Growth Behavior of Coatings Formed by Vapor Phase Aluminizing Using Fe-Al Pellets of Varying Composition

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Abstract: Growth behavior of coatings formed by AlF₃ activated vapor phase aluminizing on an Ni-base superalloy substrate was investigated at 1353 K for up to 4 h using FeAl, FeAl₂, Fe₂Al₃, and FeAl₅ pellets as aluminum donors, with an aim of understanding the kinetics under the different aluminum activities. The coatings consist of an outer δ-Ni₂Al₃ layer, a middle β-NiAl layer, and an inner diffusion layer of γ-Ni₃Al. The thickness of the δ-Ni₂Al₃ layer remarkably increases with an increase of the coating time and of the aluminum content of the donor pellet. Contrarily, the aluminum concentration at the coating surface increases only a little, which might be due to the strong dependence of the aluminum activity on composition of solid Ni-Al alloys. The amount of aluminum deposition shows parabolic time dependence in all the cases, and the deposition rate becomes higher for the donor pellet of higher aluminum content. Except for the case of the FeAl pellet, the parabolic rate constants are similar to the reported value calculated from the diffusion rate of aluminum in solid Ni-Al alloys. This suggests that the rate of aluminum deposition is dominantly controlled by solid diffusion in the coating. However, the rate falling occurs in the last stage due to the phase transformation of FeAl₁ → Fe₂Al₃ → FeAl₅ → FeAl caused by the depletion of aluminum in the pellet. It is supposed that the gaseous diffusion of aluminum or the other process might contribute to the rate-controlling when a sufficiently thick FeAl layer covers the pellet surface.

Keywords: vapor phase aluminizing, iron-aluminum pellet, nickel-base superalloy, nickel-aluminide coating

1. Introduction

Nickel-base superalloy blades and vanes are used in the hot sections of gas turbines or jet engines. Protective coatings are applied to these components to improve their oxidation and corrosion resistance at elevated temperatures. The most widely used coating is aluminide diffusion coating. It is based on the formation of intermetallic compounds of the Ni-Al system that act as a reservoir of aluminum for maintaining a protective Al₂O₃ scale on the material surface during high-temperature service. The Ni-Al layer is formed by the interdiffusion of nickel and aluminum through the heat-treatment for several hours. Aluminum is normally supplied to the substrate surface as gaseous aluminum halides generated by the reaction of an aluminum donor alloy and halide activators.

There are a variety of methods for aluminizing, but the most traditional one is pack cementation.¹) In this method, components to be coated are buried in a powder mixture of an aluminum donor alloy, a halide activator, and an inert filler such as Al₂O₃. The pack aluminizing process has been studied extensively. The next appeared is the method²) holding articles above the pack sources out of contact. It does not need unpacking. Recently, a further developed method called vapor phase aluminizing (VPA)³) is becoming major because of its profitable cost performance. The characteristic of this method is to use the donor alloy of not powder but pellets. It makes the inert filler unnecessary, which is the main constituent of the pack source, and reduces waste management cost. In addition, the pellets are easy to be recycled and thus the cost of source materials will be reduced.

The basic mechanism of VPA is the same as that of the pack aluminizing, however the kinetics of VPA is not as well known as the pack aluminizing yet. Therefore, it is important to understand the kinetics of coating formation for the appropriate process controlling. There are a lot of factors influencing the coating formation. The important one is the aluminum activity in the system.

This paper deals with the growth behavior of coatings formed by VPA using donor pellets of various aluminum contents for understanding the kinetics under the different aluminum activities. We chose Fe-Al alloys, which have been commercially used as a donor in the pack aluminizing and are promising in VPA also.

2. Experimental

FeAl, FeAl₂, Fe₂Al₃, and FeAl₅ alloys were made by button melting as aluminum donors for aluminizing. These intermetallic compounds were identified by X-ray diffraction (XRD). After a heat-treatment at 1373 K for 24 h, the alloys were crushed and sieved by particle size. Those of 2–4 mm diameter were selected and used for aluminizing. The Ni-base superalloy IN100 with chemical composition of 15.0Co-10.0Cr-5.5Al-4.7Ti-3.0Mo-1.0V-0.18C-0.06Zr-0.014B-bal. Ni (in mass%) was used as the substrate. The specimens measuring 20 × 10 × 3 in mm were prepared by machining, polishing with emery paper, and ultrasonic cleaning in acetone.

