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Influence of NH_4Cl Powder Addition for Fabrication of Aluminum Nitride Coating in Reactive Atmospheric Plasma Spray Process

Mohammed Shahien, Motohiro Yamada, Toshiaki Yasui, and Masahiro Fukumoto

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Reactive plasma spray is the key to fabricating aluminum nitride (AlN) thermally sprayed coatings. It was possible to fabricate AlN/Al composite coatings using atmospheric plasma spray process through plasma nitriding of Al powders (Al 30 μm). The nitriding reaction and the AlN content could be improved by controlling the spray distance and the feedstock powder particle size. Increasing the spray distance and/or using smaller particle size of Al powders improved the in-flight nitriding reaction. However, it was difficult to fabricate thick and dense AlN coatings with an increase in the spray distance and/or when using fine particles. Thus, the coatings thickness was suppressed because of the complete nitriding of some particles (formation of AlN particles) during flight, which prevents the particle deposition. Furthermore, the excessive vaporization of Al fine particles (due to increased particle temperature) decreased the deposition efficiency. To fabricate thick AlN coatings in the reactive plasma spray process, improving the nitriding reaction of the large Al particles at short spray distance is required to decrease the vaporization of Al particles during flight. This study investigated the influence of adding ammonium chloride (NH_4Cl) powders on the nitriding process of large Al powders and on the microstructure of the fabricated coatings. It was possible to fabricate thick AlN coatings at 100 mm spray distance with small addition of NH_4Cl powders to the Al feedstock powders (30 μm). Addition of NH_4Cl to the starting Al powders promoted the formation of AlN through changing the reaction path to vapor-phase nitridation chlorination-nitridation sequences as confirmed by the thermodynamic analysis of possible intermediate reactions. This changes the nitriding reaction to a mild way, so it is more controlled with no explosive mode and with relatively low heating rates. Thus, NH_4Cl acts as a catalyst, nitrogen source, and diluent agent. Furthermore, the evolved gases from the sublimation or decomposition of NH_4Cl can prevent the Al particles coalescing after melting.

Keywords aluminum nitride, ammonium chloride, reaction pathway, reactive plasma spray

1. Introduction

Among nonoxide ceramics, aluminum nitride (AlN) has received a great deal of interest in recent years because of its outstanding properties such as high thermal conductivity (up to 320 W/m K for pure single crystal) and high corrosion/oxidation resistance (Ref 1). Moreover, AlN has high hardness (HV 1400), physical/chemical stability, low thermal expansion coefficient (similar to Si), and high electrical resistivity (Ref 1-3). The combination of these properties makes AlN a key candidate for a diverse range of applications such as: heat sinks, electronic substrates, semiconductor packages, crucibles and vessels for handling corrosive chemicals and molten metals, parts of semiconductor equipment, and reaction chambers for etching (Ref 1). It is possible to improve a lot of characteristics due to formation of AlN ceramic coatings onto the material surface. Usually, AlN ceramic films are produced by chemical vapor deposition (CVD) or physical vapor deposition (PVD) processes. While these processes enable fabrication of thin and pure nitride ceramic films, it is difficult to produce thick coatings (more than 100 μm) because of the relatively low deposition rates (Ref 4). Nitride ceramic thin films are useful for a wide variety of electrical applications (Ref 5). However, it is difficult to apply these thin films for structural parts and power devices that require thick coatings. Among the coating processes, thermal spray has

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Mohammed Shahien, Motohiro Yamada, Toshiaki Yasui, and **Masahiro Fukumoto**, Toyohashi University of Technology, 1-1, Tempaku-cho, Toyohashi 441-8580, Japan. Contact e-mail: mo.shahien@yahoo.com.

been widely used to produce thick coatings. Furthermore, the fabrication of thermal sprayed AlN coatings will enable cost-effective solutions for a number of applications (Ref 6). However, deposition of the AlN particles in the thermal spray process has been impossible because of the particle decomposition under high temperature without a stable melting phase. In order to fabricate thermal sprayed AlN coatings, some methods were developed: spraying of AlN and Al_2O_3 powders by detonation spray (Ref 6) or low-pressure plasma spray (LPPS) (Ref 7). Fabrication of AlN coatings through the carbon reduction of Al_2O_3 by plasma spraying was also investigated (Ref 8, 9). However, the coatings fabricated by those studies included a relatively small amount of AlN phase. Consequently, the establishment of a thermal spraying technology to fabricate AlN coating is very much required.

