

Aluminide Coatings Fabricated on Nickel by Aluminium Electrodeposition from DMSO₂-Based Electrolyte and Subsequent Annealing

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A new cost-effective process to fabricate aluminide coatings was developed. Coating layers consisting of nickel aluminides could be formed by electrodeposition of Al layers from a dimethylsulfone-AlCl₃ electrolyte on Ni substrates and subsequent annealing in air or vacuum at temperatures of 700–1150°C. Analysis of the intermetallic layers by XRD, SEM and EDX indicated the formation of Al₃Ni and Al₃Ni₂ at 700°C, AlNi at 900°C and 1000°C, and AlNi and AlNi₃ at 1150°C. The Annealing atmosphere did not affect the resulting intermetallic products. [doi:10.2320/matertrans.M2010421]

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1. Introduction

Aluminide coatings are widely used in high-temperature applications such as aircraft turbine blades and power plants to protect metallic materials from high-temperature oxidation.¹⁾ Ni alloys, Co alloys and steels are used in such applications, and they are exposed to highly oxidative environments. However, they usually have insufficient oxidation resistance to withstand the harsh environments. The addition of elements to bulk material to improve the oxidation resistance often causes degradation of mechanical properties, and aluminisation is therefore applied on their surface. Aluminides exhibit high oxidation resistance owing to a dense and protective alumina layer formed by preferential oxidation of Al. The melting points of aluminides are generally high although that of pure Al is relatively low (660°C). A typical aluminide AlNi, for instance, has a melting point of 1638°C, which is even higher than that of pure Ni, due to the strong interaction between Al and Ni atoms. Thus aluminides can be used as oxidation-resistant coatings with thermal stability for high temperature applications.

Many processes such as hot dipping,²⁾ pack cementation,^{1,3)} thermal spray,⁴⁾ sputtering,^{5,6)} and high-temperature molten salt electrolysis⁷⁾ have been studied to form aluminide coatings. Among them, pack cementation is widely used in industrial applications today. In the pack cementation process, the objects to be coated are heated in a pack, which is a mixture of Al powder and halide activator. While heating, Al halide gas forms and it reacts on the surface of the objects to deposit metallic Al. The surface Al diffuses into the object, forming the aluminide coating. Although the pack cementation is relatively simple, this process uses aluminum halide gas, which is highly corrosive and hazardous.

We propose an alternative low-cost process to form aluminide intermetallics. The process consists of two steps: electrodeposition of Al layer on the objects and heat treatment to form aluminide coatings. Electrodeposition can

be carried out with simple apparatus, keeping the process cost low. Furthermore, electrodeposition can easily be used to control the coating thickness by varying the electrical charge and can be applied on surfaces with complex shapes. The heat treatment can also be carried out with a normal furnace, since this process essentially does not require the generation of halide gas.

Since Al cannot be electrodeposited from aqueous solutions, depositions from non-aqueous media, such as NaCl-AlCl₃ system⁸⁾ and [EMIm]Cl (1-ethyl-3-methyl-imidazolium chloride)-AlCl₃ system,⁹⁾ have been studied. NaCl-AlCl₃ requires a relatively high deposition temperature ($\geq 150^\circ\text{C}$) and suffers from high vapor pressure of corrosive AlCl₃. The [EMIm]Cl-AlCl₃ system can overcome the problems of the deposition temperature and AlCl₃ vapor, but the electrolyte is quite expensive.

A dimethylsulfone (DMSO₂)-AlCl₃ electrolyte^{10–14)} was used for the Al deposition in the present work. This electrolyte has some advantages over the systems noted above: DMSO₂ has the melting point of 109°C, which allows deposition at around room temperature. The problematic vaporization of AlCl₃ is suppressed in this system since DMSO₂ coordinates to Al ions and stabilizes them.¹²⁾ Furthermore, DMSO₂ is available at less than 1/5 the price of [EMIm]Cl.

