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High temperature corrosion study on yttrium modified aluminide coatings on IN 713C

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Abstract. — The addition of active elements in high temperature materials may improve corrosion resistance extensively. In general, the active elements are incorporated in the form of an alloying element either in the bulk or in overlay coatings, as an oxide dispersion, or by ion implantation. In this experiment, yttrium was incorporated by an ion plating method either before or after pack aluminizing to maximise the corrosion resistance of IN 713C. Various combinations of pack aluminizing and yttrium ion plating were examined with respect to coating sequence, aluminium activity, and corrosion environment. From all the various coating combinations examined, the best corrosion resistance was obtained from the H/A + Y (high activity aluminizing + Y-ion plating) type multilayer coatings. Uniformity of the Y deposition was greatly dependent upon the surface condition of the aluminide coating layer. The high activity aluminide coating gave better uniformity of Y deposition than did the low activity aluminide coating. Improvement of corrosion resistance by the Y-modified aluminide multilayer coatings of H/A + Y type may occur because Y present between the Al_2O_3 columns improves the Al_2O_3 scale adherence and substantially prohibits depletion of Al in the aluminide coating layer.

1. Introduction.

Pack aluminizing is widely used as the protective coating method for high temperature materials because of its practical advantages over the other coating methods. Of various coating processes commercially available today, this process is still considered as the most convenient and effective one. The corrosion resistance of the pack aluminized coatings depends primarily on the integrity of the Al_2O_3 scale forming on the aluminide coating layer. The integrity of the Al_2O_3 scale is dependent upon the stable supply of Al from the aluminide coating layer. Under thermal cyclic conditions, however, the coating layer formed by pack aluminizing easily spalls because of the loss of Al_2O_3 scale integrity under severe thermal stress. One of the recent major efforts for the pack cementation process has been with improvement of the Al_2O_3 scale adherence by incorporating an active element such as yttrium [1-3].

To improve the scale adherence, the oxygen active elements (OAE) are added into the high temperature materials which are designed to form Al_2O_3 or Cr_2O_3 scales for corrosion protection [4, 5]. The OAE are also added to the alloy systems for overlay coatings such as MCrAlY [6]. Yttrium (Y), cerium (Ce), and hafnium (Hf) are the OAE most commonly used in the high temperature systems. The beneficial effects of OAE for the oxide scale adherence have been discussed in numerous literature studies [4-8]. Nevertheless, the mechanisms are not yet clearly understood. The most frequently mentioned effects include: 1) mechanical keying effect; 2) improvement of the scale plasticity; 3) modification of scale morphology and structure and 4) curtailment of transient oxidation.

The OAE can be incorporated into the high temperature metallic and coating systems in different ways:

- 1) by addition of pure OAE to the bulk metal;
- 2) by dispersion of OAE oxide in the bulk metal;
- 3) by ion implantation and
- 4) by overlay coatings such as MCrAlY.

The first two methods effect a modification of the bulk alloy, while the latter two methods provide surface modification. The ion implantation method is not yet fully developed for industrial applications. The MCrAlY overlay coatings are achieved by electron beam physical vapor deposition (EB-PVD) as well as by the plasma spray coating. Recently, plasma spray technology for the overlay coatings has advanced to low pressure plasma spray (LPPS) and shrouded plasma spray (SPS) [9, 10].

All the coating processes commercially available for addition of the OAE are line-of-sight methods which restrict the uniform coating of components with complex geometries such as air passages of turbine airfoils. To overcome such restrictions, it is desirable to combine the pack aluminizing process and overlay coating process. Although a few efforts have been made for this purpose; the results are still controversial [1-3]. The purpose of this study is to establish a multilayer coating process of the pack aluminizing and Y-ion plating, and to evaluate the performance of this Y-modified aluminide multilayer coating by cyclic hot corrosion tests at elevated temperatures.

2. Experimental procedures.

2.1 SPECIMEN PREPARATION. — The substrate material used in this study was a commercial grade of IN 713C. The IN 713C ingot was sectioned into $15 \times 10 \times 2$ mm specimens by electrical discharge machining (EDM). All the specimens were polished by 600 grit paper and ultrasonically cleaned in acetone.

2.2 PACK CEMENTATION. — The IN 713C specimens were coated by the pack aluminizing process. According to the activity of the Al source, the pack aluminizing process can be divided into either a high activity process or a low activity process. In the high activity process, pure Al powder (99.9%) was used, while in the low activity process, a powder of Ni_2Al_3 alloy was used. The Ni_2Al_3 alloy ingot was cast in a vacuum arc melter with a mixture of 41 w/o Al and 59 w/o Ni, and this ingot was converted to powder by crushing. In the cementation pack, NH_4Cl powder was used as an activator, Al_2O_3 powders as a filler material, and Ar as the carrier gas. The typical pack cementation processes used in this experiment are listed in table I. For the high activity process, a post-coating heat treatment was performed to obtain a uniform coating layer of NiAl.

