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Article

In Situ Fabrication of AlN Coating by Reactive Plasma Spraying of Al/AlN Powder

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Abstract: Reactive plasma spraying is a promising technology for the *in situ* formation of aluminum nitride (AlN) coatings. Recently, it became possible to fabricate cubic-AlN-(*c*-AlN) based coatings through reactive plasma spraying of Al powder in an ambient atmosphere. However, it was difficult to fabricate a coating with high AlN content and suitable thickness due to the coalescence of the Al particles. In this study, the influence of using AlN additive (*h*-AlN) to increase the AlN content of the coating and improve the reaction process was investigated. The simple mixing of Al and AlN powders was not suitable for fabricating AlN coatings through reactive plasma spraying. However, it was possible to prepare a homogenously mixed, agglomerated and dispersed Al/AlN mixture (which enabled in-flight interaction between the powder and the surrounding plasma) by wet-mixing in a planetary mill. Increasing the AlN content in the mixture prevented coalescence and increased the nitride content gradually. Using 30 to 40 wt% AlN was sufficient to fabricate a thick (more than 200 µm) AlN coating with high hardness (approximately 1000 Hv). The AlN additive prevented the coalescence of Al metal and enhanced post-deposition nitriding through N_2 plasma irradiation by allowing the nitriding species in the plasma to impinge on a larger Al surface area. Using AlN as a feedstock additive was found to be a suitable method for fabricating AlN coatings by reactive plasma spraying. Moreover, the fabricated coatings consist of hexagonal (*h*-AlN), *c*-AlN (rock-salt and zinc-blend phases) and certain oxides: aluminum oxynitride (Al_5O_6N), cubic sphalerite $Al_{23}O_{27}N_5$ (ALON) and Al_2O_3. The zinc-blend *c*-AlN and ALON phases were attributed to the transformation of the *h*-AlN feedstock during the reactive plasma spraying. Thus, the zinc-blend *c*-AlN and ALON phases were not included in the feedstock and were not formed through nitriding of the Al.

Keywords: reactive plasma spray; feedstock additives; aluminum nitride coating; zinc-blend cubic-AlN

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1. Introduction

Current progress in integrated circuit, power supply unit and microelectronics technologies have increased demand for silicon-compatible substrates with superior thermal conductivity and dielectric properties. Among advanced ceramics, aluminum nitride (AlN) has attracted much attention from researchers in this field due to its outstanding properties. Aluminum nitride possesses an excellent combination of high thermal conductivity (up to 320 W/mK for a pure single crystal and 180−220 W/mK for hot pressed material), high dielectric resistivity, appropriate thermal expansion coefficient (close to silicon and GaAs), high electrical insulation, high mechanical strength and high hardness (Hv 1400). In addition, AlN has good chemical/physical stability at fairly high temperatures and high resistance to molten metals, wear and corrosion [1-4]. This makes it an ideal material not only for use as an electronic substrate, a heat sink, and packaging for electronic components, but also as semiconductor packaging, material for crucibles and vessels handling corrosive chemicals and molten metals, parts of semiconductor equipment and reaction vessels for etching.

Moreover, it has been reported that the fabrication of thermal sprayed AlN coatings will enable cost-effective solutions for a number of applications [5], especially for structural parts and power devices that require thick coatings (approximately 100 µm or more). However, it has been impossible to fabricate AlN coatings by conventional thermal spray processes directly from AlN powder due to the thermal decomposition of AlN during spraying, which occurs without a stable melting phase (AlN dissociates at ~2572 K). Thermal spray processes basically depend on the spraying and deposition of molten or semi-molten (heat-softened) materials for coating formation. Various methods have been developed for the fabrication of AlN coatings by thermal spraying such as detonation spraying [5] and low pressure plasma spraying (LPPS) of AlN and Al_2O_3 powder [6,7]. Moreover, carbon reduction of Al_2O_3 by plasma spraying has been investigated [7,8]. However, the coatings fabricated by those studies have included a number of AlN phases.

Reactive plasma spraying (RPS) is a promising technology for the *in situ* formation of both AlN coatings and nitride ceramic coatings such as titanium nitride (TiN) and silicon nitride (Si_3N_4) [9-14]. The principle of RPS is based on a reaction between the feedstock powder and surrounding reactive gaseous species present in the plasma. In our previous studies [15-18], it was possible to fabricate cubic aluminum nitride (*c*-AlN)/Al composite coatings through reactive plasma spraying of Al feedstock powder in N_2/H_2 plasma using a conventional atmospheric plasma spray system.

However, it was difficult to fabricate a coating with high AlN content and suitable thickness by controlling the in-flight nitriding reaction. Thus, the in-flight nitriding reaction affected the deposition behavior of particles sprayed on the substrate and thereby reduced their deposition efficiency. Due to the complete nitriding of some particles (the formation of AlN particles during flight prevents particle deposition) and the excessive vaporization of fine Al particles (due to increased particle temperature). Therefore, to fabricate coatings with high AlN content and suitable thickness, enhancing the nitriding reaction and nitride content at short spray distances (decreasing the in-flight time) is required. This means that improving the nitriding reaction after deposition on the substrate is also required in order to avoid the coalescence and agglomeration of molten Al particles upon collision with the substrate.

Generally, to promote the nitridation conversion in the direct nitriding method, various means of decreasing the nitriding commencement temperature have been investigated such as the nitridation of Al salts (e.g., Al_2S_3) [19], using mixtures of nitrogen and ammonia gases instead of pure nitrogen gas [20] and incorporating certain additives (e.g., Mg [21,22], Li-salts [23,24]). Some other studies have mixed Al powder with a dispersion agent such as carbon black [25] or ammonium chloride (NH_4Cl) [26,27] and then nitrided the mixture under high temperature conditions. The addition of a dispersion agent to the starting Al powder can prevent the formation of Al agglomerates and promote the formation of AlN powder. In this study, the possibility of using AlN as a dispersant to prevent Al coalescence and to the nitriding reaction after deposition in a reactive plasma spray process was investigated. The AlN selected as the dispersant does not contain materials such as water or carbon dioxide, which may interfere with the nitriding reaction or cause the nitrided product to form undesired impurities that require further purification. Furthermore, AlN contamination in the coatings will improve the nitride content and so there is no need to remove it from the fabricated coatings.

This study investigated the possibility of using AlN additives as a dispersion agent to prevent the coalescence of Al particles and to enhance the nitriding reaction after deposition on a substrate. The Al to AlN powder mixing ratio was optimized for the reactive plasma spray process. The formation mechanism of the synthesized nitride contents was also clarified in this paper.

2. Results and Discussion

2.1. Spraying of Simply Mixed Al/AlN Powders

Al/AlN powders simply mixed at AlN weight ratios of 10, 20, 30 and 40 wt% were sprayed. The feedstock hexagonal AlN phase started to appear in the fabricated coatings when spraying the 30 wt% AlN/Al mixture as shown in the XRD spectra in Figure 1 (AlN: JCPDS-file No. 025-1133 with a main peak around 33° of 2θ value). The spectra revealed that the outside layer of the fabricated coating (after fine polishing to provide a smooth surface) mainly consists of *c*-AlN phase [Figure 1 (a)] and the central layers consist of *c*-AlN/Al composite [Figure 1 (b)]. As we have explained in detail in our previous studies [15-18], the main peak of the *c*-AlN phase with JCPDS-file No. 046-1200 (rock salt AlN) lies around 44° of the 2θ value and the main peak of Al with JCPDS-file No 004-0787 lies around 38° of the 2θ value.

Moreover, the fabricated coating contains oxides like alumina (Al_2O_3) and aluminum oxynitride (Al_5O_6N). This indicates that the simple addition of AlN did not affect the nitriding process of the Al particles. Thus, the fabricated coating consists of a surface *c*-AlN layer and *c*-AlN/Al central layers, and it is almost the same as the case of using only Al powder under the same spray conditions as shown in Figure 2.

This means that using AlN additives and simple mixing has no significant effect on the RPS process using Al powder. Thus, the Al particles in the mixture easily coalesce and coagulate together after colliding on the substrate due to the low melting point of Al (660 °C) [20,26,27]. This prevented continuous nitrogen access and the realization of complete nitriding. The surface layer completed its reaction after deposition on the substrate due to N_2 plasma irradiation and the lack of further particle deposition. Furthermore, the coating's thickness strongly decreased with increasing the amounts of AlN additive. Moreover, when the AlN content in the feedstock was increased to 40 wt%, it was difficult to supply the powder due to increasing fine particle content. This indicates that the simple mixing of AlN additive with Al powder has no effect on the nitriding of Al powder in the RPS process. Furthermore, it is not suitable for the fabrication of thick coatings.

