. For the cyclic oxidation test, the time of one cycle was 3.6 ks.

3. Results and Discussion

3.1 Cathodic polarization behavior

Figures 2(a) and 2(b) show the cathodic polarization curves of Ni at 1023 K in an NaCl-KCl molten salt and in the molten salts with 3.5 mol%ZrF₄ and those in the NaCl-KCl molten salt and the molten salt with 3.5 mol%AlF₃, respectively. No cathodic current was detected in the NaCl-KCl molten salt even when the potential was decreased to -1.5 V , but a cathodic current rise due to reduction of Na⁺ or K⁺ was detected in the potential region less noble than -2 V . In contrast, a rise in the cathodic current became detectable from around -1.0 V in the NaCl-KCl molten salt

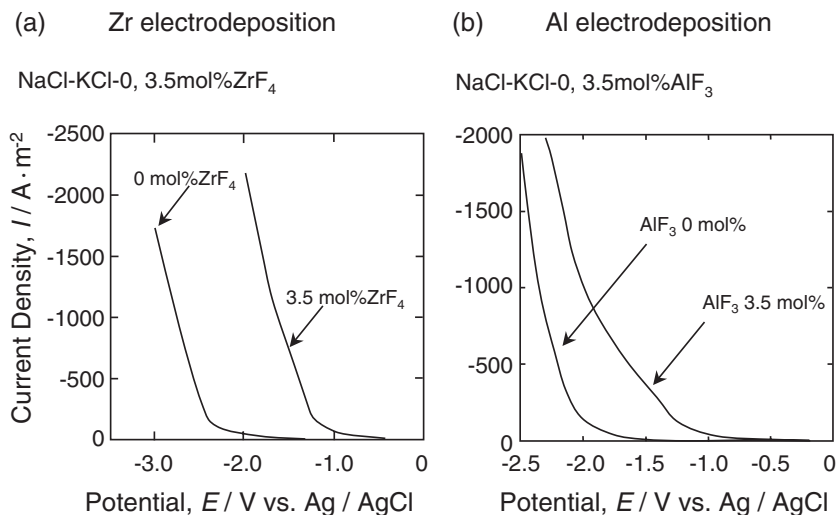


Fig. 2 Cathodic polarization curves of Ni measured at 1023 K in the NaCl-KCl melts with and without 3.5 mol%ZrF₄ (a) and those with and without 3.5 mol%AlF₃ (b).

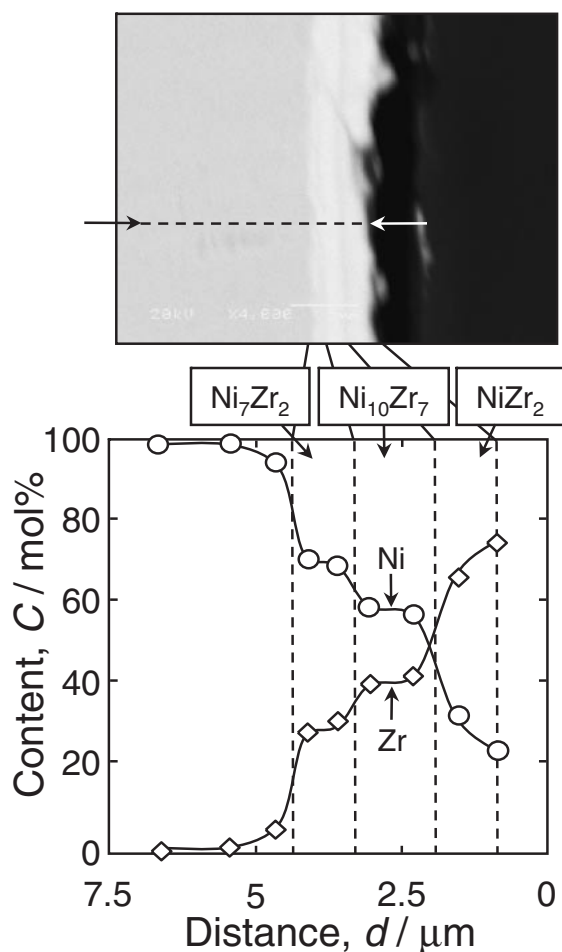


Fig. 3 Cross-sectional micrograph and concentration profiles of Ni and Zr across Ni specimen with Zr deposit.

with ZrF_4 , implying the occurrence of a cathodic reduction of Zr ion at potentials less noble than -1.0 V. A rise in the cathodic current also became detectable from around -1.0 V in the NaCl-KCl molten salt with 3.5 mol% AlF_3 , implying the occurrence of a cathodic reduction reaction of Al ion at potentials less noble than -1.0 V.