Aluminizing was conducted in a box of Ni-base alloy as the cross-section is shown in Fig. 1. The pellets were placed at the bottom of the box with the halide activator AlF₃. The pellets and activator powder were well mixed together with a spoon. The specimens were laid at a height of 10 mm from the bottom. The amount of the pellet was measured by
making the total volume to be the same as that of the FeAl pellet of 5 g. By this way the total surface area of the pellets became nearly equal for each pack of the different pellet. The amount of activator was 0.5 g, which was found enough to maintain the aluminum activity throughout the aluminizing by preliminary experiments. The distance between the pellet and the specimen was about 7 mm. The box was closed with a lid (it was not tightly sealed), and heated for 0.5, 1, 2, and 4 h at 1353 K in a steady flow of argon gas. After the prescribed time of treatment, the box was naturally cooled to room temperature in the furnace. Cross-sectional microstructures of the coatings and of the pellets were observed by optical microscopy and scanning electron microscopy (SEM).

Composition depth profiles were obtained by electron probe micro analysis (EPMA), and some points were analyzed by energy dispersive X-ray fluorescence spectrometry (EDX).

3. Results

3.1 Microstructure

The cross-sectional microstructures and composition profiles of the lower sides (that is closer to the aluminum sources) of the coatings formed by 4 h aluminizing are shown in Fig. 2. All the coatings consist of three layers: an outer layer of $\delta$-Ni$_2$Al$_3$, a middle layer of $\beta$-NiAl, and an inner diffusion layer. It is said$^4$ that $\delta$-Ni$_2$Al$_3$ is formed by inward diffusion of aluminum when aluminum is supplied faster than it can react to form $\beta$-NiAl, and that nickel-rich $\beta$-NiAl is formed when aluminum supply is slower than diffusion of nickel through $\beta$-NiAl. The former is called high-activity type and the latter low-activity type.$^5, 6$ The diffusion layer is formed as a result of Ni depletion due to its outward diffusion, accompanying the precipitation of substrate elements.$^7$

The coating formed by the FeAl pellet has a very thin $\delta$-Ni$_2$Al$_3$ layer and a relatively thick $\beta$-NiAl layer, which is close to the case of the low-activity type. Small voids form a
line at about 20 µm depth from the surface (in the β-NiAl layer), and some granular precipitates are present below the line. The EDX showed that the precipitates are carbides rich in Cr. This line is supposed to be the initial surface of the substrate, which is the evidence of outward diffusion of Ni.7)

The other three coatings have much thicker δ-Ni2Al3 layers and thin β-NiAl layers, which are close to the case of the high-activity type. Small granular precipitates are scattered in the bottom part of the δ-Ni2Al3 layer. They contain Al besides C and Cr. The initial substrate surface is supposed to be the coating surface, which indicates the inward diffusion of Al.7)

The thickness of the δ-Ni2Al3 layer increases with an increase of the aluminum content of the donor pellet. It is about 3, 30, 55, and 90 µm for FeAl, FeAl2, Fe2Al5, and FeAl3, respectively, in Fig 2. Contrasting to the remarkable difference of coating thickness, the aluminum concentration at the coating surface, Cc, varies only slightly with the donor pellet: about 60, 62, 63, and 64 at% for FeAl, FeAl2, Fe2Al5, and FeAl3, respectively. The aluminum concentration is almost constant in the δ-Ni2Al3 layer, and it decreases gradually toward the substrate level through β-NiAl and the diffusion layers.