Figure 1. XRD spectra of the fabricated coatings after using 30 wt% AlN and simple mixing: **(a)** surface layers and **(b)** central layers.

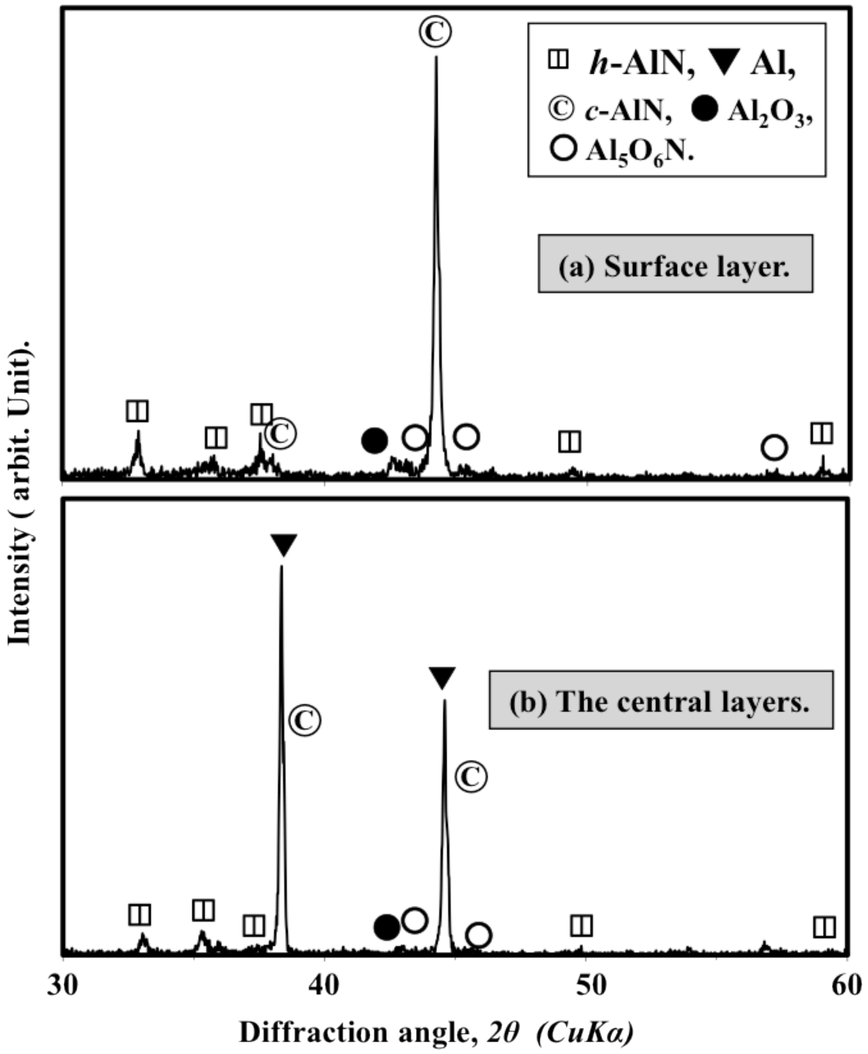
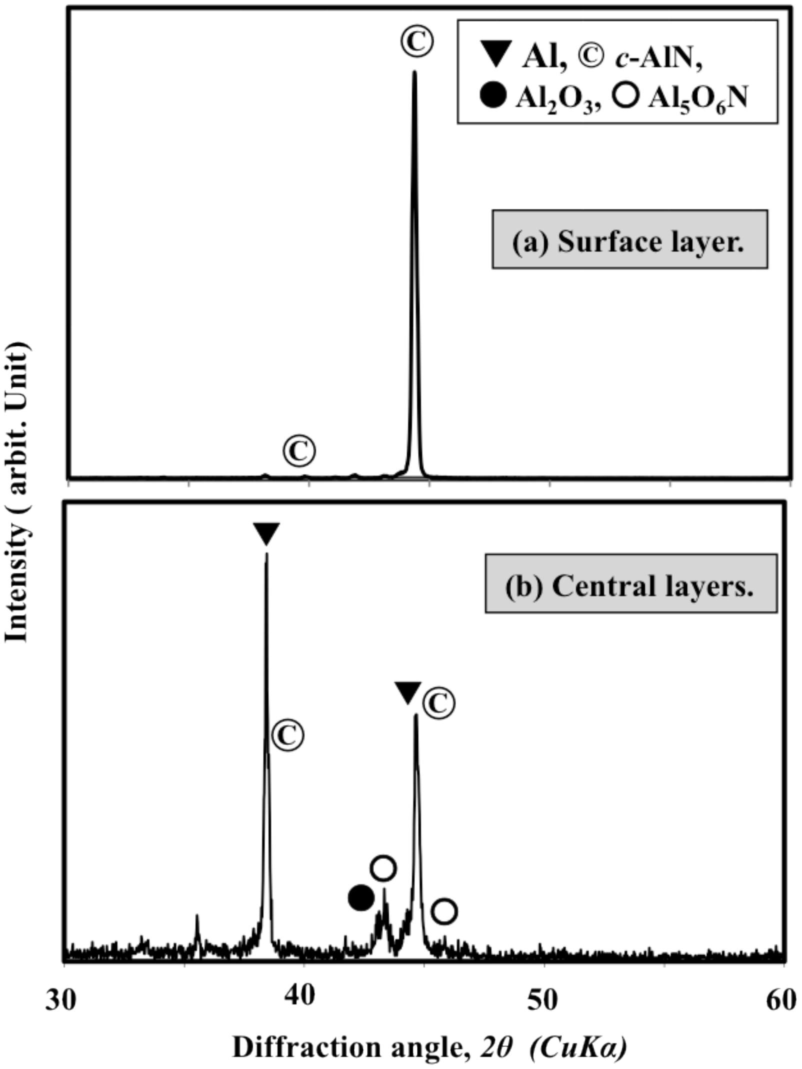


Figure 2. XRD spectra of the fabricated coatings with only Al powder: **(a)** surface layers and **(b)** central layers.



2.2. Spraying of Wet-Mixed Al/AlN Powders

To prepare a suitable Al/AlN feedstock mixture, the powders were wet mixed by planetary milling in ethanol and then dried. Figure 3 shows the XRD spectra of Al powder and AlN/Al mixed powders at different AlN weight ratios: 20, 40 wt% and pure AlN powder. The powders after mixing consisted of Al and AlN without any impurities or oxides. Figure 4 shows the SEM morphology of the 30 wt% AlN/Al mixture and its cross-section after drying. It is clear that the powders were homogenously mixed, agglomerated and the AlN was dispersed in the Al powders, which would enable the in-flight interaction between the powders and the surrounding plasma.

Figure 3. XRD spectra of **(a)** Al powder, **(b)** 20 wt. % AlN/Al, **(c)** 40 wt. % AlN/Al and **(d)** AlN powder.