In this paper, we examined the feasibility of the new process for the formation of aluminide coatings on nickel prior to Ni alloy, which is frequently used as a material for gas turbine blades.¹⁾ Electrodeposition of a dense Al layer with a good adhesion to Ni substrate from a DMSO₂-based electrolyte was confirmed and the effects of annealing temperature and atmosphere on the formation of aluminide phases were investigated.

2. Experimental

2.1 Electrodeposition of Al layer

The electrodeposition of Al layer was performed in an Ar-filled glove box equipped with a circular system. The electrolyte for the electrodeposition was prepared by mixing

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DMSO₂ (Fluka, $\geq 98.0\%$ purity) with AlCl₃ (Fluka, anhydrous $\geq 99\%$ purity) in a glass vessel at ambient temperature. The mol ratio of AlCl₃ to DMSO₂ was 2 to 10. DMSO₂ had been dried in a vacuum oven at 60°C for over 10 h prior to use. AlCl₃ had been stored in the glove box and was used as received. After mixing, the electrolyte was melted at 110°C. A simple two-electrode cell was employed for the electrodeposition. Ni plates (Nilaco, 99% purity 0.3 mm thickness) were used as substrates. The Ni plates were polished with SiC papers (#1200), followed by ultrasonic cleaning in ethanol and immersion in hydrochloric acid and then dried. A part of the Ni plates was covered with PTFE tape so that only certain areas (4 cm²) would be exposed. The anode was an Al plate (Nilaco, 99% purity 0.5 mm thickness). Al can dissolve into DMSO₂-based electrolytes by anodic polarization.¹³⁾ Thus Al concentration in the plating bath can be maintained constant throughout the electrodeposition and oxidative decomposition of DMSO₂ at the anode can be avoided. Before use, the anode was polished and rinsed in ethanol.

The deposition of Al layer was carried out galvanostatically at 40 mA·cm⁻² for 40 min. The total electrical charge was 96 C·cm⁻², which theoretically yields an Al layer with a thickness of 33 μ m assuming 100% current efficiency. The temperature of the electrolyte was maintained by a thermostat at 110°C during the deposition.

2.2 Anneal

After the electrodeposition, samples were cut into an appropriate size (~ 1 cm $\times$ 2 cm) and annealed in an electric furnace. The anneal was performed in air or in vacuum (< 0.4 Pa) pulled by a diffusion pump. The annealing temperatures were varied in the range from 700 to 1150°C. The samples were first heated to the annealing temperatures from ambient temperature in an hour, and then kept at the annealing temperatures for an hour. Finally, they were slowly cooled in the furnace. The annealing conditions examined are summarized in Table 1.

2.3 Characterization

After the anneal, samples were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDX). XRD was measured from the surface of the sample. For cross-sectional observation by SEM, samples were cut and polished with diamond paste (1 μ m) followed by ultrasonic cleaning.

3. Results and Discussion

The Al layer was galvanostatically electrodeposited on the Ni substrate from the DMSO₂-based electrolyte. The obtained deposit was smooth and white. Figure 1 shows the cross-sectional SEM images of the as-deposited Al layer. The formation of a dense Al layer with a uniform thickness of approximately 25 μ m was confirmed. The Al layer did not crack while either cutting or polishing, showing that the Al layer electrodeposited from the DMSO₂-based electrolyte had good adhesion to the Ni substrate. It should be noted that the current efficiency may be estimated from the thickness (25 μ m) to be 75%, but this value is underestimated because

Table 1 Annealing conditions.