3.2 Coating growth

Figure 3 shows the variations of aluminum concentration profile in the coating with the coating time. It can be seen that Cc hardly changes by the coating time. It reaches the high level at the early stage of aluminizing, and remains almost constant throughout 4 h. For the FeAl and FeAl2 pellets, Cc tends to decrease slightly with the increasing time, however the decrease is very small. On the other hand, the thickness of the δ-Ni2Al3 layer strongly depends on the coating time. The growth behavior of the δ-Ni2Al3 layer varies with the donor pellet. In the case of the FeAl pellet, the thickness of the δ-Ni2Al3 layer increases during the first one hour and remains constant in the next one hour, and decreases after then. In the other three cases, it keeps increasing throughout 4 h, however the increasing rate decreases with the coating time.

3.3 Aluminum deposition

The amount of aluminum deposition per area, w (mol cm⁻²), was calculated using the following equation,

$$w = \int \rho_i(C_x - C_{sub})dx$$

where \(\rho_i\) is aluminum density of the phase i (mol cm⁻³), \(C_i\) is aluminum concentration at depth x from the surface, and \(C_{sub}\) is aluminum concentration in the substrate. The value of \(\rho_i\) was obtained from the molar volume of the binary Ni-Al system. Here, the influences of the other elements and the transition regions are neglected. Besides, the aluminum concentration profile was measured in a typical part of the entire cross-section but only along one line. Thus, a few error
margins would be included in the value of \( w \). The parabolic plot of \( w \) against the coating time is shown in Fig. 4. It seems that \( w \) follows a parabolic law in all the cases, although it exhibits negative deviation at 4 h, especially in the case of the FeAl \(_2\) pellet. The aluminum deposition is faster for the donor pellet of higher aluminum content.

### 3.4 Pellet analysis

The variations of aluminum concentration profiles and microstructures of pellet cross-sections are presented in Fig. 5. It is obvious that the aluminum concentration in the pellet, \( C_p \), decreases with time. In the case of the FeAl pellet, \( C_p \) decreases by 6–7 at% from the initial value of \( C_{p,0} = 50 \) at% in 4 h. It decreases gradually from 300–400 \( \mu \)m depth toward the surface.

The decreases of \( C_p \) in the FeAl\(_3\) and FeAl\(_2\) pellets are more significant. In the case of the FeAl\(_3\) pellet, \( C_p \) in the surface part of about 30 \( \mu \)m in depth decreases to 58 at% from the initial value of \( C_{p,0} = 66 \) at% in only 1 h. While, \( C_p \) in the central part remains at 63 at%. \( C_p \) in the surface part has further decreased to 50–53 at% in 2 h, and this aluminum depletion part has expanded to the depth of about 350 \( \mu \)m in 4 h. This part, which looks white in the SEM image, may be FeAl. In the case of the FeAl\(_2\) pellet, \( C_p \) decreases to 66 at% from the initial value of \( C_{p,0} = 71 \) at% almost uniformly in the whole area. \( C_p \) in the surface part of about 100 \( \mu \)m in depth has further decreased to 63 at% in 2 h, and to 49–50 at% in 4 h. \( C_p \) in the part from 100 \( \mu \)m to 300 \( \mu \)m in depth also has decreased to 63 at% in 4 h. The surface part of 100 \( \mu \)m in depth, which looks white in the SEM image, may be FeAl\(_2\) phase. And the part of 100–300 \( \mu \)m in depth, which looks bright gray, may be FeAl phase. \( C_p \) in the FeAl\(_3\) pellet decreases uniformly in the whole area during 2 h. The degree of this decrease is larger for the first one hour, such that it falls to 68 at% from the initial value of \( C_{p,0} = 71 \) at%. While, \( C_p \) decreases only by 1.5 at% in the subsequent one hour. \( C_p \) in the surface part of about 50 \( \mu \)m in depth has decreased to 62–64 at% in 4 h. This part may be FeAl\(_2\), which looks white in the SEM image and is only locally observed.

#### 4. Discussions

The present VPA system may consist of the following processes:

- Solid diffusion of aluminum in the pellet.
- Reactions between the pellet and the activator represented by the following equations,

\[
\begin{align*}
\text{AlF}_3 (s) & = \text{AlF}_3 (g) \\
\text{AlF}_3 (g) + 2 \text{Al} & = 3 \text{AlF} (g) \\
2 \text{AlF}_3 (g) + \text{Al} & = 3 \text{AlF}_2 (g)
\end{align*}
\]

where \( \text{Al} \) means aluminum in the pellet, \( w \) and \( m \) the whole area.