2.3 YTTRIUM ION PLATING. — Yttrium (Y) was deposited by an ion plating process. The Y source was placed in a crucible with ZrO_2 lining, and vaporized by heating with an electron beam source. The initial vacuum level of the chamber and the substrate temperature were set to 10^{-5} torr and 400°C , respectively. The Ar flow rate was 40 scm. The acceleration voltage of the electron beam was 10 kV, and the biased voltage applied to the substrate was -200 V. The thickness of the Y layer was primarily controlled by the deposition time.

Table I. — *Experimental conditions for pack cementation process.*

Process	Pack Composition	Condition	Heat Treatment
High Activity	15% Al + 3% NH ₄ Cl + 82% Al ₂ O ₃	800°C x 2h	1100°C x 4h
Low Activity	15% Ni ₂ Al ₃ + 3% NH ₄ Cl + 82% Al ₂ O ₃	1100°C x 10h	--

2.4 HOT CORROSION TEST. — Evaluation of hot corrosion behavior was carried out by a high temperature hot corrosion test (HTHC). Specimens with the multilayer coatings were evaluated along with the specimens with a single layer coating to observe the difference between them. All the hot corrosion tests were performed under thermal cyclic condition to examine the effect of thermal stress on the adherence of the coating layer to the substrate.

The HTHC type is generally defined as the hot corrosion occurring due to exposure of a specimen to a Na₂SO₄ liquid film in an air or oxygen environment. The HTHC test is usually performed above the 884 °C melting point of Na₂SO₄. An aqueous solution of Na₂SO₄ was sprayed onto the coated specimen which was preheated to 300 °C. The amount of Na₂SO₄ was about 2 mg/cm². Specimens with Na₂SO₄ films were exposed in a box furnace in air at 900 °C for 20 hours. The weight change was measured after every 20 hours of exposure. After each cycle of weight change measurement, the same processes were repeated.

3. Results and discussion.

3.1 FORMATION OF MULTILAYER COATING.

3.1.1 Al + Y type multilayer coating. — The IN 713C specimens were coated by two different coating sequences. One was coated by pack aluminizing followed by Y-ion plating(Al + Y type) and other by the reverse order(Y + Al Type). But no Y was detected by EPMA analysis from the Y + Al multilayer coatings. The instability of the ion-plated Y during the subsequent pack aluminizing process has been thoroughly examined through various experiments [11].

Since the Y + Al type multilayer coating was not possible, an Al + Y type multilayer coating has been studied. For the pack aluminizing process, both low and high activity types were used. From the low activity process, the total coating thickness was 100 μm including 50 μm of interdiffusion layer. From the high activity process, the coating was 180 μm with 30 μm of interdiffusion layer. In the interdiffusion layers obtained from both processes, carbides of M₆C and M₂₃C₆ types along with Cr and Mo were precipitated out of the NiAl phase. In the outer zone of the coating layer, Cr was dissolved in the NiAl phase for the low activity process, whereas a Cr-rich phase precipitated out of the NiAl phase for the high activity process.

The Y-ion plating was performed for both types of specimens from two different pack aluminizations. Figure 1 shows the x-ray mapping of Y on both types of specimens. For the low activity process, Y deposition was not uniform due to the uneven surface condition of the

aluminide coating layer. In fact, particles of Al_2O_3 filler materials were often embedded in the NiAl coating layer. Due to these uneven surfaces, Y did not find adequate nucleation sites and in some cases Y deposition was clustered because of the shadow effect by the protrusions on the NiAl coating surface. In the case of the high activity process, in contrast to the low activity process, Y deposition was relatively uniform, and its thickness was about $1.8\text{ }\mu\text{m}$. The x-ray analysis for Y deposit showed metallic Y peaks as the primary peaks and Y_2O_3 peaks as the minor peaks. In fact, the uniformity of Y deposition was one of the key factors for corrosion resistance of the Al + Y type multilayer coatings, as is shown later. To improve the surface condition of the diffusion type coating process, a CVD type [12] or an out-of-contact type of pack cementation [13] may be recommended for the multilayer coatings.

Fig. 1. — SEM micrograph and EPMA mappings of the surfaces of aluminizing + Y-ion plating specimens.

3.2 HOT CORROSION TESTS.

3.2.1 Cyclic high temperature hot corrosion test. — Figure 2 shows the weight changes for IN 713C specimens with various coatings after cyclic HTHC tests. The uncoated IN 713C alloy and the specimens with a single aluminide coating started to deteriorate severely after 100 hours and were completely destroyed after 200 hours. However, the specimens with Y-modified coatings showed a much slower degradation rate. The specimen with a H/A + Y type multilayer coating showed outstanding corrosion resistance. It survived up to 600 hours (or 30 cycles) without any discernible surface degradation, but it was severely deteriorated after 680 hours.