Sample	Temperature (°C)	Atmosphere
a	700	air
b	900	air
c	1000	air
d	1150	air
e	700	vacuum
f	900	vacuum
g	1000	vacuum

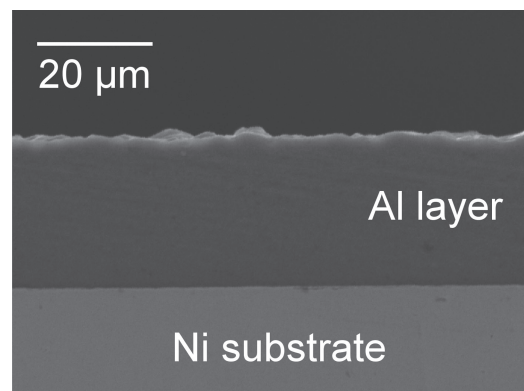


Fig. 1 Cross-sectional SEM image of Al layer electrodeposited on Ni substrate from DMSO₂-based electrolyte at 110°C and 40 mA cm⁻².

the electrodeposition of Al occurred more intensively at the edge of the substrate than at the center, where the SEM image (Fig. 1) was taken. The current efficiency for the total Al electrodeposition should be almost 100% under these conditions.¹⁴⁾

The Ni substrate with the electrodeposited Al layer was annealed in air or vacuum to form an aluminide layer. Annealing at temperatures lower than the melting point of Al (660°C) caused delamination of the electrodeposited Al layer. In contrast, annealing at higher temperatures produced a reaction layer which stayed firm on the surface of the substrate. The delamination of the Al layer could be the result of the Kirkendall effect:¹⁵⁾ the intensive Al inward diffusion begins at the interface between the Al layer and the substrate, resulting in void condensation at the interface and therefore the Al layer delaminates. If the Al layer is in a liquid state, it can stay on the surface because the liquid Al can easily fill up the voids. Annealing above the melting point of Al therefore led to the formation of the dense intermetallic layers.

Figure 2 shows the XRD patterns of the samples annealed at temperatures of 700–1150°C. The patterns confirm the formation of Al-Ni intermetallic phases. The intermetallic phases varied with the annealing temperature. The patterns indicate the formation of Al₃Ni and Al₃Ni₂ at 700°C, AlNi at 900°C and 1000°C, and AlNi and AlNi₃ at 1150°C, meaning that Ni-rich phases emerge as the temperature rises. This tendency of the phase formation is reasonable since the Ni content of the aluminide phases should become high as the diffusion proceeds. Of these intermetallic phases, the AlNi phase is often used as an oxidation-resistant coating since