3.2 Morphology and composition of coating layer

Figure 3 shows cross-sectional micrograph and concentration profiles of Ni and Zr for Ni specimen after polarization at -1.7 V in a NaCl-KCl-3.5 mol% ZrF_4 melt for 1.8 ks. The electrodeposited layer of $5 \mu m$ thickness adhering tightly to the substrate was observed. The electrodeposited layer consisted of Ni_7Zr_2 , $Ni_{10}Zr_7$ and $NiZr_2$. It was considered that the formation of these intermetallic compounds was caused by mutual diffusion of deposited Zr and Ni substrate during Zr electrodeposition at 1023 K.

Figure 4 shows the cross-sectional micrograph and concentration profiles of Ni and Al across the Ni specimen after polarization at -1.4 V in NaCl-KCl-3.5 mol% AlF_3 at 1023 K for 3.6 ks. The electrodeposition layer of $33 \mu m$ thickness adhering tightly to the substrate was observed on the Ni specimen. The electrodeposition layer consisted of Ni_2Al_3 . It is considered that the layer was formed by the mutual diffusion of the deposited liquid Al and Ni substrate during Al electrodeposition at 1023 K.

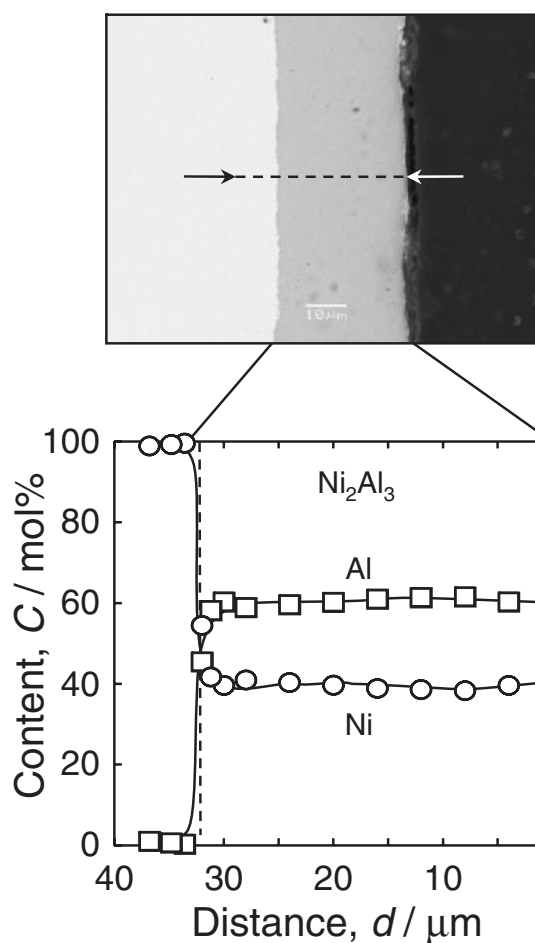


Fig. 4 Cross-sectional micrograph and concentration profiles of Ni and Al across Ni specimen with Al deposit.

Figures 5(a), 5(b) and 5(c) show cross-sectional micrographs and concentration profiles of Ni, Zr and Al across the Ni specimens with Zr deposition in NaCl-KCl-3.5 mol% ZrF_4 at -1.7 V for 0.06 ks, followed by Al depositions at -1.4 V for 3.6 ks in NaCl-KCl-3.5 mol% AlF_3 at 1073, 1153 and 1173 K, respectively. The layers formed by the electrodepositions of Al at 1073 and 1153 K had about $20 \mu m$ thickness. The layer formed by the electrodeposition of Al at 1173 K had about a $60 \mu m$ thickness. These electrodeposited layers consisted of Ni_2Al_3 . For the deposited layer at 1073 K, Zr was concentrated in surface region of the deposited layer. The Zr concentration of this point was about 10 at%. For the deposited layer at 1153 and 1173 K, on the other hand, the Zr did not segregate in the surface region. The Zr concentration in the surface region for the both layers was about 0.2 at%. It is thought that the fact that there was no segregation of Zr in the surface region for the layer deposited at 1153 and 1173 K resulted from an occurrence of the mutual diffusion of Ni and Zr, which was promoted when the temperature of the Al electrodeposition was high.

