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Synthesis of Al₂O₃-AlN Coatings by Low Pressure Plasma Spraying and Nitriding †

Akira OHMORI*, Mototaka WAKAMATSU** and Kazuo KAMADA***

Abstract

AlN has some attractive properties for many applications including high thermal conductivity and a lower thermal expansion. The formation of AlN coating was not seen through the reaction of Al powder with N₂ atmosphere by LPPS in N₂ atmosphere. In order to form Al₂O₃-AlN composite coatings Al₂O₃-Al and Al₂O₃-C composite coatings obtained by low pressure plasma spraying, were heated at high temperature in an N₂ atmosphere. For the direct nitridation of Al in Al₂O₃-Al coatings, AlN contents in coatings increased with the increase of heating temperature and time.

When the carbothermal reduction of Al₂O₃-C composite coatings was carried out in N₂ atmosphere, the formation of AlN in Al₂O₃-C coatings was depended greatly on the existence of C powders on the surface of Al₂O₃-C coatings during heat-treatment.

KEY WORDS: (Al₂O₃-Al coating) (Al₂O₃-C coating) (LPPS) (Nitriding) (Carbon reduction)

1. Introduction

Aluminum nitride (AlN) offers characteristics which make it suitable for a wide range of applications. Such characteristics include high thermal conductivity, low thermal expansion, and good electrical properties. As a result, AlN is attracting a great deal of interest from the electronics industry for application in integrated circuits, packages, and so on. AlN powder for sintering can be synthesized by the direct nitridation of aluminum and by carbon reduction of aluminum oxide (Al₂O₃) in the presence of nitrogen.¹⁾ Low pressure plasma spraying (LPPS) has recently become accepted as an effective process for depositing a dense, noncontaminated coating.²⁻³⁾

It is well known that a metal and ceramic composite coating can be formed through the reaction of metal powder with an intentionally reactive atmosphere. Because some ceramics are difficult to spray directly because of decomposition, reactive spraying has been used to synthesize TiN-Ti coatings through the reaction of titanium powder in an N₂ atmosphere.⁴⁻⁵⁾

In this report, the formation of aluminum nitride coatings was examined through reaction of aluminum powder in an N₂ atmosphere with a nitrogen plasma jet.

Moreover, Al, Al₂O₃-Al and Al₂O₃-C coatings obtained by low pressure plasma spraying were heated in an N₂ atmosphere to obtain AlN.

2. Materials and Experimental Procedure

The powders used in this experiment were commercially available Al₂O₃ (METCO, DMC-12SF) with a particle size of about 17 μm, aluminum with an average particle size of 70 μm, and carbon (Wako Junyaku) with a particle size of 7.5 μm. The substrate used was sintered Al₂O₃ plate.

Formation of an AlN coating was performed by plasma spraying onto the substrate and heating in a furnace. The spraying powder used for direct nitriding was a mixed powder of Al₂O₃ and aluminum, at a mole ratio of 1 to 2. For carbothermal reduction nitriding, a mixed powder of Al₂O₃ and carbon at a mole ratio of 1 to 3 was used with a stoichiometric amount of carbon.

Figure 1 shows the laser-hybrid low pressure plasma spraying (LPPS) apparatus employed. A plasma spray gun was horizontally installed inside a chamber equipped with an exhaust system. An 1kw CO₂ laser was inserted into the chamber in the direction shown in Fig. 1. Table 1 shows the typical LPPS conditions. Heat treatment in an N₂ atmosphere was carried out at a

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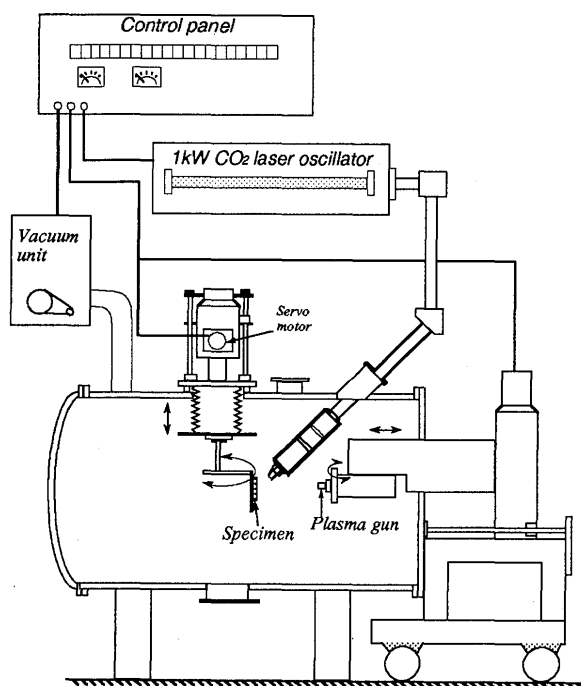


