Low-temperature Formation of Aluminide Coatings on Ni-base Superalloys by Pack Cementation Process

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Abstract

This article investigates the low-temperature formation of aluminide coatings on a Ni-base superalloy by pack cementation process. The pack cemented coatings characteristic of high density and homogeneity possess a two-layer structure. The top layer mainly consists of Al\(\text{3}\)Ni\(\text{2}\) and Al\(\text{3}\)Ni, while the bottom layer of Al\(\text{3}\)Ni\(\text{2}\). Great efforts are made to elucidate the effects of different experimental parameters on the microstructure and the constituent distribution of the coatings. The results show that all the parameters exclusive of the pack activator (NH\(\text{4}\)Cl) content produce effect on the coating thickness, but do not on the microstructure and the constituent distribution. The pack activator (NH\(\text{4}\)Cl) content affects neither the coating thickness nor structure and constituent distribution. The parabolic relationship between the coating thickness and the deposition time suggests that the process is diffusion-controlled. Furthermore, the article demonstrates a linear relationship between the coating thickness and the reciprocal deposition temperature.

Keywords: low-temperature aluminizing; aluminide coatings; nickel alloys; pack cementation process; experimental parameters

1. Introduction

Aluminide coatings have been frequently applied to Ni-base superalloys to improve their high-temperature oxidation resistance due to the formation of a stable Al\(\text{2}\)O\(\text{3}\) scale which acts as a protective barrier separating the substrate material from aggressive agents in environment\([1-3]\). It is well known that nickel aluminides such as Al\(\text{3}\)Ni\(\text{2}\), AlNi and AlNi\(\text{3}\) are constituents of Al\(\text{2}\)O\(\text{3}\) scales immune against high-temperature oxidation\([1, 4]\).

As a versatile and economical process, the pack cementation process is usually used to deposit aluminide diffusion coatings on Ni-base superalloys\([5-7]\). The pack cementation process is essentially an in-situ chemical vapour deposition process (CVD) and a thermal diffusion process\([8]\). This process has been widely and chronically used to treat components of various dimensions and geometries. However, it is seriously limited by requiring thermal activation to boost chemical reaction and interdiffusion kinetics\([2,8-10]\). As a result, most of the processes are carried out at a temperature higher than 900 °C and last a long time. This would for certain lead to fatal degradation of the mechanical properties of the substrate alloy due to the microstructure changes associated with grain coarsening and carbide precipitation\([9,11-12]\). To settle this problem, the pack aluminizing process is required to be conducted at temperatures below 800 °C.

Some works\([2-3,13-15]\) systematically reported the dependence of the low-temperature pack aluminizing parameters (e.g., temperature) on the growth kinetics and resultant microstructures of the aluminide coatings prepared on steels. A few works\([4-6]\) laid focus on the low-temperature formation of the aluminide coatings on Ni-base superalloys by modified pack cementation process in which ball impact was provided by a vibrating generator. As a result, the process is more complex and expensive than the traditional pack cementation process. So far, there is no meaningful literature or published reports available on the application of low temperature pack cementation process to fabricate aluminide coatings on nickel-base superalloys. This study was thus undertaken to systematically investigate the effects of pack compositions and deposition conditions on the aluminide coating formation for a Ni-base superalloy. An extensive discussion is
also led about the relationship between the coating thickness and the deposition temperature based on the Arrhenius theory.

2. Experimental

2.1. Specimens preparation

A Ni-base superalloy named K3 was used as the substrate in the experiments. The nominal composition (wt%) of the alloy was Ni (balance)-C (0.11-0.18)-Cr (10-12)-W (4.5-5.5)-Mo (3.8-4.5)-Ti (2.3-2.9)-Al (5.3-5.9)-Co (4.5-5.5). Prior to the experiments, the material was cut into rectangular specimens with dimensions of 15 mm×10 mm×2 mm. Then they were manually ground to a 500-grade finish by using SiC abrasive paper and washed with acetone in an ultrasonic bath for 5 min.