3.3 Cyclic-oxidation resistance of specimens with coating

Figure 6 shows the results of the cyclic oxidation test at 1423 K in air for the specimens treated with Zr deposition, followed by Al deposition at 1073, 1153 and 1173 K. For

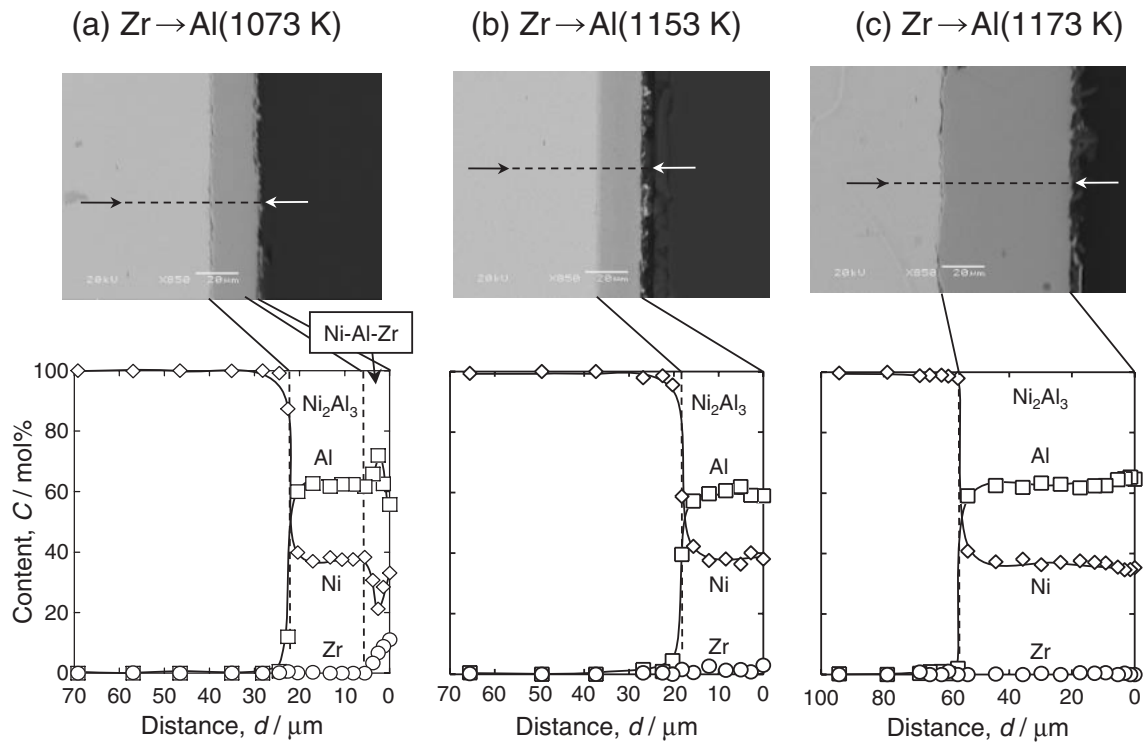


Fig. 5 Cross-sectional micrographs and concentration profiles of Ni, Al and Zr across Ni specimens with Zr and Al deposits.