- Gaseous diffusion of aluminum fluorides that transport aluminum to the substrate (coating) surface.
- Aluminum deposition on the substrate (coating) surface represented by the equations,

\[
\begin{align*}
3 \text{AlF} (g) & = \text{AlF}_3 (s) + 2 \text{Al} \\
3 \text{AlF}_2 (g) & = 2 \text{AlF}_3 (s) + \text{Al}
\end{align*}
\]

- Solid diffusion of aluminum in the substrate (coating).

#### 4.1 Gaseous diffusion

The above equations imply that aluminum fluoride vapors, \( \text{AlF} \) and \( \text{AlF}_2 \), contribute to the aluminum transport, and that their partial pressures dominantly influence the rate of aluminum deposition. Their partial pressures at the pellet surface, \( p_{\text{AlF}} \) and \( p_{\text{AlF}_2} \), should be higher than those at the coating surface, \( p_{\text{AlF}}' \) and \( p_{\text{AlF}_2}' \). This gap should be the driving force for aluminum transport through the gas phase, and its rate, \( dw_g/dt \), might be given by,

\[
dw_g/dt = \sum \sigma_i D_i(p_i - p_i')/RT
\]

where \( \sigma_i \) is the ratio of aluminum bearing species \( i \), \( D_i \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( l \) is the diffusion distance (cm), \( R \) is the gas constant (= 82 atom cm\(^3\) mol\(^{-1}\) K\(^{-1}\)), \( T \) is absolute temperature (K). As indicated by the eqs. (5) and (6), \( \sigma \) should be 2/3 and 1/3 for \( \text{AlF} \) and \( \text{AlF}_2 \), respectively.

Since \( l \) is constant in this case, the amount of aluminum transported in time \( t \) should be expressed by,

\[
w_g = \left( \frac{2}{3} D_{\text{AlF}} (p_{\text{AlF}} - p_{\text{AlF}}') \right) + \left( \frac{1}{3} D_{\text{AlF}_2} (p_{\text{AlF}_2} - p_{\text{AlF}_2}') \right) t/RT
\]

Since a large part of vapor molecules might be deposited on the inner wall of the box or go outside without reacting, \( w_g \) should not be identical to the amount of aluminum deposited on the substrate. In addition, the gas flow might exist and influence the aluminum transport. However, it should be true that \( w_g \) increases with an increase of the gap between \( p_i \) and \( p_i' \). If a gas-metal interface is in equilibrium, partial pressures of aluminum bearing species at the metal surface should balance with the aluminum activity in the metal, which generally increases with increasing aluminum concentration. It is supposed that the higher aluminum concentration in the pellet, \( C_p \), achieves the higher \( p_{\text{AlF}} \) and \( p_{\text{AlF}_2} \) (hereafter expressed as \( p_{\text{AlF}, \text{AlF}_2} \)) by increasing the aluminum activity at the pellet surface, \( a_p \). The higher \( p_{\text{AlF}, \text{AlF}_2} \) may accelerate the diffusion of these halide vapors by increasing the gap.
Fig. 5 Cross-sectional microstructures and aluminum concentration profiles of (a) FeAl, (b) FeAl₂, (c) Fe₂Al₅, and (d) FeAl₃ pellets.
with $p_{\text{AlF}_{2}}$. The increase of diffusion rate will lead to the higher ratio of solid diffusion in the coating, aluminum concentration at the coating surface, $a_{c}$, will become higher corresponding to the increasing $a_{c}$. A schematic image of the distribution of aluminum activity is shown in Fig. 6. The higher $a_{c}$ will enable the higher rate of aluminum deposition. If the rate of aluminum deposition is higher than the rate of aluminum diffusion in the coating, aluminum concentration at the coating surface, $C_{p}$, should increase. In addition, $C_{c}$ should become higher corresponding to the increasing $a_{c}$. However, in our results, $C_{c}$ increased only a little in spite of the increase of $C_{p}$. As the reason for this, the strong dependence of the aluminum activity on composition in solid Ni-Al alloys can be thought. It varies by three orders of magnitude in the $\beta$-NiAl region at 1273 K, and varies by one order of magnitude or more in the narrow $\delta$-Ni$_{2}$Al$_{3}$ region where the composition changes only by several percent. It is supposed that the composition $C_{c}$ hardly changes even if the aluminum activity $a_{c}$ is much different.