Fig.1 Schematic diagram of laser-combined low pressure plasma spray system

pressure of 1.0×10^5 Pa with an N₂ flow rate of $5 \text{ cm}^3/\text{s}$ using a vacuum furnace as shown in Fig. 2. Heat treatment was carried out at a temperature of 973K to 1573K for the Al₂O₃ and aluminum composite coatings, and at 1773K for the Al₂O₃ and carbon composite coatings. The content of AlN formed in the Al₂O₃ coating was semi-quantitatively estimated by X-ray diffraction analysis according to the following equation:

$$\text{AlN Ratio} = I_{\text{AlN}} / (I_{\text{AlN}} + I_{\text{Al}_2\text{O}_3})$$

where the ratio of AlN is an index number which denoted the coatings AlN content, and I_{AlN} and $I_{\text{Al}_2\text{O}_3}$ were the peak of AlN(100) and Al₂O₃ (104) in the X-ray diffraction pattern.

3. Results and Discussion

K.Kassabji reported the formation of AlN in an N₂ plasma sprayed Al coating using hydrogen as the secondary gas.⁶⁾ However, when a direct nitride reaction of aluminum powder with an N₂ plasma jet was tried, changing the hydrogen flow rate from 0 to $267 \text{ cm}^3/\text{s}$, no AlN formation was observed. Similarly, no formation of AlN was observed when carbothermal reduction nitration of Al₂O₃-C was carried out under the same plasma spray conditions. The most likely reasons that no AlN was formed are that the reaction time was too short in a plasma jet, or there was a dense film of Al₂O₃ on the surface of the aluminum particles.

Table 1 Conditions of plasma spraying

Spraying distance	417 mm
Arc current	750 A
Arc voltage	53 V
Arc power	40 kW
Primary flow (N ₂)	$0.83 \text{ cm}^3/\text{s}$
Secondary flow(H ₂)	$0.05 \text{ cm}^3/\text{s}$
Pressure(N ₂)	$1.3 \times 10^4 \text{ Pa}$

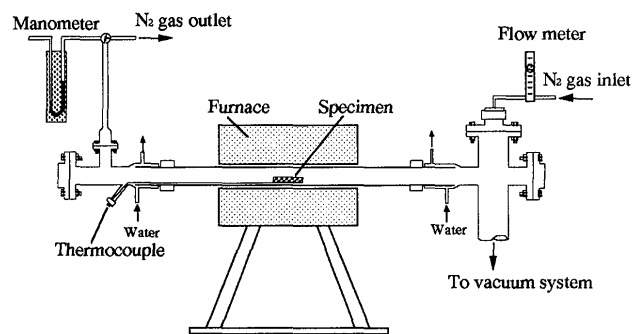


Fig.2 Schematic diagram of vacuum furnace for nitridation

To overcome these problems, an aluminum coating obtained by LPPS was heated in a furnace with an N₂ atmosphere at temperatures from 1123 to 1573K for different durations, ranging from 10.8 to 25.2 ks, to form AlN by direct nitriding. The result was the formation of AlN, which could be recognized by its X-ray diffraction pattern.

Below a temperature of 1273K, AlN formed just a very thin film just on the surface, and the amount of AlN did not increase with the heat treatment time. At a temperature of 1573K, the amount of AlN greatly increased, but the AlN obtained was in the form of fine white particles laid on the surface of the coating. Therefore, in order to form a dense AlN coating, formation of an Al₂O₃-AlN composite coating was tried.

3.1 Direct nitriding of Al₂O₃-Al composite coatings

Figure 3 shows the cross sections of as-coated and heat treated Al₂O₃-Al composite coatings. Figure 4 shows the X-ray diffraction patterns of Al₂O₃-Al composite coatings before and after direct nitriding as shown in following reaction: $2\text{Al} + \text{N}_2 \rightarrow 2\text{AlN}$. From these results, the formation of AlN was observed by direct nitriding of Al₂O₃-Al composite coatings.