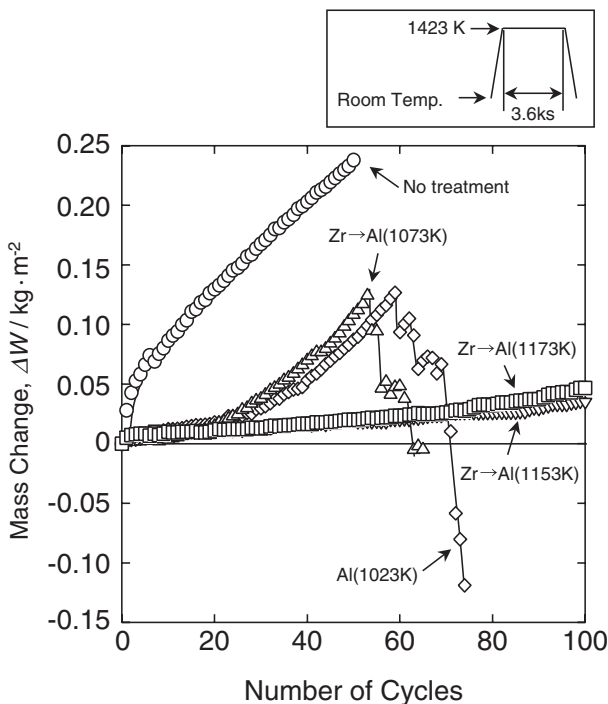


Fig. 6 Mass change-cycle number curves of Ni with and without Al and Zr deposits during cyclic oxidation at 1423 K in air.

comparison, this figure contains the results of the specimen of no treatment and that treated with only Al deposition at 1073 K. For the specimen of no treatment, mass gain was largely increased with a time. For the specimen treated with only Al deposition, the mass gain increased after about 20 cycles, and the mass started to decrease due to the spallation of the scale after 50 cycles. For the specimen treated with Zr

deposition, followed by Al deposition at 1073 K, the mass gain also increased after about 20 cycles, then the mass started to decrease due to the spallation of the scale after about 50 cycles. The increase in the mass for this specimen seems to result from the fact that Zr was preferentially oxidized because of the high Zr concentration in the surface region of Ni aluminide layer. For the specimens treated with Zr deposition, followed by Al deposition at 1153 and 1173 K, on the other hand, the mass gain was small, and no mass decrease due to spallation of the scale was observed. It is postulated that this resulted from the fact that the Zr concentration in the surface region of the Ni aluminide decreased because the Zr diffused into the Ni aluminide during the Al deposition at high temperatures, such as 1153 K and 1173 K.

Figures 7(a) and 7(b) show cross-sectional micrographs and concentration profiles of Al, Zr, Ni and O for the specimen treated with the Zr deposit, followed by an Al deposit at 1073 K and those for the specimen treated with the Zr deposit, followed by an Al deposit at 1153 K, respectively, after cyclic oxidation at 1423 K for 100 cycle in air. A thick scale mainly consisting of Ni oxide was formed on the specimen treated with the Al deposit at 1073 K. For this sample, the coating surface contained 10 mol% Zr. It was observed for this sample that the scale of initial oxidation period consisted of Al_2O_3 and ZrO_2 . It was estimated that in the scale consisting of a mixture of Al_2O_3 and ZrO_2 , a large internal stress was generated due to that there was a difference in the growth rate between Al_2O_3 particle and ZrO_2 particle in the scale. It was thought that this stress accelerated the spallation of scale, in addition to the thermal stress due to the thermal cycle. The spallation and regeneration of scale consisting mainly of the Al_2O_3 increased Ni