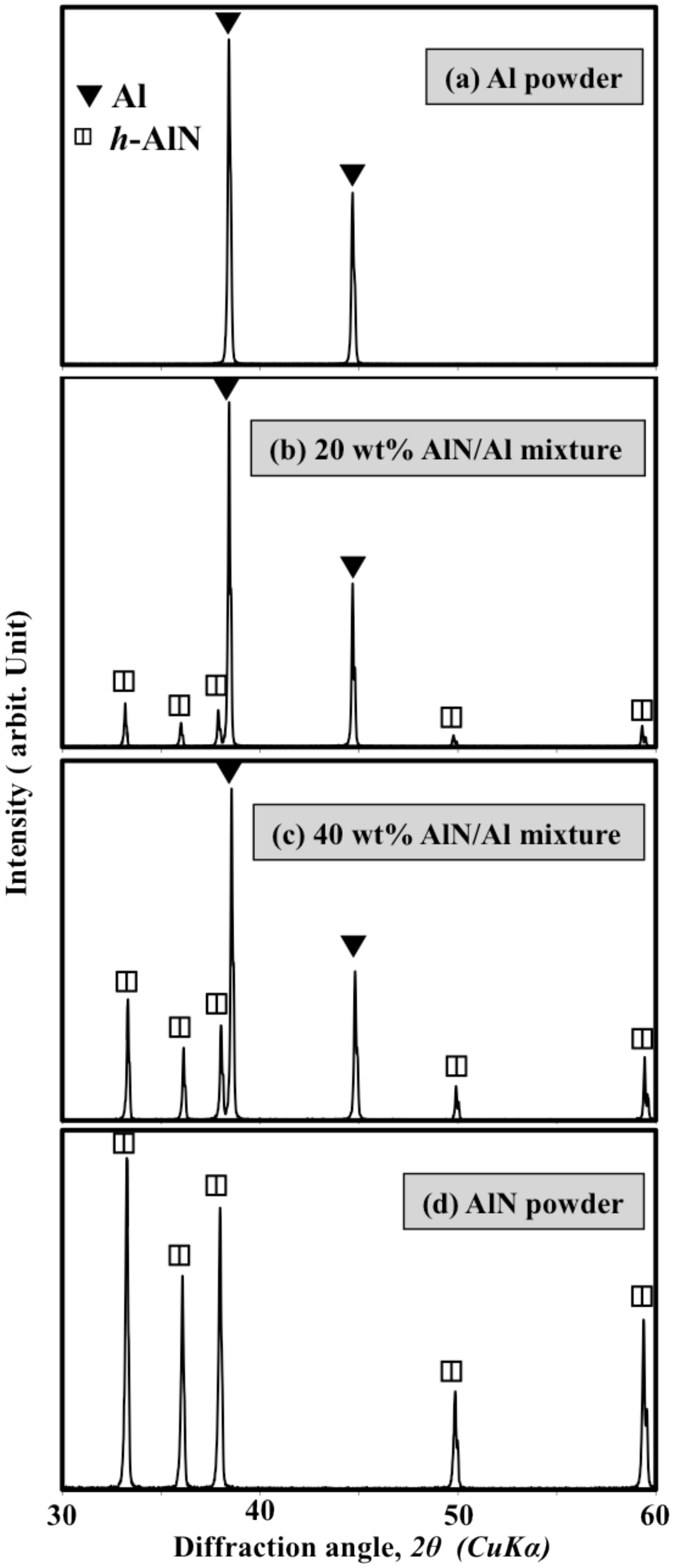


Figure 4. SEM morphology of 30 wt% AlN/Al wet-mixed powders: **(a)** the powder mixture and **(b)** the mixture in cross-section.

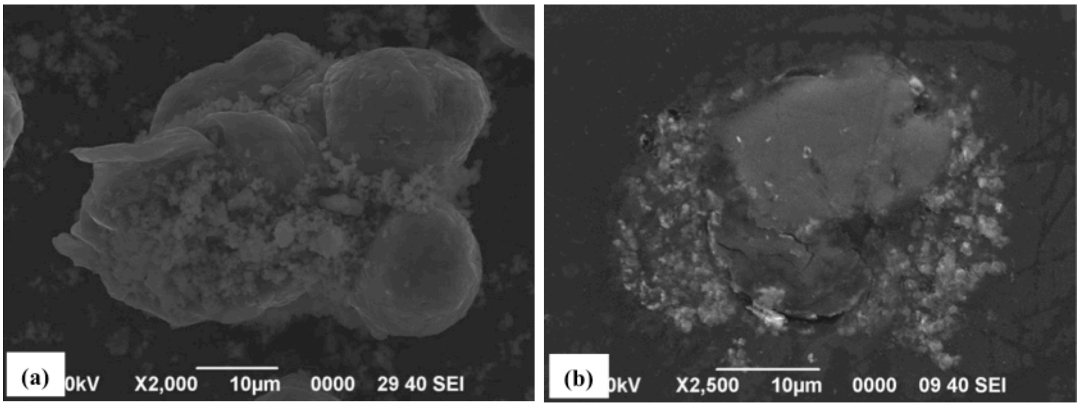


Figure 5 shows the XRD spectra of the fabricated coating after using wet-mixed 10 wt% AlN/Al powder. The outside layer of the coating consists of mainly *c*-AlN phase as shown in Figure 5(a). The hexagonal phase also appeared in the fabricated coatings. This indicates that the hexagonal AlN from the feedstock mixture started to deposit on the substrate through the Al molten phase. Furthermore, a new *c*-AlN phase (Zinc-blend phase) was detected in the XRD spectra after using the AlN additive. The zinc-blend phase did not appear during the reactive plasma nitriding of only Al powder as shown in our previous studies [15-18] and in Figure 2. Some oxides like aluminum oxynitrides (Al_5O_6N) and Al_2O_3 (which appeared during the nitriding of Al powder) were detected in the XRD spectra. Moreover, cubic sphalerite, $Al_{23}O_{27}N_5$ (ALON), also appeared in the coating after using the AlN additive. However, after removing the surface layer (approximately 250 µm), the coating mainly consists of Al, *h*-AlN and *c*-AlN composite, and the main phase is Al as shown in Figure 5(b). This indicates that AlN can easily deposit after preparing a suitable Al/AlN mixture by wet mixing. However, 10 wt% AlN is not enough to prevent the coalescence of Al particles and achieve the complete nitriding of the Al particles. The complete nitriding of the surface layer is related to the N_2 plasma irradiation after deposition on the substrate and the lack of further particle deposition. The incomplete nitriding of Al particles in the center part is related to the aggregation of the Al particles as explained above in Section 2.1. Thus, a significant amount of Al remains in the mixture, the particles easily coalesce and 10 wt% AlN additive is not enough to prevent this coalescence.

Furthermore, both *c*-AlN (zinc-blend phase) and oxide phases (Al_2O_3, Al_5O_6N) were detected in the XRD spectra of the central of the coatings as shown in Figure 5(b). The cubic sphalerite $Al_{23}O_{27}N_5$ (ALON) phase did not appear in the spectra of the center parts of the coatings.

A cross-section of the fabricated coatings after using 10 wt% AlN/Al mixed powders is shown in Figure 6. The thickness of the fabricated coating is approximately 700 µm, and the coating is dense, as shown in the high magnification parts of Figure 6 (b and c). The hardness of this coating is approximately 320 Hv. Therefore, using 10 wt % of AlN additive and wet-mixing with Al powder is a suitable way to directly deposit AlN in the APS process. It was possible to fabricate thick AlN (hexagonal and cubic)/Al coatings with high hardness with 10 wt% AlN additive. However, 10 wt% AlN is not enough to prevent Al coalescence and achieve the complete nitriding of all the Al particles in the RPS process.

Figure 5. XRD spectra of the fabricated coatings after using 10 wt% AlN additive: **(a)** surface layers and **(b)** central layers.