Figure 5 shows the effect of the temperature of heat treatment on the ratio of AlN. These figures clearly show that the formation of AlN in the coating increased as the temperature of heat treatment increased and an

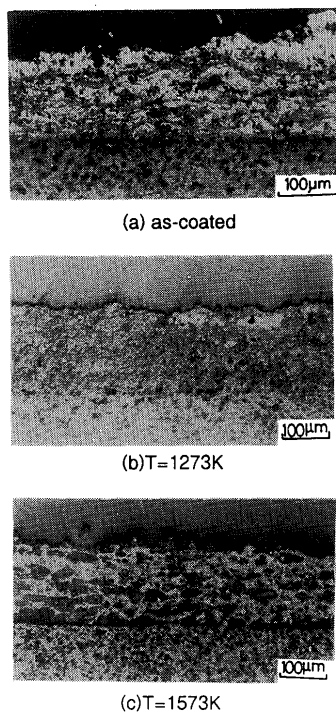


Fig.3 Cross sections of as-coated and heat treated Al_2O_3 -Al composite coatings

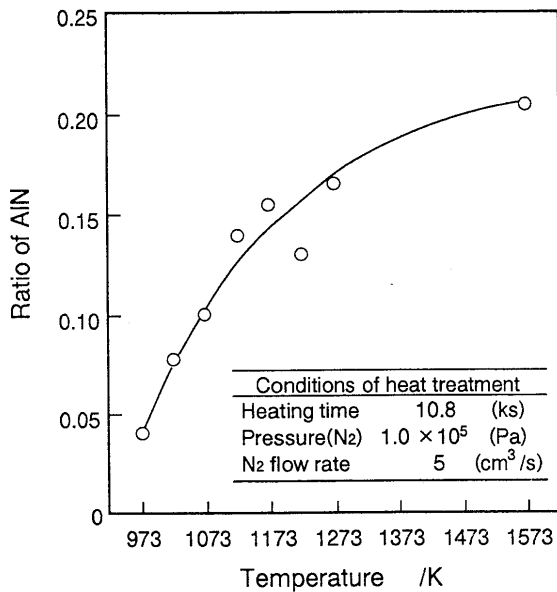


Fig.5 Effect of temperature of heat treatment on the ratio of AlN in Al_2O_3 -Al coatings

amount of Al in the coating decreased with the increase temperature in N₂ atmosphere. Figure 6 shows the effect of the temperature on the cross section of heat treated Al_2O_3 -AlN composite coatings. Amount of Al (white part) in the coating decreased with the increase of temperature. Figure 7 shows how the distance from the surface correlates with the ratio of AlN in Al_2O_3 -AlN

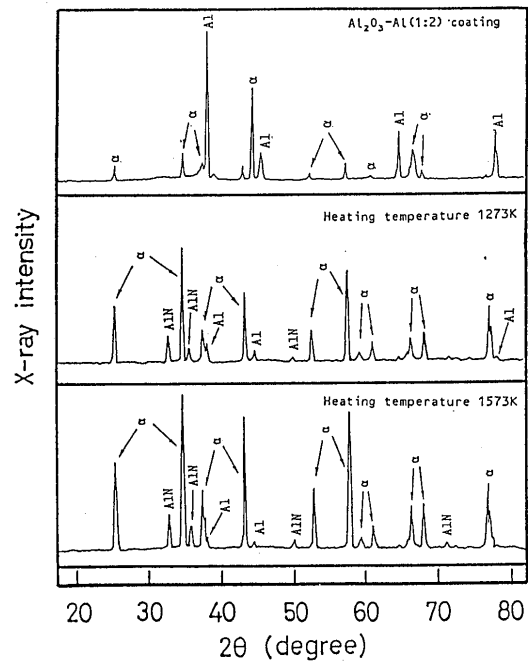


Fig.4 X-ray diffraction patterns of as-coated and heat treated Al_2O_3 -Al composite coatings