In our previous studies (Ref 10-13), it was possible to fabricate thick cubic-AlN/Al composite coatings by atmospheric reactive plasma spraying. The nitride content in the fabricated coatings was enhanced through increasing the spray distance gradually, thus increasing the reaction time between the Al particles and the surrounding N_2 plasma. However, it was difficult to fabricate dense and thick coatings with high AlN content because of the decrease in particle temperature and the complete reaction of some particles during flight, which suppressed the coating thickness (Ref 11). On the other hand, the nitriding ratio was also improved with decreasing the particle size of the feedstock powder, thus improving the nitriding reaction during flight (Ref 12, 13). However, with decreasing the particle size of the feedstock powders the coating thickness was suppressed because of the loss of the powders during the injection, increase in the in-flight particle temperature (which leads to excessive vaporization of Al particles), and completion of the nitriding reaction of some fine Al particles during flight. Therefore, enhancement of the nitriding reaction of reactive plasma sprayed Al particles with larger particle size at shorter spray distance is essential in order to fabricate thick AlN coatings.

It is well known that the aggregation of Al particles is the main problem during fabrication of AlN powders through the direct nitriding of Al powders because of the low melting point of Al (660 °C) (Ref 14, 15). Moreover, a coherent nitride skin is usually formed on the surface of Al particles (Ref 15, 16). Both phenomena prevent continuous nitrogen access and the realization of complete nitridation. In the reactive plasma spray process, the accelerated molten or semimolten Al particles collide with the substrate. These particles easily coagulate and aggregate together, which prevents the nitrogen access to some of the particles. Some recent developments on the direct nitridation method have been investigated to promote nitridation conversion such as nitridation of Al salts (e.g., Al_2S_3) to decrease the nitriding commencement temperature (Ref 17). Using mixtures of nitrogen and ammonia gases instead of pure nitrogen gas (Ref 14), or incorporating some additives (e.g., Mg, Ref 18, 19, Li-salts, Ref 20, 21). Some other reports prevented the formation of the agglomerates through using a dispersion agent such as AlN or carbon black (Ref 22), and adding ammonium chloride (NH_4Cl) additives (Ref 15, 16) to the starting Al powders to promote the formation of AlN powders.

In this study, the availability of using NH_4Cl additives to improve the nitriding reaction of Al powders in the reactive plasma spray process and its effect on the coatings structure were investigated. The influence of the mixing ratio of NH_4Cl and Al powders for the reactive plasma spray process was optimized in this study.

2. Experimental Procedure

Pure aluminum powder (Toyo Aluminium K. K., Osaka, Japan) with average particles size of 30 μm was used as feedstock powder. The morphology of the aluminum powder is shown in Fig. 1(a). The particles are quasi-spherical in shape. Table 1 presents the typical impurities

Table 1 Content of impurities in aluminum powder

Element, mass%			
Fe	**Ti**	**Si**	**Ni**
0.243	0.153	0.053	0.004

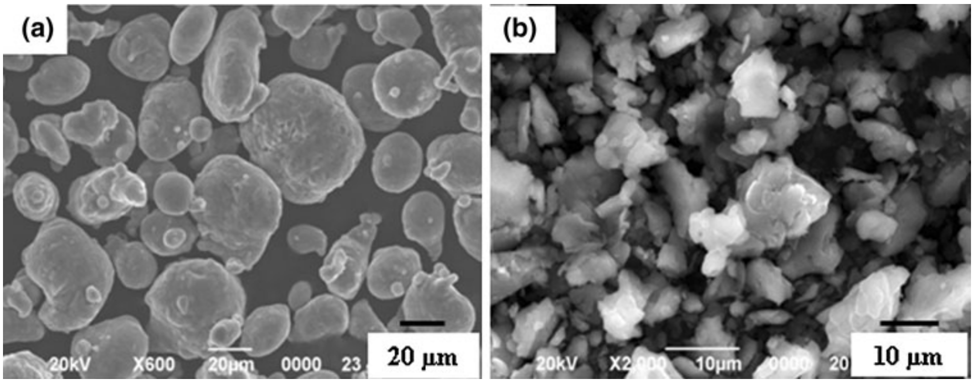

Fig. 1 Morphology of (a) Al powders with average particle size 30 μm and (b) NH_4Cl powders

Table 2 Typical spray conditions

First gas	N_2
Pressure, kPa	330.9
Flow rate, L/min	100
Second gas	H_2
Pressure, kPa	344.7
Flow rate, L/min	5
Carrier gas	N_2
Flow rate, L/min	2
Substrate materials	SS400
Spray distance, mm	100