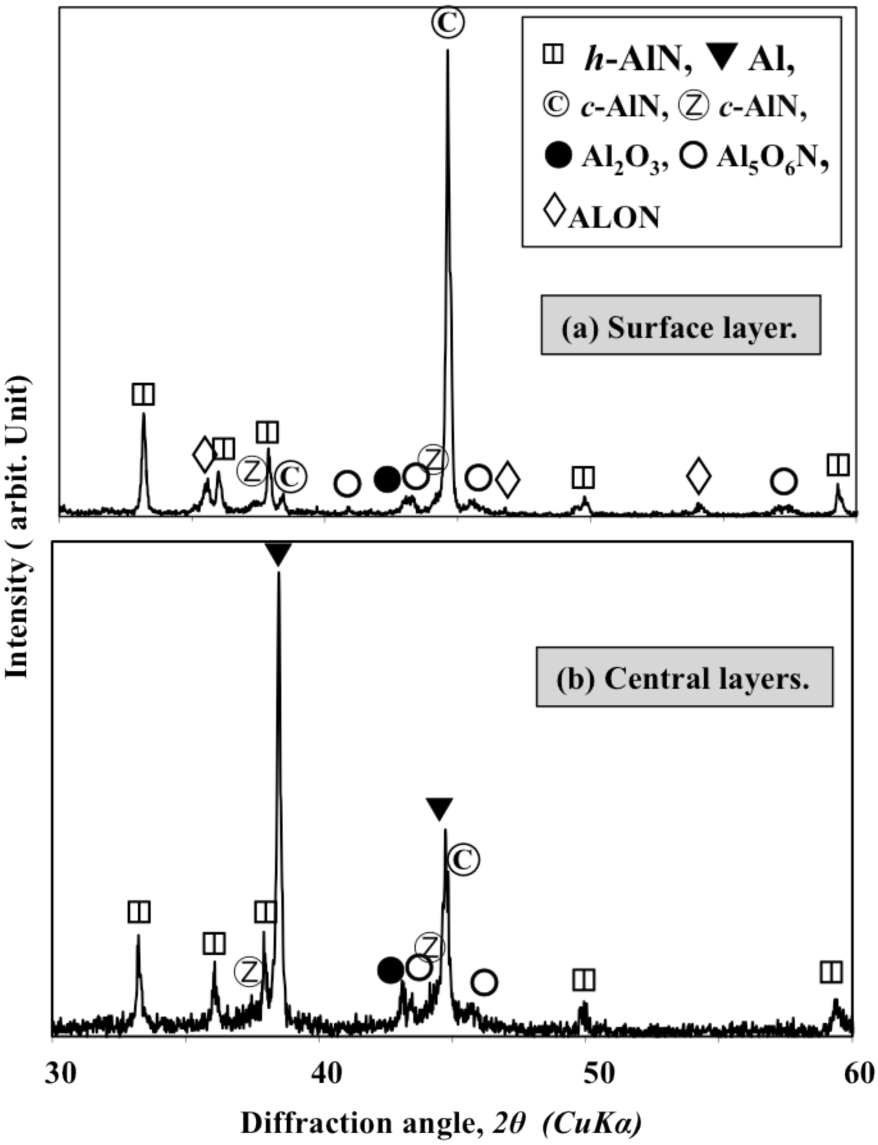
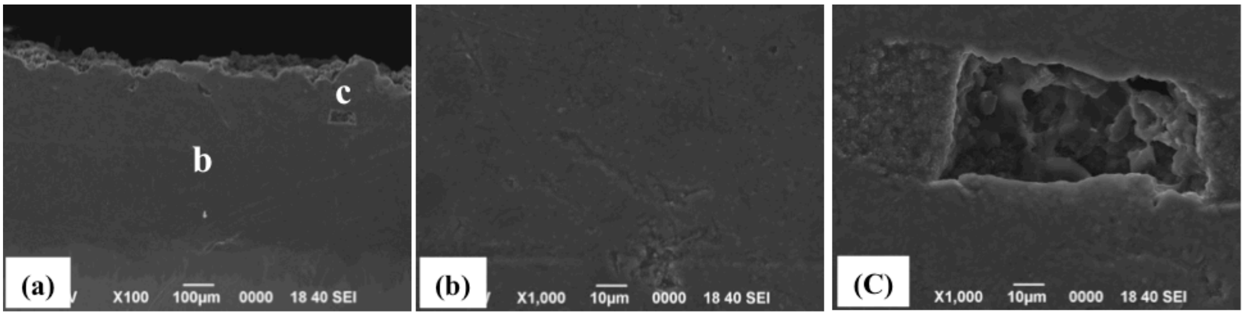
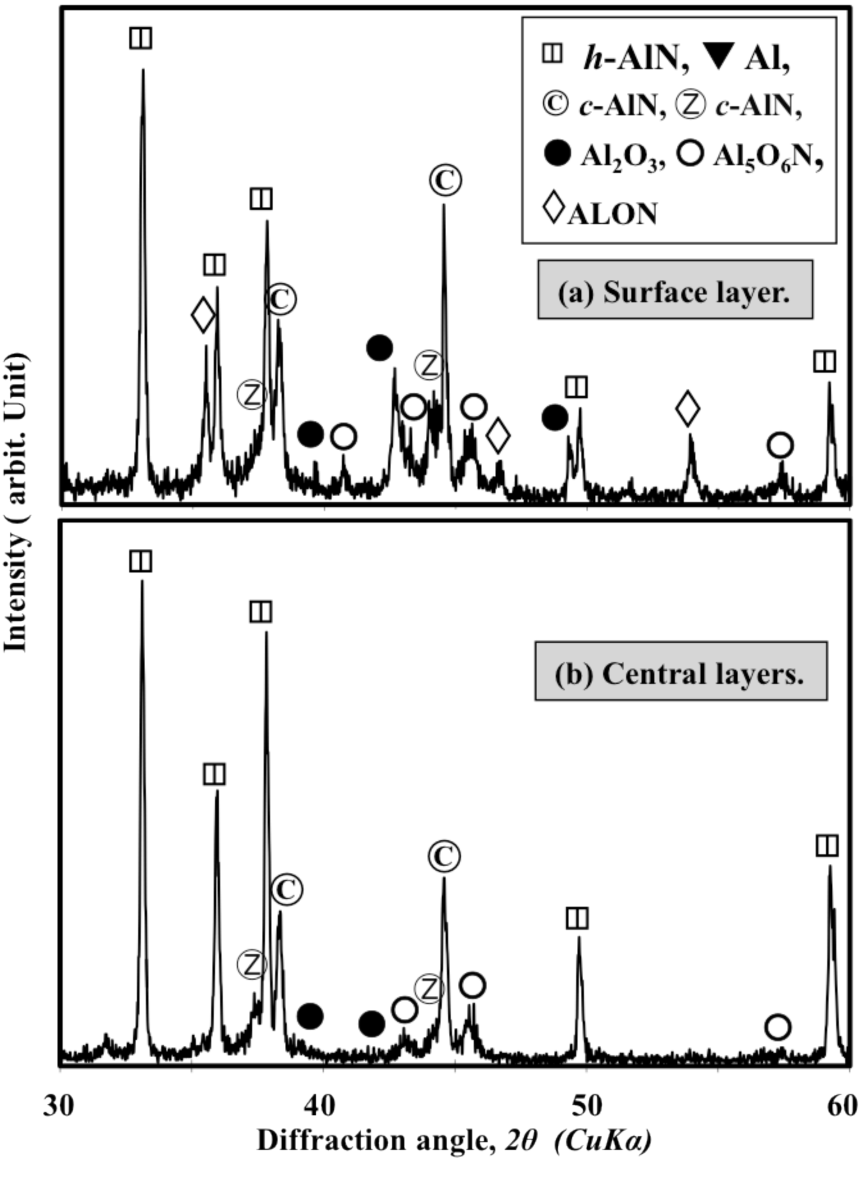


Figure 6. (a) SEM cross-section morphology of the fabricated coating after using 10 wt% AlN additive, **(b)** high magnification of the b parts from **(a)**, **(c)** high magnification of the b parts from **(a)**.



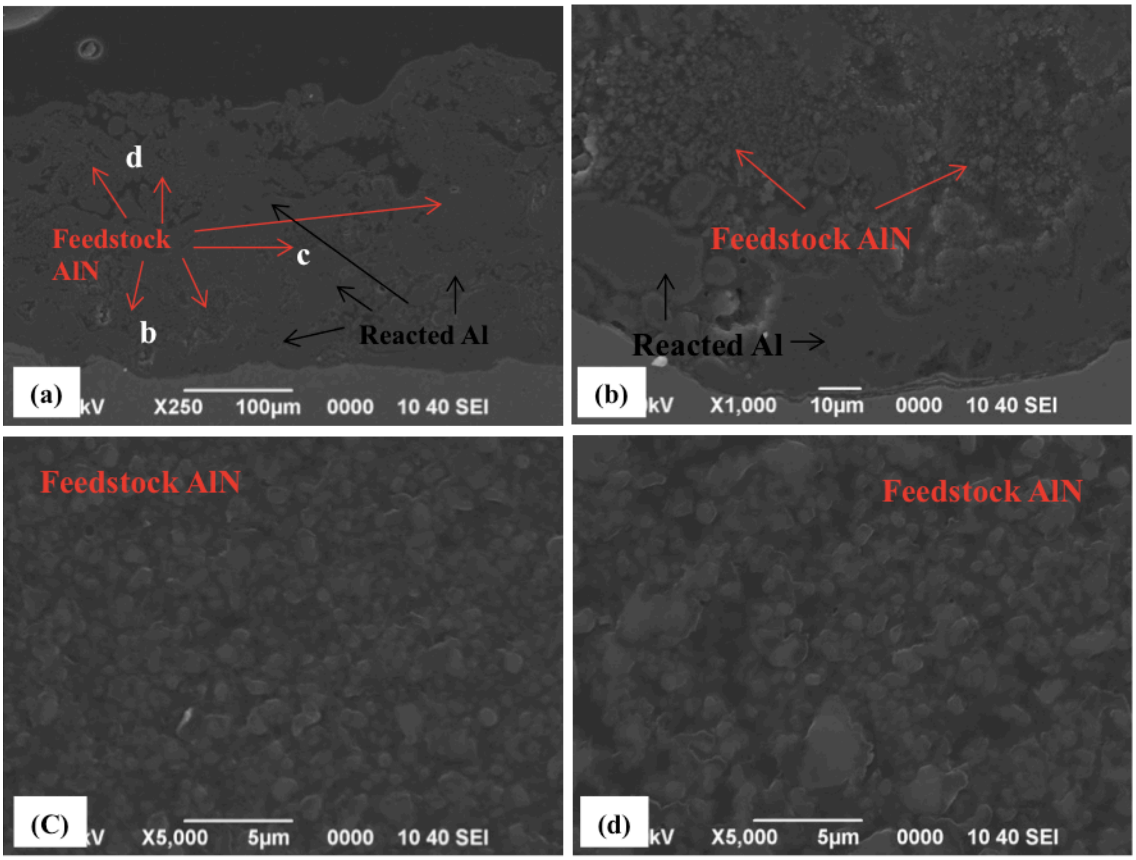
By increasing the amount of AlN additive in the feedstock mixture, the Al content in the fabricated coatings decreased gradually, and it was possible to reach almost complete nitriding with 30 wt% AlN/Al mixed powder. Figure 7 shows the XRD spectra of the fabricated coating after using 30 wt% AlN additive. The surface layer of the coating consists of *h*-AlN, *c*-AlN, *c*-AlN phase (zinc-blend phase), ALON and Al_5O_6N as shown in Figure 7(a). This result agrees with the previous result after using 10 wt% AlN wet mixture. It is clear that the *h*-AlN and ALON contents increased with increasing amounts of AlN in the feedstock mixture, and the main phase is mainly *h*-AlN. Figure 7(b) shows the XRD spectrum of the central layer of the coating. This reveals that the nitriding reaction was almost complete and no peaks related to Al phases appear in the spectrum. Furthermore, the cubic sphalerite, $Al_{23}O_{27}N_5$ (ALON) phase did not appear in the spectrum of the central part of the coatings. It is concluded that using 30 wt% AlN and wet mixing is a suitable way of preventing Al coalescence and reaching almost complete nitriding of the Al particles in the RPS process.