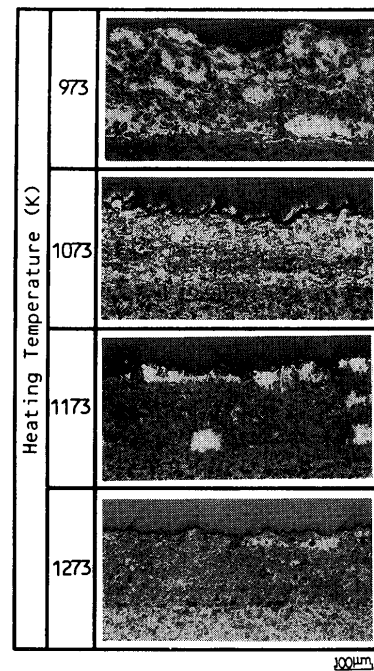


Fig.6 Effect of temperature of heat treatment on the microstructure of Al_2O_3 -Al composite coatings

composite coatings heated at 1123K for 10.8Ks. The formation of AlN in the coating decreases with the coating thickness, but AlN still exists at the interface of the coating and the substrate. It is thought the reason for this is that N₂ gas flows from the surface of the coating to the interface through pores or microcracks in the coating, with the result that AlN forms from the direct

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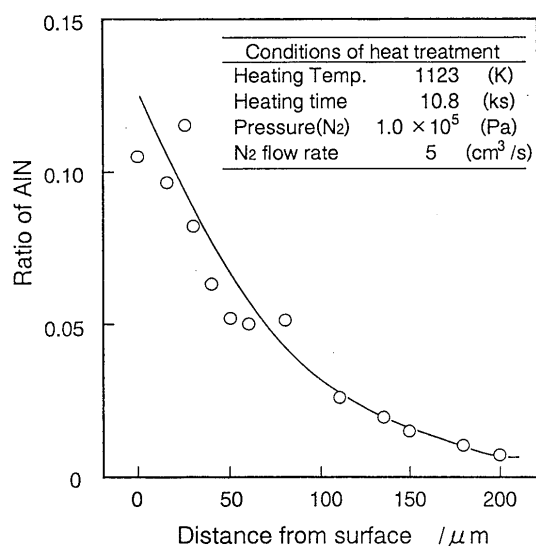


Fig.7 Effect of the distance from the surface on the ratio of AlN in Al₂O₃-Al coatings

reaction of the N₂ gas and aluminum. Thus, the existence of clearances such as cracks and pores is an important factor into the formation of AlN by direct nitriding. **Figure 8** shows the SEM microstructure and EPMA analysis of N distribution in the cross sections of heat treated Al₂O₃-Al composite coatings. AlN was seen entirely from the surface to the interface.

3.2 Carbothermal reduction nitriding of Al₂O₃-C composite coatings

The formation of AlN could not be detected after heat treatment of an Al₂O₃-C composite sprayed coating in an N₂ atmosphere as shown in **Fig. 9(b)** and **(c)**. However, for Al₂O₃-C pellet, AlN was observed as shown in **Fig. 9(a)** according to following reactions :

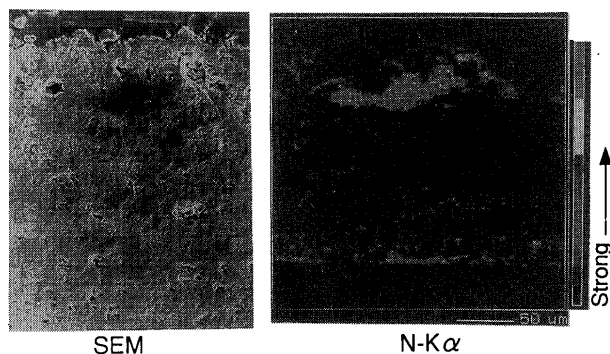


Fig.8 SEM microstructure and distribution of N by EPMA at a cross section of heat treated Al₂O₃-Al composite coatings

$\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \rightarrow 2\text{AlN} + 3\text{CO}$. When X-ray diffraction was used to compare the amount of carbon in the spraying powder with the carbon content of the sprayed Al₂O₃-C coating, it was found that the sprayed coating had a much lower carbon content. For this reason, to increase the amount of carbon for the carbothermal reaction, the surface of the Al₂O₃-C coatings was coated with carbon powder mixed with acetone, which was then let dry. Schematic illustration is shown in **Fig.10**.