2.2. Experimental processes

The pack powders (20 g in total) consists of pure Al powder, α-Al2O3 filler and NH4Cl activator. Before being put into the retort, these substances were manually ground with a mortar and a pestle. Then the specimens were buried in the pack powders charged into a cylindrical alumina retort (30 mm in diameter and 40 mm in length). Then the retort was heated to an appropriate temperature, at a heating rate of 5 °C/min and was held at this temperature for a required duration. The furnace was then cooled to room temperature naturally by switching off its power supply while keeping the gas-argon flowing.

2.3. Microstructure characterization

Surface and cross-sectional observations of the coated specimens were performed on a scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) analysis of the surface layer of as-coated specimens was carried out with 40 kW, Cu-Kα radiation of λ = 0.154 18 nm, and small steps of 2θ = 0.02°.

3. Results and Discussion

3.1. Features of coatings

Fig.1 presents the cross-sectional microstructure and the constituent distribution of a treated specimen after the treatment at 700 °C for 8 h. In the processing, the content (wt%) of pack Al, Al2O3 and NH4Cl were 10, 80 and 10, respectively. It can be seen that the aluminide coating has a two-layer structure with the top layer about 90 μm thick. As shown in Table 1, the contents of nickel and aluminum in the top layer are about 40wt% and 50wt%, respectively. The XRD patterns identify that the top layer consists mainly of Al3Ni2 and Al3Ni with a small quantity of Al-Cr intermetallics (see Fig.2).
Table 1  Content of the elements in top layer and bottom layer

<table>
<thead>
<tr>
<th>Layer</th>
<th>Element</th>
<th>wt%</th>
<th>at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top layer</td>
<td>Al</td>
<td>50.42</td>
<td>68.46</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>1.03</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>5.77</td>
<td>4.07</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>3.50</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>39.29</td>
<td>24.52</td>
</tr>
<tr>
<td>Bottom layer</td>
<td>Al</td>
<td>44.66</td>
<td>63.26</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>1.25</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>6.46</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>3.83</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>43.79</td>
<td>28.51</td>
</tr>
</tbody>
</table>

The bottom layer of the coating about 30 μm thick is characterized by high density, homogeneity and excellent adherence to the substrate. The contents of the elements in bottom layer measured by EDS are shown in Table 1 which indicates that the chief constituent of the bottom layer is Al₃Ni₂.

3.2. Effect of pack Al content

To investigating the effect of pack Al content on the aluminizing process, the pack Al content varied from 5wt% to 30wt% while keeping pack NH₄Cl content constant at 10wt%. All the experiments are undertaken at the temperature of 700 °C for 8 h. Fig.3 shows the cross-sectional microstructures of the aluminide coatings under the treatment with different pack Al content. It can be seen that all the coatings have the similar characteristic with two layers.

Fig.3  Cross-sectional microstructures of various aluminide coatings prepared using the aluminizing powder mixtures containing different Al contents.

Fig.4 illustrates the XRD patterns of surfaces of aluminide coatings of different pack Al contents. The results show that the top layer is mainly composed of Al₃Ni₂, Al₃Ni and Al₆Cr₁₄. Similar to the sample discussed firstly, the bottom layer is mainly composed of Al₃Ni₂.

Fig.4  XRD patterns of surfaces of aluminide coatings under treatment with various pack Al contents.
Fig. 5 plots the coating thickness as a function of pack Al content. It indicates that the coating thickness increases rapidly from 73.24 μm to 230.19 μm as the content of pack Al increases from 5wt% to 20wt%. Nevertheless, as the Al pack content increases from 20wt% to 30wt%, the increase in coating thickness amounts to only 15.96 μm. This indicates that the relationship of coating thickness with pack Al content may follow an approximately parabolic relation.

Fig. 6 illustrates the variation of the thickness of the coatings on the Ni-base superalloy as a function of the pack NH₄Cl contents. The coating thicknesses (μm) are 110.74, 113.97, 114.42 and 114.93 with the corresponding pack NH₄Cl contents (wt%) being 5, 10, 20 and 30, respectively. These data indicate that when the deposition temperature and time keep constant, the coating thickness is only affected by pack Al content within error of the measurements.