Figure 7. XRD spectra of the fabricated coatings after using 30 wt% AlN additive: **(a)** surface layers and **(b)** central layers.



With increasing AlN content in the feedstock mixture, the fabricated coating thickness decreased gradually. Figure 8 shows a cross-section of the fabricated coatings after using 30 wt% AlN additives. The coating is approximately 250 µm and the *h*-AlN phase is homogeneously dispersed across the coating as shown in the high magnification parts of Figure 8 (b–d). The average hardness of this coating is approximately 980 Hv. Therefore, it was possible to fabricate a thick (hexagonal and cubic) AlN coating with high hardness with 30 wt% AlN additive.

Figure 8. **(a)** SEM cross-section of the fabricated coating after using 30 wt% AlN additives, **(b)** high magnification of b region in **(a), (c)** high magnification of c region in **(a), (d)** high magnification of d region in **(a)**.



To optimize the AlN/Al mixing ratio for the reactive plasma spray process, the AlN content was increased up to 50 wt%. Figure 9 shows the XRD spectra of the coating fabricated using 40 wt% AlN additive. The fabricated coating (both the surface and the central layers) has almost the same phase composition as the coating fabricated using 30 wt% AlN. However, the thickness of the coating was slightly decreased to approximately 200 µm when the AlN content was increased to 40 wt%, as shown in Figure 10. The average hardness of the coating was approximately 1050 Hv. A cross-section showed the homogeneous dispersion of the *h*-AlN phase in the coating, as shown in the highly magnified parts of Figure 10 (b–d).

However, with an AlN content in the feedstock mixture of 50 wt%, it was difficult to supply the mixture due to the increased amount of fine particles in the mixture. Therefore, it is possible to directly deposit AlN particles in thermal spray processes by spraying wet-mixed AlN/Al feedstock powder.

Increasing the AlN content in the feedstock mixture is a promising method for preventing coagulation and promoting the nitriding of the Al particles in the RPS process. The dispersed AlN phase deposited with the partially reacted Al particles played a passive role in completing the nitriding reaction by preventing Al coagulation. The hardness of the fabricated coatings increased gradually with increasing AlN content in the feedstock mixture, as shown in Figure 11. The optimal amount of AlN in the feedstock is 30 to 40 wt%.

Figure 9. XRD spectra of the fabricated coatings after using 40 wt% AlN additive: **(a)** surface layers and **(b)** central layers.

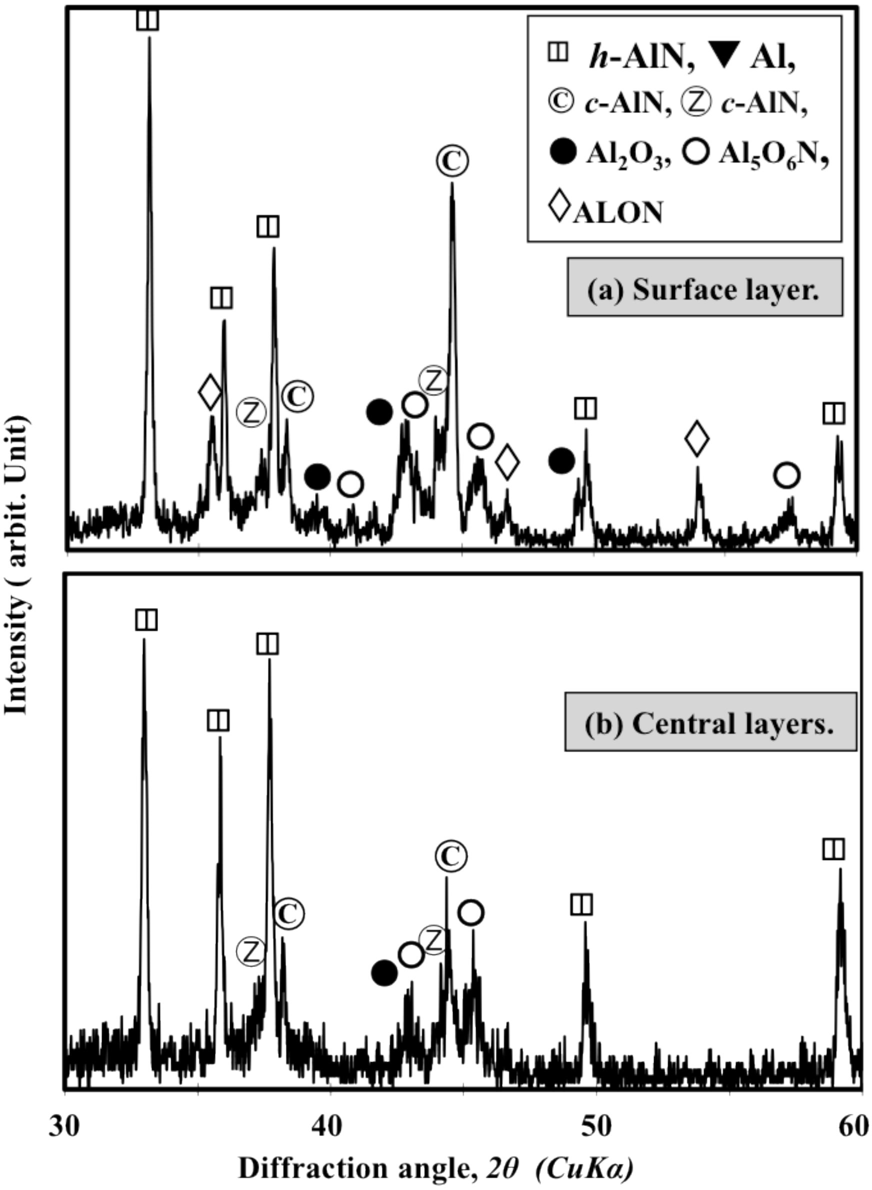
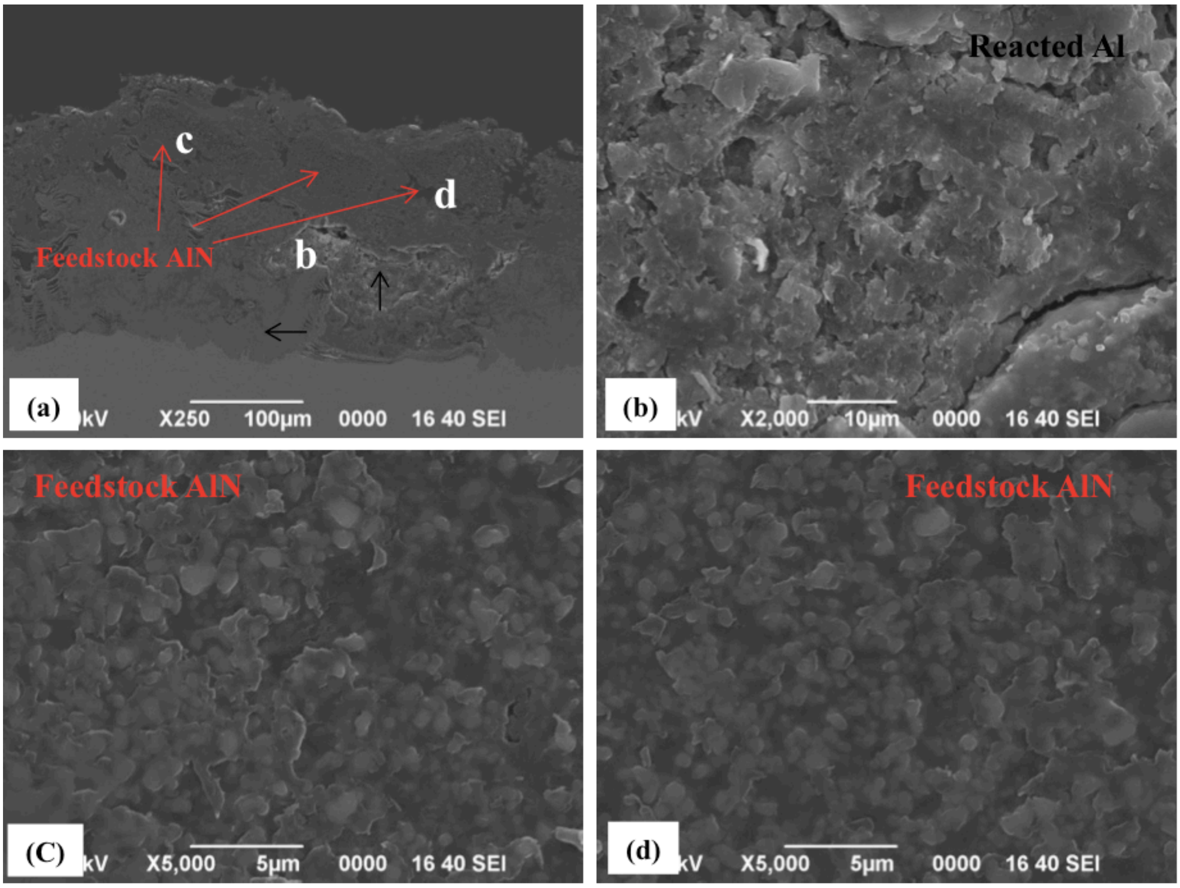