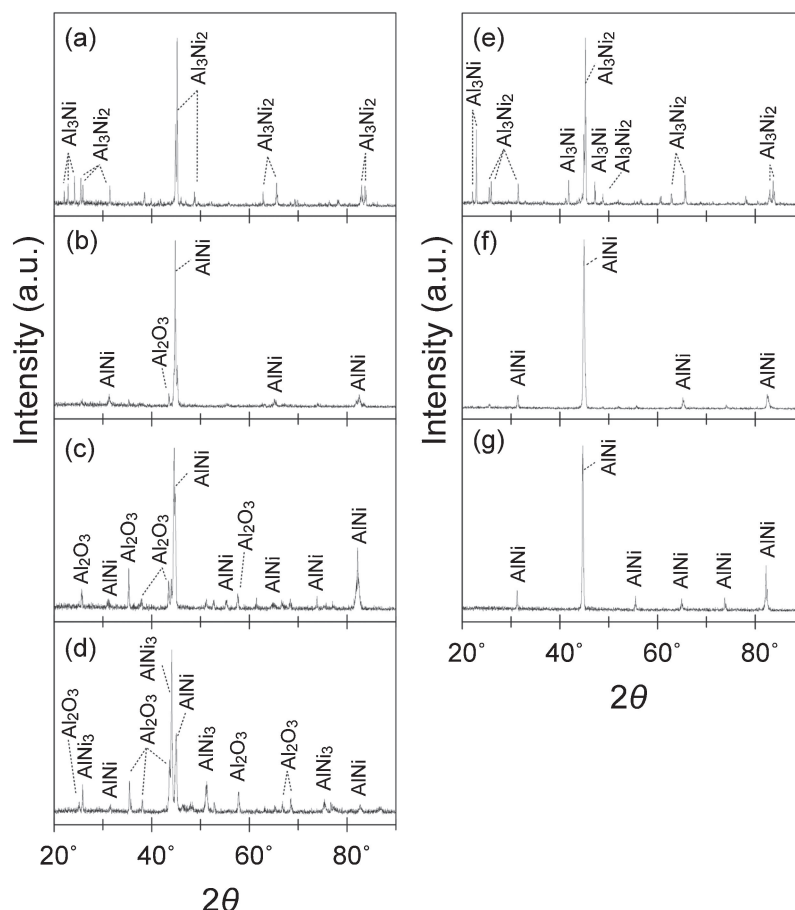


Fig. 2 XRD patterns of the samples annealed under the conditions listed in Table 1.

it is superior in terms of oxidation resistance. As evidenced by the XRD patterns, oxidation of the Al layer occurs during annealing in air at 900°C and higher temperatures (Figs. 2(b)–(d)). The intensities of the diffraction peaks of Al_2O_3 imply that the degree of oxidation increases with an increase in the annealing temperature. However, the diffraction intensities of the Al_2O_3 phase were still much smaller than those of the Al–Ni intermetallic phases even in the sample annealed at 1150°C. The surface Al_2O_3 layer could have prevented the intermetallic phase from further oxidation in the same manner as aluminide coatings do. This oxidation can be avoided by performing the annealing in vacuum; no evidence of oxidation could be seen in the patterns of the vacuum-annealed samples. Except for the generation of Al_2O_3 , the same intermetallic compounds were obtained as the major phases by annealing in air and in a vacuum at the same temperature.

The cross-sectional SEM pictures reveal the formation of layered structures of the intermetallic compound phases (Figs. 3 and 4). The thickness of the aluminide layers in total is in the range of 30 and 60 μm , and tends to increase as the annealing temperature increases because the diffusion of Al proceeds more at higher temperatures. A porous layer can be observed at the outermost part of some samples, while only the sample annealed at 1150°C included voids at the interface between the substrate and the intermetallic layer. Judged by the surface appearance, the porous layer seems to be generated under all annealing conditions. However, since it is

quite fragile and easily peeled off while polishing for the cross-sectional SEM observation, the porous layer disappears from the SEM pictures of some samples. The formation of the porous layer cannot be ascribed to oxidation, since the same porous layer is formed on the surface of the samples annealed in vacuum. There is a possibility that the Kirkendall effect¹⁶⁾ could be involved in the formation of the porous layer. In general, Al inward diffusion is predominant in the parts where Al activity is high. As a result, voids are left in the outermost part, and the accumulation of the voids forms the porous layer. However, detailed mechanism of the pore formation is not clear and is now under investigation. In contrast, Ni outward diffusion is dominant in the parts where Al activity is low. In this case, voids could be formed at the interface of the substrate and the intermetallic layer. The voids formed at 1150°C are likely caused by this mechanism.

The phase of each layer was assigned from line analysis of the composition with reference to the Al–Ni phase diagram¹⁷⁾ (Fig. 5). The layers with Al concentrations of approximately 60%, 34–50% and 25% were determined to be Al_3Ni_2 , AlNi and AlNi_3 , respectively. Here we should note that the reliability of the composition data in voids and at the edge of the sample is low. The phases determined by EDX are consistent with the phases of XRD analysis except that Al_3Ni is missing in the EDX measurements of samples annealed at 700°C (Figs. 3(a) and 4(a)) although it was detected by the XRD (Figs. 2(a) and 2(e)). The lack of Al_3Ni phase in the