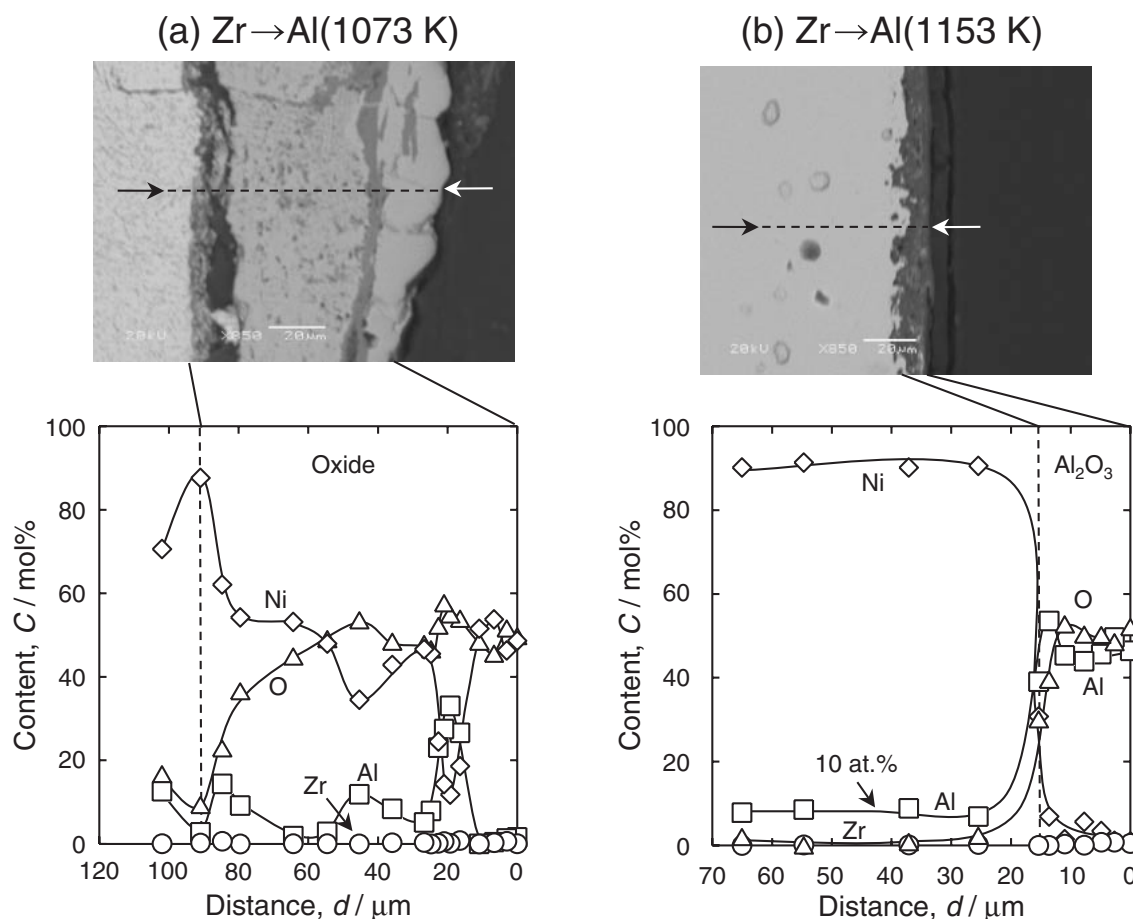


Fig. 7 Cross-sectional micrographs and concentration profiles of Ni, Al, Zr and O across Ni specimens with Zr and Al deposits after cyclic oxidation at 1423 K for 100 cycle in air.

concentration in coating surface area. Finally, it was thought that the scale consisting mainly of NiO was formed. On the other hand, it was found that an Al_2O_3 scale was formed on the specimen treated with the Al deposit at 1153 K. For this specimen, moreover, about 10 at% of Al remained in a metal below the scale. The Ni-Al binary phase diagram shows that the metal below the scale having this Al concentration is γ -Ni. It is postulated that the Al concentration of the Ni-Al alloy layer below the scale decreased due to the inner diffusion of Al into the substrate and the continual formation of Al_2O_3 during the cyclic oxidation test. However, Al is not consumed by the formation of the Al_2O_3 when spallation of the Al_2O_3 scale does not occur. Therefore, it is thought that the decrease of the Al concentration in the metal below the scale was small because the spallation of the scale did not occur for this sample during the cyclic oxidation. Moreover, it was found that for this sample the Al_2O_3 scale had a spiked shape that locally penetrated into the Ni substrate. As a result, it is thought that for this sample, the adhesion of the Al_2O_3 scale to the Ni substrate was improved, and the spallation resistance of the scale was improved.