Figure 10. SEM cross-section of the fabricated coating after using 40 wt% AlN additive, **(b)** high magnification of parts b from **(a)**, **(c)** high magnification of parts c from **(a)**, **(d)** high magnification of parts d from **(a)**.



2.3. Discussion

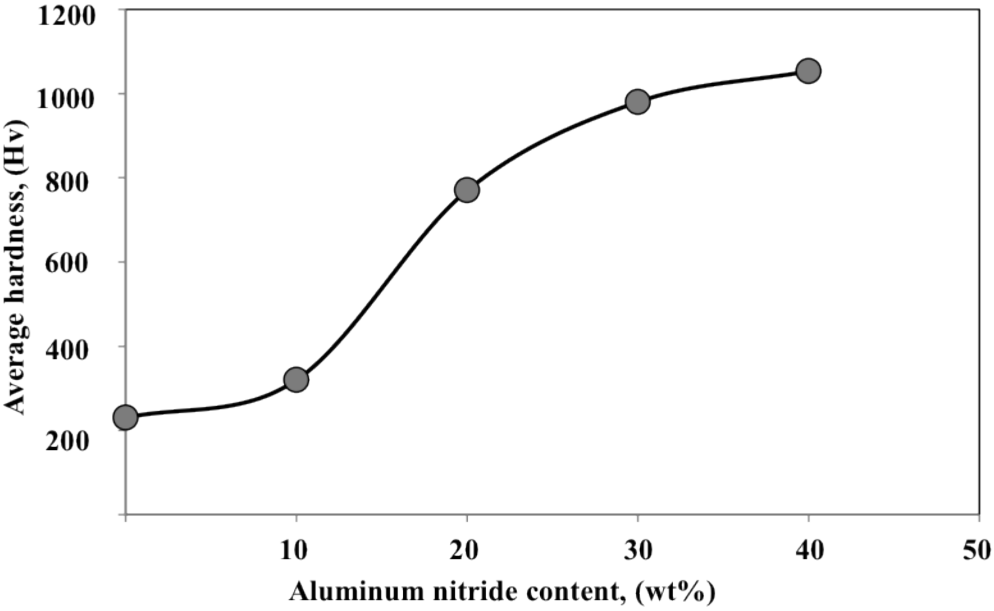
It was possible to fabricate thick (more than 200 μm) AlN coatings with high hardness (approximately 1000 Hv) using the APS process. Thus, the addition of AlN provides a stable compatible solid surface that allows higher conversion rates to be achieved. This promotes spreading of the molten Al, exposing it to the N_2 plasma for nitriding and AlN formation after deposition on the substrate through plasma irradiation. Furthermore, AlN is a suitable dispersant for fabricating AlN thermal sprayed coatings, and the deposition of contaminating AlN increases the nitride content in the fabricated coating. Additionally, AlN lacks materials such as water and carbon dioxide, which interfere with the nitriding process and lead to the formation of significant undesirable impurities. The optimum amount of AlN additive is approximately 30~40 wt%. Increasing the AlN content in the feedstock mixture to 50 wt% made it too difficult to supply the mixture due to the increased amount of fine particles.

Using AlN as a dispersion agent with Al feedstock powder prevented the coalescence of Al metal and thus allowed the nitriding species in the plasma to impinge on a larger surface area of Al. In other words, it promoted post- deposition nitriding and it led to the rapid and complete nitriding of Al particles. Moreover, the deposition of AlN feedstock particles increases the nitride content in the fabricated coating. Using AlN as a dispersion agent minimizes the introduction of unnecessary impurities into the reaction mixture that may interfere during the nitriding process and with the nitride product. Therefore, this approach prevents undesirable impurities from appearing in the coating.

To clarify the effects of the AlN addition on the RPS process, we will first summarize the direct nitriding of Al powder. Generally, during the direct nitriding of Al powder, molten and semi-molten particles react with the surrounding N_2 gas species through a liquid–gas mechanism according to the following equation [27]:

$$Al_{(l)} + 1/2N_{2(g)} \rightarrow AlN_{(s)}\ (\Delta H^0 = -318\ KJ/mol) \quad (1)$$

Figure 11. Average hardness of the fabricated coatings *vs*. AlN content.

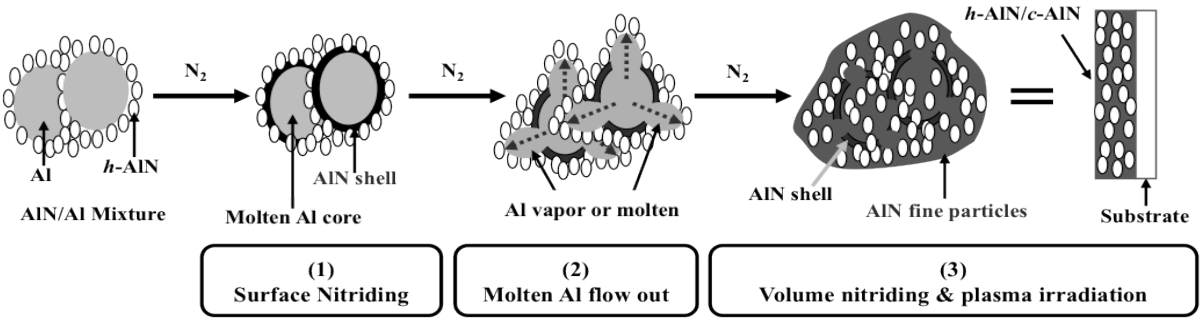


The nitrogen reacts intensely with the liquid metallic particles and the nitriding reaction occurs via three steps as clarified in more detail in our previous studies [17,18]: nitridation at the surface of the particles with the formation of a crystalline AlN shell, breakaway or outflow of molten or vaporized Al core, and volume nitridation outside the shell with a remaining hole or an empty core. Thus, under high-temperature conditions, above the Al melting point (660 °C), Al particles melt, followed by coalescence into a ball-like form due to surface tension. Nitridation occurs on the surface of these molten Al particles, forming nitride layers or shells surrounding the molten Al.