### 4.2 Solid diffusion in the coating

The results showed that the coating surface quickly reaches a steady state. If the composition at the coating surface is time-invariant, the amount of aluminum diffused into the substrate, $w_{s}$ (mol cm$^{-2}$), should obey a parabolic law, as is expressed by the following equation:

$$w_{s}^{2} = k_{s}t$$

where $k_{s}$ is the parabolic rate constant (mol$^{2}$ cm$^{-4}$ s$^{-1}$), which is determined by the diffusivity of aluminum in the solid. The rate of diffusion also depends on the surface composition. Seigle et al. calculated the growth rate of coating formed by aluminizing of pure Ni, and led $k_{s}$ as a function of surface composition. According to Seigle's calculation, the value of $k_{s}$ is $(1.2-2.2) \times 10^{-11}$ (mol$^{2}$ cm$^{-4}$ s$^{-1}$) at 1273 K and $(6.7-9.2) \times 10^{-10}$ at 1366 K for 60–61 at% of surface aluminum concentration. In our results, the coating surface composition $C_{c}$ varied only little with $C_{p}$, however, strictly speaking, the driving force of diffusion should be the gap of not concentration but activity. Thus it is possible that the rate of aluminum diffusion in the coating increases with increasing $C_{p}$, by the increase of $a_{c}$ even if $C_{c}$ varies little.

### 4.3 Solid diffusion in the pellet

Solid diffusion of aluminum in the donor pellet should be included in the aluminum transport system. The results showed that aluminum in the pellet is depleted with the coating time and the aluminum depletion zone forms near the surface in the last stage. Aluminum should be consumed at the pellet surface, and it should be supplied from the inside by solid diffusion through the depletion zone, like Levine and Caves' model. As far as considering the earlier stages, the influence of this process might be negligible. The interdiffusion coefficient in Fe-Al binary alloy is larger than that in Ni-Al at around 1353 K. Therefore, it can be thought that aluminum diffusion in the pellet is fast enough to supply aluminum at sufficient rate for the reactions with the activator, so that it scarcely influences the rate of aluminum deposition. The results of pellet analysis showing that aluminum concentration $C_{p}$ decreases entirely to the center part in the early stage also suggest a fast diffusion of aluminum. However, the decrease of $C_{p}$ is unavoidable, and thus the decrease of $a_{p}$ is. This leads to the decrease of aluminum deposition rate. Although the rate falling is unnoticeable in the early stage, it becomes significant in the last stage where $C_{p}$ reaches the critical level.

### 4.4 Degradation of the pellet

The results indicate the occurrence of phase transformations of FeAl$_{3}$ → Fe$_{2}$Al$_{3}$ → FeAl$_{2}$ → FeAl in the pellet. It is thought that the transformation occurs from the surface and its front proceeds inward according to the aluminum consumption. These transformations may cause significant fallings of aluminum deposition rate, because a transformation accompanies an abrupt decrease of the aluminum activity. Since FeAl$_{2}$, Fe$_{2}$Al$_{3}$, and FeAl$_{3}$ have very narrow composition ranges, they may readily transform to the lower aluminides by a little decrease of $C_{p}$. The negative deviations from the parabolic law of aluminum deposition in the last stage seen in the cases of the FeAl$_{2}$ and Fe$_{2}$Al$_{3}$ pellets might be attributable to the occurrence of these transformations, especially to the formation of FeAl. The relatively small rate falling in the case of the FeAl$_{3}$ pellet might be explained by the fact that only the transformation from FeAl$_{3}$ to Fe$_{2}$Al$_{3}$ occurs locally. It is supposed that the significant rate falling occurs when the pellet surface is covered with a sufficiently thick FeAl layer. Since FeAl has a wide composition range, it may hardly transform even if $C_{p}$ decreases to some degree. This might be a reason for the slight rate falling in the case of the FeAl$_{3}$ pellet seen in Fig. 4. However, a symptom of rate falling can be seen in the transition of microstructure. That is a decrease of $\delta$-Ni$_{2}$Al$_{3}$ layer in the last stage. It implies that the rate of aluminum deposition has become too low to catch up with the rate of solid diffusion in the coating. It is thought that the deposition rate for the FeAl pellet is so low from the beginning that it becomes below the diffusion rate in the coating with a slight decrease.