Besides the keying on effect described above, the following mechanisms were proposed as the reason for the improvement in the high spallation resistance of the scale due to the addition of a small amount of Zr. Kahn³⁾ reported that ZrO_2 particles were formed in the Al_2O_3 scale on the Ni aluminide, and the inner diffusion of oxygen in the Al_2O_3

scale was promoted through these particles. As a result, voids at scale/alloy interface disappeared. On the other hand, Kurokawa⁷⁾ reported that the formation of the voids at the scale/alloy interface was inhibited because the outer diffusion of Al in the Ni aluminide below the Al_2O_3 scale was promoted by adding Zr into the Ni aluminide. As shown in Fig. 7(b), this scale went into the substrate after cyclic oxidation test. Therefore, it is thought that this scale was grown by an inward diffusion of the oxygen. Consequently, this fact suggested that the effect of Zr for the spallation resistance of scale was explained by Kahn's mechanism. Based on the results of this study, the voids at the scale/alloy interface was not also observed. Therefore, it is thought that the spallation of the Al_2O_3 scale was improved by the Zr addition due to the mechanism of the disappearance of void at the scale/alloy interface together the keying on effect of scale.

4. Conclusions

A Ni aluminide layer containing a small amount of Zr was formed on Ni specimen by electrodeposition of Zr and Al in molten salt. The temperature of the Al electrodeposition was at 1023 K, 1073 K, 1153 K or 1173 K. The effect of the temperature of the Al electrodeposition on the cyclic oxidation resistance was evaluated. The following conclusions can be drawn.

(1) For the specimen treated with the Zr deposition, followed by the Al deposition at 1073 K, Zr did not inwardly diffuse into the Ni₂Al₃ layer, and was contained in the surface region of the Ni₂Al₃ layer.

(2) For the specimen treated with the Zr deposition, followed by the Al deposition at 1153 and 1173 K, Zr inwardly diffused into the Ni₂Al₃ layer, and was uniformly contained with a small amount in the Ni₂Al₃ layer.

(3) The result of cyclic oxidation at 1423 K showed that for the specimen treated by Zr deposition followed by Al deposition at 1073 K, which had a large amount of Zr in the surface region of the Ni₂Al₃ layer, the cyclic oxidation resistance was not improved. On the other hand, for the specimen treated by Zr deposition, followed by Al deposition at 1153 and 1173 K, which had a small amount of Zr in the surface region of the Ni₂Al₃ layer, the cyclic oxidation resistance was improved.

Acknowledgment

This study was supported in the part by research fund (Kaken-hi: Specially Promoted Research No. 16001004) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

- 1) T. Narita, M. Shoji, Y. Hisamatsu, D. Yoshida, M. Fukumoto and S. Hayashi: *High Temperature Corrosion and Protection 2000*, (ISIJ, 2000) pp. 351–357.
- 2) J. L. Smialek: *Metall. Trans A* **9A** (1978) 309–320.
- 3) A. S. Kahn, C. E. Lowell and C. A. Barrett: *J. Electrochem. Soc.* **127** (1980) 670–678.
- 4) T. T. Chang, Y. C. Pan and T. H. Chuang: *J. Alloy. Compd.* **243** (1996) 126–132.
- 5) B. A. Pint: *Oxid. Met.* **45** (1996) 1–37.
- 6) J. A. Haynes, B. A. Pint, K. L. More, Y. Zhang and I. G. Wright: *Oxid. Met.* **58** (2002) 513–544.
- 7) K. Kurokawa, S. Kawata, A. Yamauchi, S. Watanabe and T. Narita: Report of 123rd committee on high temperature metals and alloys, Japan Soc. for Promotion of Science, **46** (2005) pp. 311–316.
- 8) M. Fukumoto, M. Hara, Y. Sato, T. Kidachi and T. Nagataki: *J. Japan Inst. Metals* **66** (2002) 684–689.
- 9) M. Fukumoto, M. Hara and T. Nagataki: *Zairyo-to-Kankyo* **51** (2002) 510–515.
- 10) M. Fukumoto, T. Nagataki and M. Hara: *J. Soc. Mater. Eng. Resources Jpn.* **16** (2003) 7–13.
- 11) M. Fukumoto, M. Hara and T. Fujimori: *J. Surf. Finish. Soc. Jpn.* **54** (2003) 798–805.
- 12) M. Fukumoto, T. Saruta, M. Hara and T. Narita: *J. Japan Inst. Metals* **71** (2007) 41–46.