Aluminizing of Nickel-Based Superalloys Grade IN 738 by Powder Liquid Coating

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Nickel-based superalloy grade IN738 has superior creep resistance, however, oxidation resistance is the main limitation of this alloy for practical applications at high temperature. Coating of nickel aluminate compounds which have high oxidation resistance on the IN738 alloys surface can remarkably increase the oxidation resistance by formation of Al2O3 film as protective layer. Aluminizing by powder liquid coating methods is applied in this research. Mixed slurries of Al and Al2O3 powders are pasted onto IN 738 samples and heated at 1273 K in argon atmosphere for 3.6 to 14.4 ks (1 to 4 h). Slurries can be classified into four different ratios of Al : Al2O3: 10 : 0, 7 : 3, 5 : 5 and 3 : 7. The microstructure was investigated by scanning electron microscope (SEM) and optical microscope. Phases in the coated layer are characterized by Glancing Incident-angle X-ray Diffractometer (GIXD) and Electron Probe Micro Analysis (EPMA). The results show that the coated layer is formed by dissolution of nickel into liquid aluminum at aluminizing temperature resulting in formation of intermetallic compound layer. The coated layer consists of Ni3Al as a main phase with small amount of NiAl and AlCr2. AlCr2 exists mostly at the layer adjacent to the top surface. For 8.1 and 14.4 ks (2.25 and 4 h) holding time, formation of AlCr2 at the interface of matrix and coated layer occurs due to diffusion of aluminum from coated layer into nickel matrix. The effect of time shows that longer aluminizing time leads to formation of a uniform coated layer. The Al : Al2O3 ratio of either 10 : 0 or 7 : 3 will create a uniform coated layer with thickness more than 200 μm.

Keywords: aluminizing, nickel aluminate, IN738, powder liquid coating

1. Introduction

Nickel-based superalloys grade IN738 is well known as a high temperature material due to its superior creep resistance.1 However, this alloy suffers from low oxidation and corrosion resistance. In order to apply nickel-based superalloys grade IN738 as machine parts in hot section under severe oxidative and corrosive atmosphere, surface modification to improve oxidation and corrosion resistance is necessary. Many research attempts related to protective film coating have been done to improve hot corrosion and oxidation resistance of IN738.2–5 Formation of intermetallic compound, for example nickel aluminate, covering entire surface is one way to increase oxidation resistance of IN738. The nickel aluminate layer acts as an aluminum sink, therefore, alumina film can form at high temperature as a protective layer retarding oxygen diffusion as well as oxidation.6 Several methods to increase aluminum content at the surface yielding formation of nickel aluminate on the surface of IN 738. A recently developed process is the so-called powder liquid coating process applied for aluminizing steel. This process employs pasting slurries, which act as a source for coating materials, on to the surface followed by subsequent heat treatment. The slurry contains coating metal powder, which is aluminum powder for aluminizing, mixed with other high melting point powder, such as Al2O3. Addition of Al2O3 powder helped retaining and dispersing molten aluminum to cover all coating areas, preventing coalescence of molten aluminum into separate pools. Therefore coating layer was formed uniformly and evenly on the entire surface.7 The purpose of this study was to apply powder liquid coating process to fabricate nickel aluminate layer which was well known as a protective layer for oxidation in nickel base superalloys. Effect of processing parameters which were slurry composition and heat treatment time on microstructure and phases of the fabricated layer was investigated.

2. Experimental Procedure

2.1 Sample preparation

Nickel-based superalloy grade IN738 (chemical composition shown in Table 1) was cut into rectangular shape with the size of 5 mm × 10 mm × 5 mm. All samples were polished by SiC paper to number 4000 grade. The samples were then rinsed in acetone by ultrasonic cleaning machine for 300 seconds.

2.2 Coating

Coating slurries were prepared from a mixture of Al and Al2O3 powders with various Al : Al2O3 ratios: 10 : 0, 7 : 3, 5 : 5 and 3 : 7. Alumina powder with a size of 160 μm was mixed with 3 μm aluminum powder. Ethylene glycol was added into the mixture of Al and Al2O3 powders to liquefy the mixture and this became the coating slurries. The slurries were pasted onto the samples with density of 1 kg/m2 (0.1 g/cm2) and were heated under argon atmosphere at 473 K, and held at this temperature for 5.4 ks in order to remove the ethylene glycol. After that, the temperature was increased to aluminizing temperature at 1273 K, and held for 3.6 ks (1 h), 8.1 ks (2.25 h), and 14.4 ks (4 h). The coating conditions are summarized in Table 2.

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Table 1 Chemical composition of IN738.

<table>
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<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Ti</th>
<th>Al</th>
<th>W</th>
<th>Mo</th>
<th>Ta</th>
<th>C</th>
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<td>mass%</td>
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<td>8.5</td>
<td>3.4</td>
<td>3.4</td>
<td>2.6</td>
<td>1.75</td>
<td>2.65</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>at%</td>
<td>17.5</td>
<td>8.2</td>
<td>4.0</td>
<td>7.2</td>
<td>0.8</td>
<td>1.0</td>
<td>0.8</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>
2.3 Characterization

Surface and cross-sectional microstructure of the coated samples were observed by an optical microscope and a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) and electron probe micro analysis (EPMA) were performed to investigate the distribution of elements in the coated layer. Phase formation in the coated layer was characterized by an X-ray diffractrometer (XRD) and a glacing incident angle X-ray diffractometer (GIXD) at the incident angle of 5 degree.