### 4.5 Rate controlling step

The rate of coating growth should be determined by the balance between aluminum supply to the coating surface and aluminum diffusion in the coating. The rate of aluminum...
deposition would be equal to the smaller of these two rates. If sufficient aluminum is supplied to the coating surface, the deposition rate should be limited by the rate of solid diffusion in the coating. Otherwise, it should be limited by the rate of aluminum supply, which is controlled by gaseous diffusion and/or solid diffusion in the pellet.

It is difficult to clarify the rate controlling mechanism of coating growth, because of the influence of aluminum depletion in the last stage besides the lack of data. However, the aluminum deposition $w$ seems to follow the parabolic law: $w^2 = kt$, as shown in Fig. 4. The parabolic rate constants $k$, which can be obtained from the slopes of the straight lines in Fig. 4, are 0.1, 0.5, 1.5, and $2.5 \times 10^{-11}$ (mol$^2$ cm$^{-4}$ s$^{-1}$) for FeAl, FeAl$_2$, Fe$_2$Al$_5$, and FeAl$_3$, respectively. Except for the case of FeAl, the values of $k$ are similar to the reported value of $k_s$ which is calculated by Seigles from the diffusion rate of nickel and aluminum in the binary Ni-Al alloy.$^8$ This implies that the rate of aluminum deposition is dominantly controlled by the solid diffusion in the coating. The rate of aluminum diffusion in the coating depends on the aluminum activity at the coating surface achieved by each pellet, and it determines the rate of aluminum deposition. The $k$ values determined in this study are a little smaller than the $k_s$ values determined by Seigles, this deviation could be partly attributable to the effect of solutes derived from the substrate. The diffusion of aluminum in the alloy containing various solute elements may slower than that in pure nickel. Levine and Caves also had suggested this possibility.$^4$ On the other hand, the value of $k$ for the FeAl pellet is smaller by almost two orders of magnitude than the Seigles’ result of $k_s$. It is supposed that the process other than the solid diffusion in the coating contributes to the rate-controlling. When the FeAl pellet is used or a sufficiently thick FeAl layer is formed on the surface of the pellet of higher aluminum content, the rate of aluminum supply from the gas phase to the coating surface is thought to be lower and it might be lower than the rate of aluminum diffusion in the coating. It is possible in this case that the gaseous diffusion of aluminum or the other process influence the rate of aluminum deposition. There is a possibility that $w$ only pretends to obey the parabolic law because the rate of aluminum supply from the gas phase decreases due to the aluminum depletion in the pellet.

5. Summary

Time dependence of aluminum deposition follows a parabolic law in all the cases. The parabolic rate constant increases with an increase in the aluminum content of the donor pellet. Except for the case of the FeAl pellet, the rate constants are similar to the reported values of rate constants of aluminum diffusion into pure nickel substrate, which were calculated using the diffusion coefficients in solid Ni-Al alloys. This implies that the rate of aluminum deposition is dominantly controlled by solid diffusion in the coating. However, the rate falling occurs in the last stage due to the occurrences of phase transformations caused by the depletion of aluminum in the pellet. The gaseous diffusion of aluminum or the other process might contribute to the rate-controlling when a sufficiently thick FeAl layer covers the pellet surface.

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