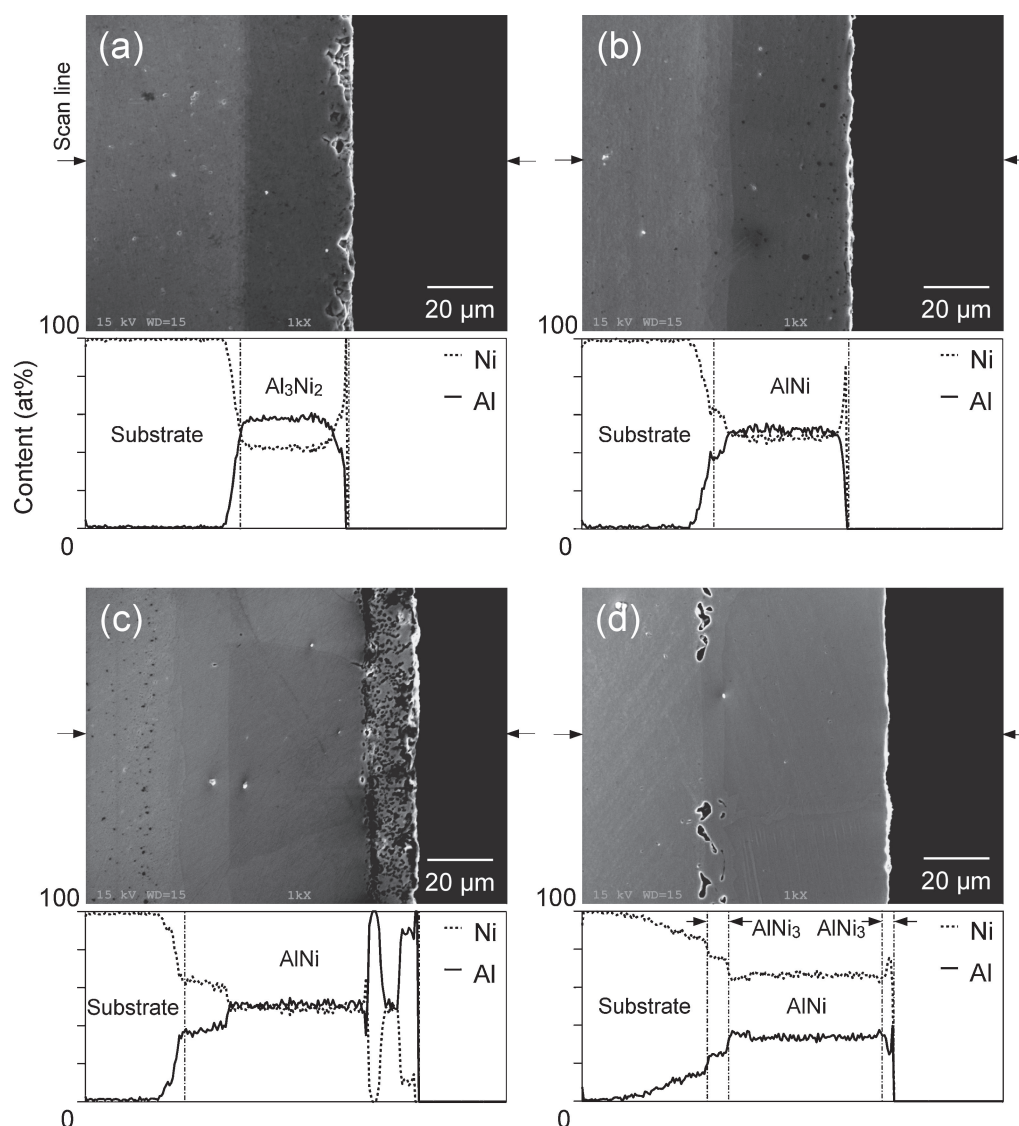


Fig. 3 Cross-sectional SEM images and EDX line analysis of the samples annealed in air at (a) 700°C, (b) 900°C, (c) 1000°C and (d) 1150°C.

cross sectional SEM images should be due to the delamination of the outermost parts described above.