As explained in our previous studies, in RPS processes the Al particles start to react with N_2 plasma during flight and deposit on the substrate to complete their reaction through N_2 plasma irradiation. However, not all the particles are completely reacted by the N_2 plasma irradiation to give a pure AlN coating. Thus, the accelerated molten and semi-molten particles easily coagulate together after colliding on the substrate. Although the process seems simple (as shown in Equation 1), it is more difficult than it first appears because Al melts at approximately 660 °C, and under such high-temperature conditions, the molten Al particles easily coalesce, which prevents intimate contact between the reactants (N_2 and Al). This prevents the N_2 from accessing all the particles to complete the nitriding reaction and thereby form pure AlN. The surface layer completed its reaction after deposition on the substrate due to the N_2 plasma irradiation and the lack of further particle deposition. It is well known that the aggregation of Al particles is the main obstacle to fabricating AlN powder through the direct nitriding of Al powder due to the low melting point of Al (660 °C) [20,26,27]. This prevents continuous nitrogen access and the realization of complete nitriding.

When using the AlN additive, the nitriding process of the Al particles follows its normal sequence of surface nitriding, outflow of molten Al core and volume nitriding through plasma irradiation. The role of the AlN feedstock comes in the last step after collision on the substrate (during the post- deposition reaction). The effect of the AlN additive during Al powder nitriding is schematically shown in Figure 12. Thus, the presence of AlN prevents the coalescence and coagulation of the molten Al. This enables a continuous interaction between the nitriding species of the plasma and the Al phase after deposition on the substrate. It also allows the nitrogen species to impinge upon a larger surface area of Al particles, which assists the continuous nitriding occurring through N_2 plasma irradiation after deposition on the substrate. Moreover, the AlN particle size is an important factor in the nitriding process. Thus, the fine particles are preferred because they separate the Al powder more efficiently than the larger particles and thus retard the coalescence of Al more efficiently.

Figure 12. Schematic diagram of the nitriding process of Al particles after using AlN additive in the APS process.



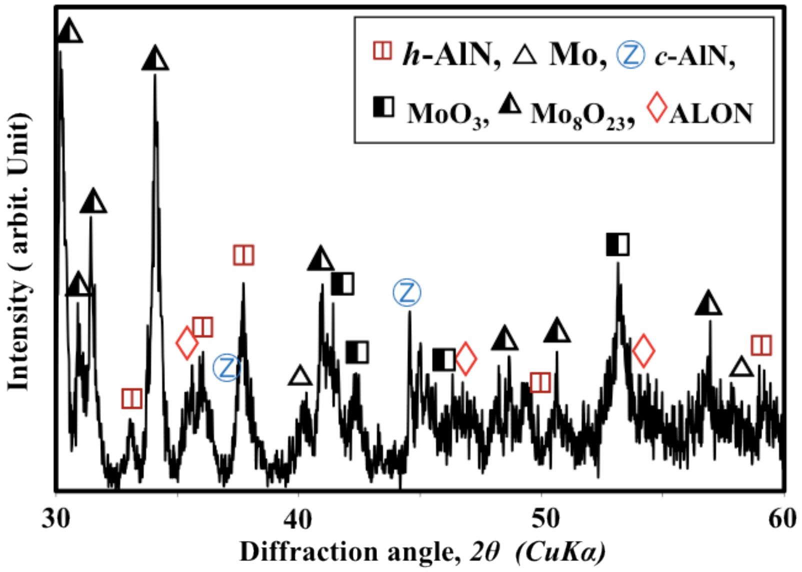
Therefore, it was possible to fabricate an AlN coating more than 200 μm thick with an average hardness of approximately 1000 Hv with AlN additive. The AlN additive prevents the coalescence of Al particles after collision on the substrate, which facilitates the nitriding of the unreacted Al particles through plasma irradiation (post-deposition nitriding). The XRD results confirmed that AlN additive improves the nitride content, promotes the nitriding process and enables the nearly complete nitriding of Al particles. However, more quantitative analyses are required regarding the transformation of Al to AlN phase during the RPS process in further studies (by EPMA or SEM with BSE).

Furthermore, using the AlN additive led to an interesting finding in the RPS process: the appearance of a zinc-blend AlN phase in the coatings. The formation of this AlN zinc-blend phase after using AlN/Al mixed powder is attributed to transformation from the hexagonal AlN feedstock powder. To confirm the transformation of AlN during spraying, the Al was replaced with molybdenum (Mo) in the 30 wt% AlN mixture. The XRD spectrum of the fabricated coating is shown in Figure 13. It is clear that the zinc-blend *c*-AlN appeared in the coating. Furthermore, the cubic sphalerite $Al_{23}O_{27}N_5$ (ALON) phase appeared in the spectrum. Therefore, the transformation of *h*-AlN feedstock powder into zinc-blend *c*-AlN and ALON phases was confirmed. However, more details regarding the transformation of the *h*-AlN feedstock phase during plasma spraying are required in further studies.

The formation of the ALON phase is attributed to an interaction between AlN and oxygen under high temperatures as reported by J. Wang *et al.* [28] and F. Boey *et al.* [29]. F. Boey *et al.* reported that the presence of oxygen can induce the AlN phase to convert to aluminum oxynitride. Furthermore, the disappearance of the ALON phase in the center of the coating is due to decreasing amounts of oxygen. Additionally, J. Wang *et al.* [28] reported that ALON can produce the *c*-AlN phase. The formation of Al_2O_3 and Al_5O_6N in the coating is attributed to the interaction of Al with the surrounding N_2 plasma and atmospheric oxygen, which agrees with its appearance only in the case of Al powder.

These results reveal the importance of the influence of ambient nitriding (the surrounding atmosphere and N_2/H_2 plasma) both during spraying and after deposition. The effect of the ambient atmosphere will be investigated with a shroud technique or a controlled gas pressure chamber and controlling the process parameters in future studies. A gas shroud significantly helps control the interaction between the ambient air and the plasma jet in conventional thermal spray processes [30,31]. Furthermore, using a gas shroud affects the particle conditions (temperature and velocity) and the coating properties [31]. Therefore, it is expected that controlling ambient nitriding will affect the reactive plasma spray process and will clarify the coating formation process in the complex RPS mode.

Figure 13. XRD spectra of coatings fabricated using Mo instead of Al (30 wt% AlN and 70 wt% Mo).



Herein, it was possible to fabricate a thick high nitride content coating in a reactive plasma spray process by spraying an Al/AlN mixed feedstock mixture. However, simple mixing was not suitable for the reactive plasma spray process. Only a small amount of AlN deposited after using simply mixed 30 wt% AlN/Al powders, and it did not show a significant effect on the nitriding process. Moreover, it was difficult to obtain a thick coating by spraying the simply mixed powders. To prepare a suitable AlN/Al mixture (homogeneously mixed, agglomerated and with the AlN dispersed in the Al powder), the powders were wet-mixed. This mixture morphology enables in-flight interaction between the mixture and the plasma. When spraying the wet-mixed powders, the feedstock AlN appeared in the fabricated coating even when using a 10 wt% AlN mixture. The fabricated coating consists of *c*-AlN (rock-salt and zinc-blend structures), *h*-AlN, Al_2O_3, Al_5O_6N and cubic sphalerite ALON. The appearance of the ALON phase is related to the transformation of AlN, and it agrees with previous reports by J. Wang *et al.* [28] and F. Boey *et al.* [29]. The formation of the AlN zinc-blend phase when using AlN/Al mixed powder is attributed to transformation from the hexagonal AlN feedstock powder. After polishing the surface layers of the coating, the Al phase appeared in the coating. Therefore, using a small amount of AlN additive was not sufficient to achieve complete nitriding of the Al powder. Increasing the amount of AlN in the feedstock powder enhanced the Al nitriding reaction gradually.

The nitriding reaction was almost complete when using 30 to 40 wt% AlN. The fabricated coating mainly consists of *h*-AlN/*c*-AlN, and it is more than 200 µm thick with a hardness of approximately 1000 Hv. Herein, it was possible to fabricate a thick AlN coating with high hardness by using AlN additive in an RPS process. Thus, using a homogeneous mixture of fine AlN/Al powders is a suitable way of fabricating thick AlN coatings in the RPS process, and the current results open the way towards multiple further studies. The effect of using fine AlN particles on the porosity of the Al/AlN feedstock mixture may play a role in the RPS process, especially during post-deposition nitriding. Moreover, heat treatment (pre-treatment, during coating formation and post-treatment) seems to be effective in the RPS process and will be conducted in future studies.