Figure 11 shows the X-ray diffraction results of Al₂O₃-C composite coatings and Al₂O₃ coating coated with C powders at a density of 0.07mg/mm² after heat-treatment at 1773K for 10.8ks in an N₂ atmosphere. The formation of AlN was seen for Al₂O₃-C composite coatings and the amount of AlN increased with the increase of amount of C in composite coatings. However, for Al₂O₃ coating coated with C powders,

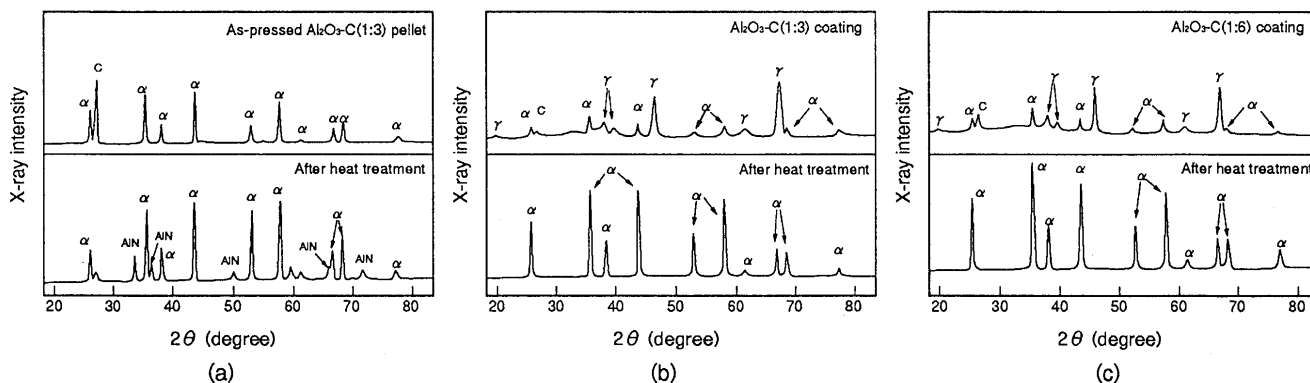


Fig.9 Comparison of (a)as-pressed Al₂O₃-C pellet, (b)as-sprayed Al₂O₃-C(1:3) and (c)Al₂O₃-C(1:6) with those heat treatment in an N₂ atmosphere respectively

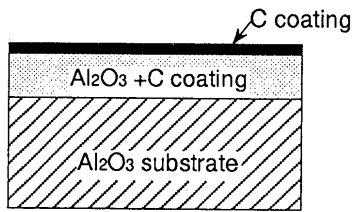


Fig.10 Schematic illustration of cross section of Al₂O₃-C coatings coated with C powder

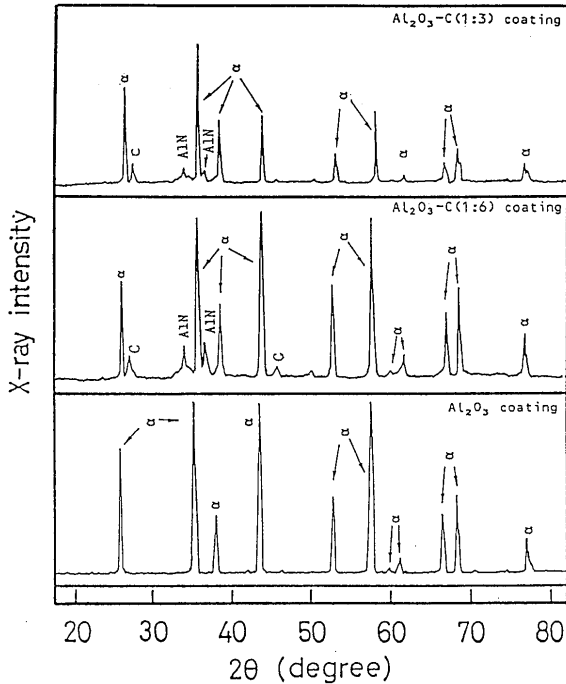


Fig.11 X-ray diffraction patterns of Al₂O₃-C (1:6) composite coatings and Al₂O₃-C(1:3) composite coatings coated with C powders(0.07mg/mm²) heat treated in N₂ atmosphere(1773K for 10.8ks)