3. Results and Discussion

3.1 Phases and microstructure characterization

Figure 1 shows a cross-sectional microstructure of samples which were aluminized by slurries with different Al : Al$_2$O$_3$ ratios for 3.6 ks (sample No. 1 to 4 in Table 2). It can be seen that the different Al : Al$_2$O$_3$ ratios affect uniformity and thickness of the coating layer. The slurry with higher Al : Al$_2$O$_3$ ratio produces thicker and more uniform coated layer. In the case of 5 : 5 and 3 : 7 mixing ratios the coated layer does not cover the entire surface of IN738 matrix. This is because the amount of aluminum in the slurries is not sufficient to be uniformly distributed. Moreover, aluminum cannot wet nickel surface because the formation of nickel aluminide layer separates the liquid aluminum and the nickel matrix below. Nickel aluminide layer prevents liquid aluminum from spreading, therefore cannot cover the entire surface of nickel substrate.8) Figure 1(d) shows the aluminized layer formed on the top surface of IN738 sample. This microstructure shows that nickel and other alloying elements are dissolved into liquid aluminum at the aluminizing temperature resulting in the formation of aluminized layer on the top surface.

GIXD analysis at the surface of Nos. 1 to 4 samples is shown in Fig. 2. The coated layer consists of NiAl$_2$, Ni$_2$Al$_3$ and AlCr$_2$, while only
Ni$_2$Al$_3$ peaks are detected on the surface of sample No. 4. It can be seen that the relative intensities, which express volume fractions, of NiAl$_3$ and AlCr$_2$ decrease with decreasing amount of Al in the slurries but volume fraction of Ni$_2$Al$_3$ increases.

The contrast in cross-sectional microstructure along the depth from the surface indicates that several phases exist in the coated layer. The coated layer can be divided into 2 sub-layers: the first sub-layer is the grey color layer located next to the IN738 matrix, and the second sub-layer is at the top surface. It is mainly white in color with some splash of grey color phase, as can be seen in Fig. 1(a). Investigation of phases existing at various depths from surface was done by GIXD as shown in Fig. 3. The GIXD profiles show that there are NiAl$_3$, Ni$_2$Al$_3$ and AlCr$_2$ at the surface. The relative intensity shows that the main phases at the top surface, which is the second sub-layer, are NiAl$_3$ and AlCr$_2$. At increasing depth from the surface, the relative intensities of NiAl$_3$ and AlCr$_2$ become lower while the relative intensity of Ni$_2$Al$_3$ becomes higher. At depth greater than 150μm from the surface, the first sub-layer, Ni$_2$Al$_3$ is the main phase.

Distribution of aluminum, nickel, and chromium elements was investigated by EDS as shown in Fig. 4. The coated layer has higher content of aluminum than that of IN738 matrix. The first sub-layer has lower content of aluminum than the second sub-layer, and vice versa for nickel and chromium contents. The distribution of these elements corresponds well with the result from GIXD, in that Ni$_2$Al$_3$ in the first sub-layer has lower amount of Al than NiAl$_3$ in the second sub-layer. EDS line analysis of the second sub-layer shows large amount of aluminum at the top surface, which becomes less at increasing depth from the surface. In contrast, nickel content is lowest at the top layer. Distribution and concentration gradient of nickel and aluminum suggests that nickel atoms diffuse through solid Ni$_2$Al$_3$ layer and then dissolve into liquid aluminum at the aluminizing temperature.

Effect of aluminizing time is shown in Fig. 5. At short aluminizing time, there are two distinct sub-layers. When the aluminizing time is increased, the thickness of the first sub-layer remarkably increases, where as the thickness of the second sub-layer decreases. At sufficiently long aluminizing time, the second sub-layer disappears; the microstructure of coated layer becomes phasic uniform and contains only the first sub-layer. Therefore, sample No. 6, which has only first sub-layer uniformly coated on the IN 738 is selected for microstructure and phase analysis.

Sample No. 6 is aluminized at 1273 K for 8.1 ks, using slurry of 7 : 3 Al : Al$_2$O$_3$ ratio. Its EDS analysis is shown in Fig. 6. The first sub-layer contains nickel, large content of aluminum and small content of chromium. Figure 7(a) shows SEM micrograph of the first sub-layer formed on surface of sample No. 6. High magnification SEM micrograph of the first sub-layer and the first sub-layer/matrix interface are
shown in Fig. 7(b) and (c), respectively. The different contrast in Fig. 7(b) indicates three distinct phases. EPMA analysis of area in Fig. 7(b) is shown in Fig. 8. GIXD analysis at various depth of this sample is shown in Fig. 9. From Fig. 8, it is found that the main phase in the first sub-layer contains aluminum with a high content of nickel, the second phase contains more aluminum and less nickel, and the third phase contains a high amount of chromium and aluminum, with very low amount of nickel. Together with GIXD analysis which shows that there are only Ni$_2$Al$_3$, NiAl$_3$, and AlCr$_2$ in the first sub-layer, it can be identified that the main phase is Ni$_2$Al$_3$, the second phase is NiAl$_3$, and the third phase is AlCr$_2$.