3. Experimental Procedures

All experiments were carried out with an atmospheric DC plasma spray system (APS: 9MB, Sulzer Metco, Switzerland) using N_2 as the primary gas and H_2 as the secondary gas. Table 1 indicates the typical spraying parameters of an APS system. Pure aluminum powder (Toyo Aluminium K. K., Osaka, Japan) with an average particle size of 30 µm (D10 = 19.77, D50 = 35.08 and D90 = 62.82 µm) was used as feedstock powder. To improve the nitriding of the Al powder, aluminum nitride (Tokuyama Co., Tokyo, Japan) additive with an average particle size of 1.14 µm was used. Figure 14 shows the particle size distribution of the AlN additive. The morphology of the powders is shown in Figure 15. The particles are quasi-spherical in shape.

Table 1. Typical spraying conditions.

First gas: Pressure, KPa Flow rate, l/min	**N_2**: 330.9 100
Second gas: Pressure, KPa Flow rate, l/min	**H_2**: 330.9 5
Arc current: A Arc voltage: V	500 70~80
Spray distance, mm	150
Carrier gas: flow rate, l/min	**N_2**: 1
Substrate material	SS400

Table 2 presents the typical impurities in the powders. The powders were mixed at AlN weight ratios of: 10, 20, 30, 40 and 50 wt%. First, lightly mixed powder (using mortar and pestle for 20 to 25 min, then the mixture was screened with a 212-µm mesh) was sprayed. Second, powder wet-mixed by a planetary mill (Fritsch Gmbt Laborgeratebau, Germany) in ethanol was used. The milling parameters are shown in Table 3. After milling, the obtained slurry was dried in an oven at 70 °C for 24 h. The mixture of dried powders was screened with a 212-µm mesh. To confirm the effects of using AlN additive on phase composition, molybdenum (Mo) powder with an average particle size approximately 63 µm was used instead of Al powder in the feedstock mixture. The feedstock powders were supplied by a PL-10NS-Technoserve (Toyohashi, Japan) powder feeder using N_2 carrier gas at a flow rate of 1 l/min. The particles were injected into the plasma jet created by the passage of N_2/H_2 gases through an electric arc under high-current conditions. Blasted 50 × 50 × 5 mm soft steel (SS400) plates were prepared as the substrate.

Figure 14. Particle size distribution profile of the AlN powder.

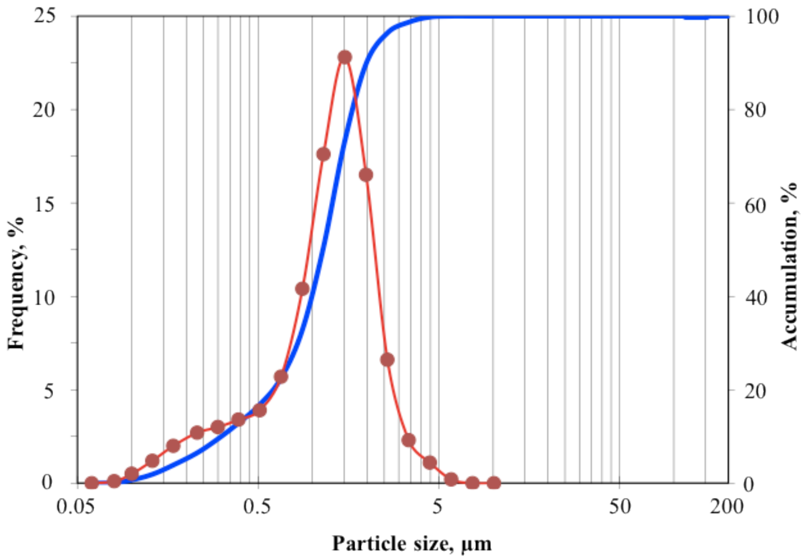
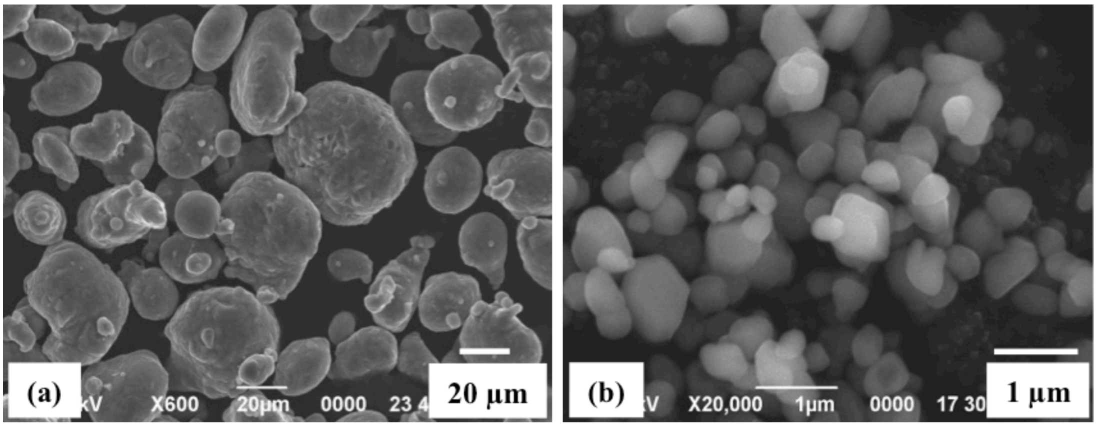


Figure 15. Morphology of **(a)** Al and **(b)** AlN powders.



The presence of AlN phase in the deposited coatings was verified by X-ray diffraction analysis (XRD: RINT-2500, Rigaku, Tokyo, Japan) with CuKα radiation. A scanning electron microscope (SEM: JSM-6390, JEOL, Tokyo, Japan) was used to observe the morphology and cross-section of the powders and the cross-section of the fabricated coatings. The hardness of the coatings was examined with a micro Vickers hardness tester (HMV-1, Shimadzu, Kyoto, Japan).

Table 2. Impurities in the aluminum and aluminum nitride powders.

Aluminum powder				**Aluminum nitride powder**				
Fe, mass%	**Ti**, mass%	**Si**, mass%	**Ni**, mass%	**O**, wt %	**C**, ppm	**Ca**, ppm	**Si**, ppm	**Fe**, ppm
0.243	0.153	0.053	0.004	0.88	210	230	43	12

Table 3. Mixing parameters in the planetary mill.

Powder		**Milling conditions**				**Ball**	**Solvent**
Al, wt%	AlN, wt%	Rotational Speed	Time, min	Repeat	Pause, min		
90~50	10~50	150	10	1	1	Al_2O_3	Ethanol

4. Conclusions

Aluminum nitride (AlN) coatings with high hardness and reasonable thickness were fabricated through reactive plasma spraying of Al/AlN feedstock mixtures. The addition of AlN played an important role in this process, and the results of this study can be summarized as follows:

1. Simple mixing is not suitable for preparing Al/AlN mixtures for reactive plasma spray processes. The AlN only weakly deposits when using simply mixed 30 wt% Al/AlN powders, and it has no significant effect on the nitriding of the Al powder.
2. Wet mixing can be used to prepare a homogenously mixed, agglomerated and dispersed Al/AlN mixture suitable for reactive plasma spraying.
3. The nitride content increased gradually with increasing AlN content in the feedstock powder. A high-nitride content coating more than 200 μm thick and with a hardness of approximately 1000 Hv was successfully fabricated by using 30~40 wt% addition of AlN powder. The fabricated coating mainly consists of *h*-AlN and *c*-AlN (rock-salt and zinc-blend structures).
4. The addition of AlN promoted the formation of the AlN phase in the reactive plasma spray process by preventing the coagulation and coalescence of the Al particles on the substrate. This promotes continuous nitriding through N_2 plasma irradiation (post-deposition nitriding). Furthermore, using AlN in the feedstock powder increased the nitride content in the coating.
5. The sprayed coatings contain cubic-AlN with zinc-blend structures, which was not used as the feedstock and was not formed during the nitriding of the Al. The formation of both the *c*-AlN zinc-blend phase and the cubic sphalerite ALON is attributed to transformation from the hexagonal AlN feedstock powder.
6. AlN content of more than 40 wt% in the mixed powder is not suitable for supplying the mixture to the plasma stream.

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