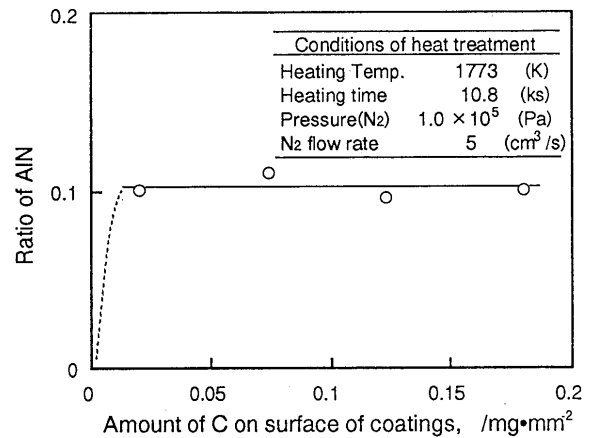
AlN was not observed in coating as shown in bottom figure.

Figure 12 shows the effect of the additional carbon on the ratio of AlN after carbothermal reduction in an N₂ atmosphere. AlN formed at a constant ratio to the amount of carbon on the Al₂O₃-C coatings.

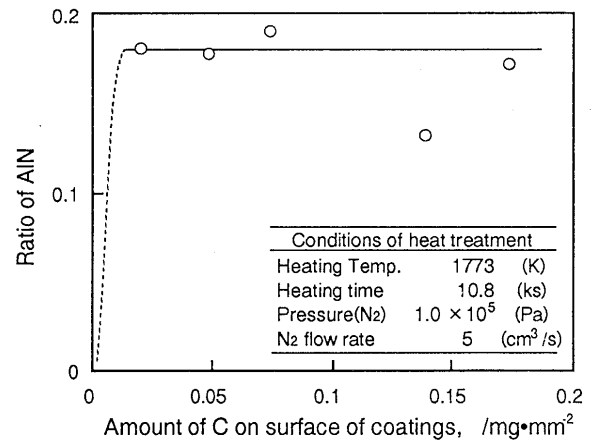
Figure 13 shows how the AlN distribution decreased as the coating thickness decreased, with nitridation occurring at a depth of 30 to 40 μm from the surface.

Figure 14 shows the SEM microstructure and EPMA analysis of the nitrogen distribution in cross sections of Al₂O₃-C composite coatings coated with carbon at a density of 0.1mg/mm², at holding times of 3.6 and 25.2 ks.

Figure 15 shows the X-ray diffraction patterns of decarbonized Al₂O₃-C coating heat-treated as shown in



(a) Al₂O₃-C(1:3) composite coating



(b) Al₂O₃-C(1:6) composite coating

Fig.12 Effect of amount C coated on the surface of Al₂O₃-C composite coatings on the ratio of AlN

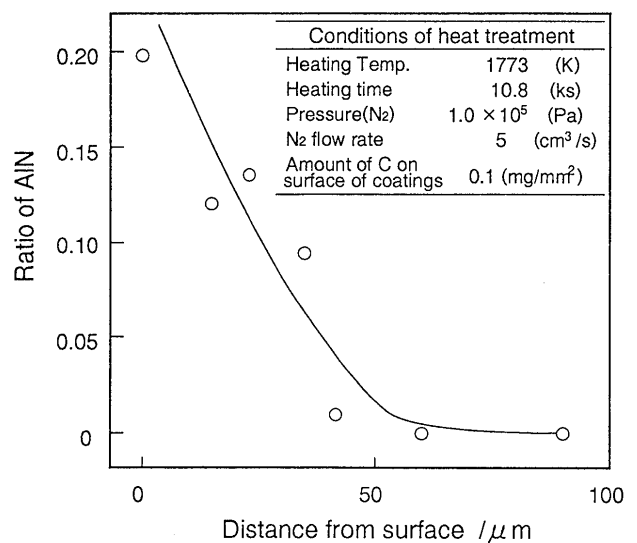


Fig.13 Effect of the distance from the surface on the ratio of AlN

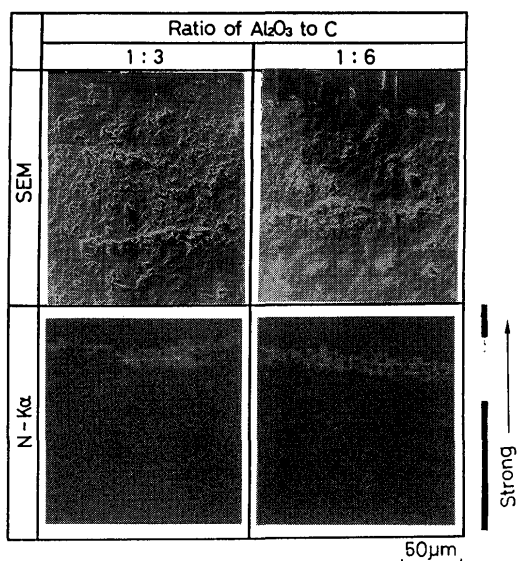


Fig.14 Effect of C content in spraying powders on the microstructure and nitriding of Al₂O₃-C coatings coated with same amount of C on the surface after heat treatment at 1773K for 10.8ks in N₂ atmosphere