The XRD and EDX analysis detected the formation of Ni-rich phase, AlNi₃, at the vicinity of the surface of the sample annealed in air at 1150°C (Figs. 2(d) and 3(d)). The enrichment of Ni at the surface was more or less observed in all the samples annealed in air, but was not in the samples annealed in vacuum. The Ni enrichment must be due to the surface oxidation of the aluminide layer.¹⁸⁾ Since Al is preferentially oxidized to form Al₂O₃, the Ni-rich phase is generated from the aluminide phase.

The Al₃Ni₂ and AlNi₃ layers have stoichiometric compositions, while the AlNi layer seemingly has two distinctly different compositions; one is stoichiometric (50 at% Al) and the other is Ni-rich (~38 at% Al). The samples annealed at 900°C and 1000°C show the clear boundary of the two different compositions in the single AlNi phase (Figs. 3(b), 3(d), 4(b) and 4(c)). The sample annealed at 1150°C has only the Ni-rich AlNi phase (Fig. 3(d)). According to the phase diagram, only AlNi phase exists in the wide composition

range, and the minimum Al contents of the AlNi phase at the annealing temperatures are close to the Al contents of the generated Ni-rich AlNi layers. The separation in the AlNi layer can be explained by kinetic factors. As reported in the literature,^{19,20)} the interdiffusion coefficient in AlNi phase drastically changes with the composition and has a minimum near the stoichiometric composition. AlNi with such a composition can work as a diffusion barrier and causes a sharp composition gradient.

We have verified that aluminide coatings can be formed on pure Ni by the present process. The diffusion behaviors in Ni based alloys used in actual applications, to which many elements are added, can be different from that in pure Ni, but we expect the present process can also be applied to the actual alloys.

4. Conclusions

We demonstrated the fabrication of aluminide coatings on Ni substrate by Al electrodeposition from a DMSO₂-based