The first sub-layer/matrix interface in Fig. 7(c) contains precipitates in form of light-colored elongated islands perpendicular to the interface in direction of the first sub-layer. EPMA analysis of the area in Fig. 7(c) is shown in Fig. 10. It shows that the precipitated islands are chromium rich phase. At depth between 160–190 µm, GIXD reveals diffraction peaks at 20.57, 42.50 and 43.55 degree corresponding to (002), (110), and (103) crystallographic planes of AlCr$_2$ and diffraction peaks of Ni$_2$Al$_3$. Therefore, the precipitated islands are identified as AlCr$_2$.

### 3.2 Mechanism of coated layer formation on IN 738

At aluminizing temperature, nickel and alloying elements in IN738 dissolve into molten aluminum. The concentration of nickel in aluminum is high at the interface between molten aluminum and matrix IN738. As soon as nickel content in molten aluminum reaches the solubility limit, Ni$_2$Al$_3$ is formed. Continuous formation of Ni$_2$Al$_3$ layer is by diffusion of nickel atoms through the newly formed Ni$_2$Al$_3$ layer into liquid aluminum. Nickel concentration in molten aluminum therefore increases and Ni$_2$Al$_3$ layer grows. With increasing aluminizing time, the Ni$_2$Al$_3$ layer, which is the first sub-layer, grows into liquid aluminum.
For short aluminizing time of 3.6 ks (1 h), distinction between the first and the second sub-layer can be easily made. The thickness of Ni$_2$Al$_3$ layer is thin due to insufficient time for nickel diffusion through Ni$_2$Al$_3$ layer. Therefore, molten aluminum remains on the top surface. During cooling down in the furnace, the remaining liquid aluminum with high nickel content transforms to Ni$_2$Al$_3$ and NiAl$_3$ during solidification. NiAl$_3$ can only precipitate stable phase at temperature lower than 1178 K. AlCr$_2$, which is found in the second sub-layer, also forms during solidification. This is due to the fact that Ni$_2$Al$_3$, which is the first phase formed at the interface, can dissolve Cr about 4 at% at 1273 K, as shown by ternary phase diagram of Ni-Al-Cr in Fig. 11. Dissolved Cr must be ejected from Ni$_2$Al$_3$ layer into adjacent liquid aluminum. This results in precipitation of AlCr$_2$ in the layer adjacent to the surface, coexisting with NiAl$_3$ in the second sub-layer.

For long aluminizing time, 8.1 and 14.4 ks (2.25 and 4 h), there is sufficient time for nickel diffusion to grow thick Ni$_2$Al$_3$ layer; therefore, all liquid aluminum is consumed and transformed to Ni$_2$Al$_3$ as a single layer. This coating layer can be considered as a high aluminum concentration layer. Aluminum can diffuse into IN738 matrix resulting in growth of Ni$_2$Al$_3$ into IN738 matrix. Ejection of
chromium out of Ni<sub>2</sub>Al<sub>3</sub> occurs as discussed above. The ejected chromium reacts with aluminum and precipitates as AlCr<sub>2</sub> islands as shown in Fig. 10.

4. Conclusions

Nickel aluminide layer is successfully formed by powder liquid coating. The appropriate Al : Al<sub>2</sub>O<sub>3</sub> ratios are 7 : 3 or 10 : 0. Thickness of coated layer reaches to more than 200 μm after aluminizing for 8.1 ks (2.25 h). This coated layer consists of Ni<sub>2</sub>Al<sub>3</sub> as a main phase coexisting with NiAl<sub>3</sub> and AlCr<sub>2</sub>.

For short aluminizing time, the coated layer can be divided into two sub-layers: Ni<sub>2</sub>Al<sub>3</sub> rich layer besides the IN738 matrix and NiAl<sub>3</sub> rich layer at the surface. For long aluminizing time, the coated layer is uniform consisting of mainly Ni<sub>2</sub>Al<sub>3</sub> with some precipitates of NiAl<sub>3</sub> and AlCr<sub>2</sub>. The formation of the coated layer is firstly controlled by reaction of Ni<sub>2</sub>Al<sub>3</sub> formation between liquid aluminum and nickel. After Ni<sub>2</sub>Al<sub>3</sub> layer is formed, diffusion of nickel atoms through Ni<sub>2</sub>Al<sub>3</sub> layer controls growth of Ni<sub>2</sub>Al<sub>3</sub> layer into liquid aluminum. AlCr<sub>2</sub> islands are also found at the interface between the coated layer and the matrix due to low solubility of chromium in Ni<sub>2</sub>Al<sub>3</sub>.

REFERENCES