Fig. 7 shows the relationship between coating thickness and treatment duration. The effect of treatment duration on the coating formation was studied at 700 °C with a pack content of 10wt% Al, 80wt% Al₂O₃ and 10wt% NH₄Cl. The structures of the coatings treated for different durations varied from 1 h to 12 h are the same as those are discussed above. However, the thickness of the coatings with different durations varies a lot. The relationship between deposition time and coating thickness is shown in Fig. 7. When the treatment duration rises from 1 h to 8 h, the coating thickness increases rapidly (from 76.90 μm to 124.88 μm accordingly). However, it changes a little when further increasing the treatment duration to 12 h. The analysis evinces that the relationship between the coating thickness and the treatment duration follows an approximately parabolic law, which is a typical feature consistent with the diffusion controlled coating growth mechanism.

3.3. Effect of activator (NH₄Cl) content

The effect of pack NH₄Cl content on the aluminizing process is investigated by varying pack NH₄Cl content from 5wt% to 30wt% while keeping pack Al content constant at 10wt%. The treatment temperature and deposition time were 700 °C and 8 h respectively. The curves illustrate the variation of the thickness of the coatings on the Ni-base superalloy as a function of the pack NH₄Cl contents. The coating thicknesses (μm) are 110.74, 113.97, 114.42 and 114.93 with the corresponding pack NH₄Cl contents (wt%) being 5, 10, 20 and 30, respectively. These data indicate that when the deposition temperature and time keep constant, the coating thickness is only affected by pack Al content within error of the measurements.

3.4. Effect of treatment duration

The effect of treatment duration on the coating growth rate can be described through the following Arrhenius relationship:

\[ \ln k = -\frac{Q}{RT} + C \]

where \( Q \) is the activation energy, \( R \) the gas constant, \( T \) the absolute temperature, and \( C \) a constant. As already stated, the experimental process is diffusion controlled, so the relation of the coating growth rate \( k \) and the coating thickness \( x \) can be expressed as

\[ x = kt^2 \]

By taking the natural logarithms of both sides, Eq.(2) can be extended into

\[ \ln x = \ln k + 2\ln t \]

Inserting Eq.(1) into Eq.(3), the relation of \( x, t \) and \( k \) can be obtained as

\[ \ln x = -\frac{Q}{RT} + C + 2\ln t \]

If \( t \) is a constant, Eq.(4) can be expressed by

\[ \ln x = A + B/T \]

where \( A = C + 2\ln t \) and \( B = -Q/R \).

In this study, the pack composition used to determine the effect of temperature on coating growth was 10Al-80Al₂O₃-10NH₄Cl (wt%). The deposition tem-
perature varies from 500 °C to 800 °C while keeping the treatment duration constant of 8 h. Fig.8 illustrates the natural logarithmic of coating thickness $x$ as a function of $1/T$.

\[
\ln(x) = A + \frac{B}{T}.
\]

Fig.8 Dependence of logarithmic coating thickness on deposition temperature.

It clearly shows a linear relationship which provides strong experimental evidence supporting Eq.(5). The least squares fit of the data in Fig.8 yields a slope of 2.77. Then the activation energy $Q$ can be figured out by substituting the slope into Eq.(5). The activation energy of the coating formation process is calculated to be 23.06 kJ/mol in the temperature range under study.

4. Conclusions

(1) Aluminide coatings have been successfully produced on a Ni-base superalloy at low temperatures by pack cementation process with appropriate activator and pack composition. The coatings possessed a two-layer structure. The top layer consisted of Al$_3$Ni$_2$ and Al$_3$Ni with a small quantity of Al-Cr intermetallics. The bottom layer exhibited high density, homogeneity and a good adherence to the substrate and consisted of Al$_3$Ni$_2$.

(2) The results show that all the parameters exclusive of the pack activator (NH$_4$Cl) content have influences upon the coating thickness, but do not on the microstructure. The relationship of coating thickness with treatment duration follows an approximately parabolic law, suggesting that the process is diffusion controlled.

(3) A linear relationship exists between the coatings thickness $x$ and $1/T$ in the aluminide coatings formation process on the Ni-base superalloy at low temperatures by pack cementation process. The relationship can be expressed as $\ln(x) = A + B/T$.

References


Biography:

Lu Tong Born in 1985, he received B.S. degree from China University of Geosciences (Beijing) in 2007 and now is a postgraduate student in Beijing University of Aeronautics and Astronautics. His main research interest is protection of high temperature materials. E-mail: lutong 851221@mse.buaa.edu.cn