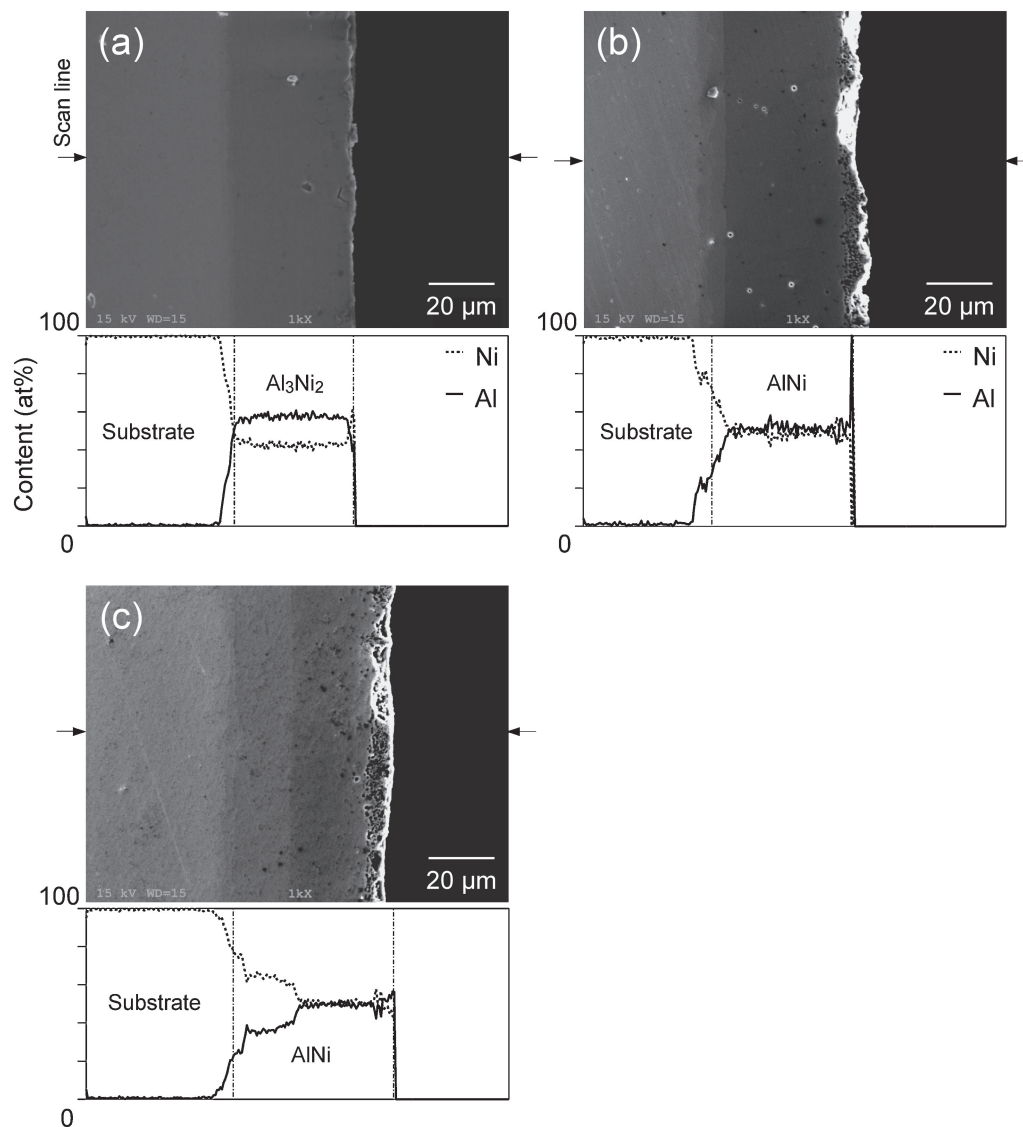


Fig. 4 Cross-sectional SEM images and EDX line analysis of the samples annealed in vacuum at (a) 700°C, (b) 900°C and (c) 1000°C.

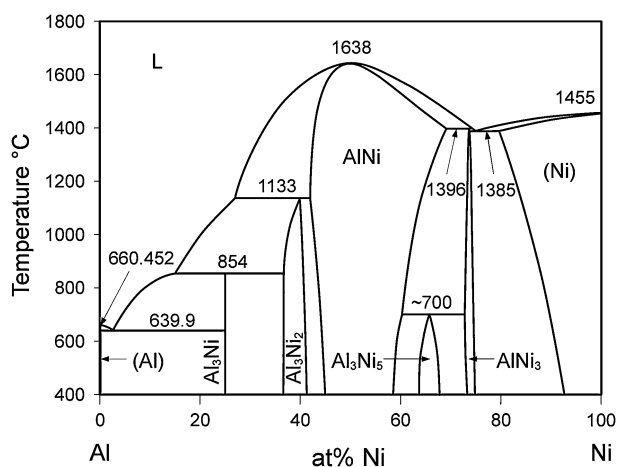


Fig. 5 The Al-Ni phase diagram.¹⁷⁾

electrolyte followed by annealing. A dense Al layer with uniform thickness and good adhesion could be electro-deposited onto Ni substrate from the DMSO₂-AlCl₃ electro-

lyte at 110°C. Layer-structured aluminide coatings were obtained by the subsequent annealing in air and in vacuum in the temperature range of 700–1150°C, which lay above the melting point of pure Al. The resulting intermetallic phases changed with annealing temperature; Al₃Ni and Al₃Ni₂ at 700°C, AlNi at 900°C and 1000°C, and AlNi and AlNi₃ at 1150°C. The Al contents of Al₃Ni₂ and AlNi₃ phases were close to the stoichiometric compositions, whereas the Al content of AlNi phase varied from 35 to 50 at%. The thickness of the coatings increased from 30 μm to 60 μm with increasing annealing temperature. Annealing in air led to oxide formation, but this was not remarkable. We believe that this simple, low-cost process can be an alternative to the conventional pack cementation process for the fabrication of aluminide coatings.

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