top figure in Fig. 16, and decarbonized Al₂O₃-C coating coated with C powders after carbothermal reduction in N₂ as shown in middle figure in Fig. 16. From Fig. 15, the formation of AlN was seen for decarbonized Al₂O₃-C coating coated with C powders.

In contrast, as shown in bottom figure in Fig. 16 the nitriding did not occur for Al₂O₃ coating coated with carbon powders. From these results, the formation of AlN in Al₂O₃-C coatings was depended greatly on the existence of C powders on the surface and the pores and the microcracks in coatings.

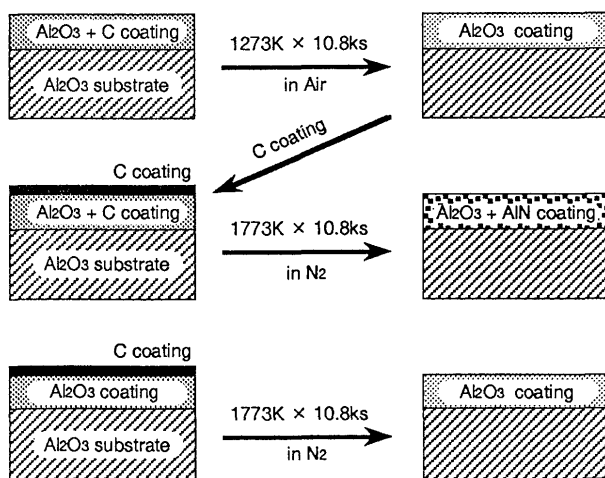


Fig.16 Schematic illustration of nitriding of Al₂O₃-C composite coating by carbothermal reduction

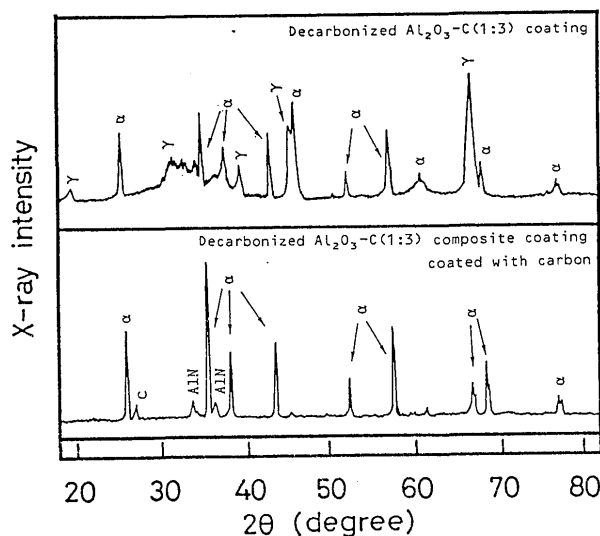


Fig.15 X-ray diffraction patterns on decarbonized Al₂O₃-C(1:3) composite coating by heat treatment in air and that of decarbonized Al₂O₃-C composite coating coated with C on the surface after nitriding at 1773K for 10.8ks in N₂ atmosphere

4. Conclusion

Nitridation does not normally occur with thermal spraying of aluminum or Al₂O₃-C mixed powder in an N₂ atmosphere using an N₂ plasma jet. In order to form AlN, heat treatment of an Al₂O₃-Al or Al₂O₃-C composite coating in an N₂ atmosphere is required. For Al₂O₃-Al composite coatings, the nitridation ratio increases as the temperature of heat treatment increases. For Al₂O₃-C composite coatings, a supply of carbon on the surface is required for nitridation, and the nitriding depth is about 40 µm from the surface of the coatings.

For both direct and carbothermal reduction nitridation of sprayed coatings clearances such as pores and microcracks are an important factor.

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