Fig. 2. — Weight change vs. time plot for coated specimens after high temperature hot corrosion tests in air at 900 °C.

Deterioration of this specimen started from a localized corrosion site which led to an overall attack. This cyclic HTHC test on the specimen with H/A + Y type multilayer coating also suggested that the uniformity of Y deposition was a key factor for improving the corrosion resistance. Therefore, the surface condition of the aluminide coating layer was a very important parameter for the success of the Y-modified multilayer coating.

According to this experiment, it is clear that the H/A + Y type multilayer coating process can be an effective method for improving the corrosion resistance of the high temperature alloys against HTHC occurring in molten Na_2SO_4 salt, for which the basic fluxing is dominant.

3.2.2 Effect of Y modification. — The effect of Y of the H/A + Y type multilayer coating on the stability of the aluminide coating was examined through various HTHC tests. The HTHC test condition was the same as the one mentioned in section 2.4. After 30 minutes exposure, the specimen with the H/A single layer coating showed a severe degradation all over the surface and many localized pits. However, the specimen with the H/A + Y type multilayer coating showed a good surface condition. Figure 3 shows the surface morphology of this specimen and Auger electron spectroscopic (AES) analyses. The protrusions or columnar structures shown in the outer most surface were identified as Al_2O_3 by both EDS and AES

analyses. The AES analysis showed the presence of only Al and O but no presence of Y at the center of the columnar structure (Marked A), and the clear existence of Y along with Al and O along the grain boundary area of the columnar structure (Marked B). The depth profile of the "Area A" suggests that an Al_2O_3 scale has grown from the NiAl coating layer. The depth profile of the "Area B" shows that the amount of Y is decreased as it goes in.

Fig. 3. — SEM micrograph and AES depth profile of H/A aluminizing + Y-ion plating specimens after high temperature hot corrosion test for 30 minutes at 900 °C: a) SEM Micrograph showing the analyzed area; b) AES Depth Profile of the area indicated by the mark A; c) AES Analysis of the Surface indicated by the mark B; d) AES Depth Profile of the area indicated by the mark B.

Figures 4 and 5 compare the SEM micrographs and EPMA mappings of the cross-sections of the H/A single and H/A + Y multilayer coating specimens after 160 hours of exposure in the HTHC condition. The H/A single coating specimen shows the development of cracks along the boundary between the NiAl coating layer and the substrate and spallation of the coating layer. EPMA mappings show clear evidences of Al depletion in the outer area of the NiAl coating layer and formation of bulk chromium sulfide by the inward diffusion of S. In contrast to this, the H/A + Y multilayer coating shows no evidence for crack development or spallation of the coating layer even though S diffused deep inside the coating layer. From EPMA mappings, Al is enriched in the outer most layer of the coating but no depletion of

Al occurred. After 500 hours of exposure in HTHC, x-ray analysis shows only β -NiAl and α - Al_2O_3 peaks. This analysis clearly indicates that the ion-plated Y assists the integrity of the Al_2O_3 scale formed on the outer surface of the NiAl coating layer. In turn, Y improved the stability of the NiAl coating layer as a whole. This improvement in corrosion resistance is attributed to the fact that the Al_2O_3 scale adherence by deposition of Y onto the NiAl coating surface prohibits crack formation and spalling of the scale and the resulting depletion of Al in the aluminide coating layer.

Fig. 4. — SEM micrograph and EPMA mappings of cross section of H/A aluminizing after high temperature hot corrosion test for 160 hours at 900 °C.

4. Conclusions.

1) From all the various coating combinations examined, the best corrosion resistance was obtained from the H/A + Y type multilayer coating. Uniformity of the Y deposition was greatly dependent upon the surface condition of the aluminide coating layer. The high activity aluminide coating gave better uniformity of Y deposition than did the low activity aluminide coating.

2) During the initial stages of high temperature hot corrosion, Al_2O_3 has grown out of the ion-plated Y deposit in the form of protrusions or a columnar structure. The presence of Y was identified only in the areas between the Al_2O_3 columns.

3) Improvement of the hot corrosion resistance for the Y modified aluminide multilayer coatings of H/A + Y type may result from the presence of Y in the areas between the Al_2O_3 columns, which improves the Al_2O_3 scale adherence and substantially prohibits the depletion of Al in the aluminide coating layer.

Fig. 5. — SEM micrograph and EPMA mappings of cross section of H/A aluminizing + Y-ion plating after high temperature hot corrosion test for 160 hours at 900 °C.

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