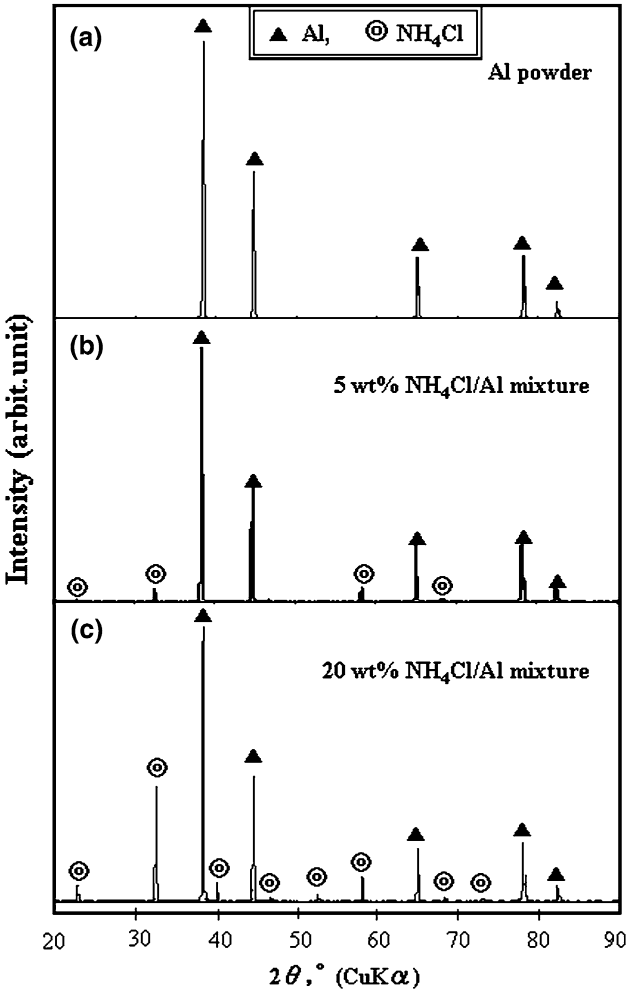

Fig. 2 XRD spectra of (a) Al powders, (b) 5 wt.% NH_4Cl/Al, and (c) 20 wt.% NH_4Cl/Al mixtures

in the aluminum powder. The morphology of NH_4Cl powder (Kishida Kagaku Co., Osaka, Japan) is shown in Fig. 1(b). The powders were mixed in different weight ratios of NH_4Cl: 2.5, 5, 10, 20, 30, 40, 50, and 60 wt.%. The powders were lightly mixed using mortar and pestle for 15-20 min. Blasted 50 × 50 × 5 mm soft steel (SS400) plates were prepared as substrate.

All experiments were carried out by an atmospheric plasma spray system (APS; 9 MB, Sulzer Metco) using primary gas of N_2 and secondary gas of H_2. The typical spraying parameters are shown in Table 2. The feedstock powders were supplied to the plasma stream using N_2 as carrier gas. The substrate was kept 100 mm from the APS gun (spray distance). The phase analysis of the raw materials and the plasma sprayed coatings were verified by x-ray diffraction (XRD; RINT-2500, Rigaku, Tokyo, Japan) using Cu Kα radiation. The powder morphologies and the cross-section microstructure of the coatings were observed by scanning electron microscopy (SEM; JSM-6390, JEOL, Tokyo, Japan). Elemental analysis of the mixed powder and plasma sprayed coatings was carried out by energy-dispersive x-ray (EDX; JSM-6300, JEOL, Tokyo, Japan).

3. Results and Discussion

3.1 NH_4Cl/Al Feedstock Characterization

Figure 2 shows the XRD spectra of Al powder and NH_4Cl/Al mixed powders at different weight ratios of NH_4Cl: 5 and 20 wt.%. The powders consist of Al and NH_4Cl without any impurities or oxides. Figure 3(a) shows the morphology of 50 wt.% NH_4Cl/Al mixed powder. The EDX images of Al and Cl are shown in Fig. 3(b) and (c), respectively. It is clear that the powders were homogenously mixed and agglomerated, which enables in-flight interaction between the powders.

3.2 Spraying of NH_4Cl/Al Mixed Powder

XRD spectra of the coatings fabricated using only Al powder and NH_4Cl/Al mixed powders at different weight ratios of NH_4Cl (2.5 and 5 wt.%) are shown in Fig. 4. The diffraction lines are assigned to a cubic AlN structure (JCPDS card No. 046-1200). It is clear that the fabricated coatings mainly consist of *c*-AlN phase with an oxide and an oxynitride phases. However, when using Al as feedstock powder the coatings still contains a residual Al phase (Fig. 4a). After using NH_4Cl/Al mixed powders, the residual Al and NH_4Cl peaks were not detected (Fig. 4b, c). This indicates that the addition of NH_4Cl to Al feedstock powder could enhance the nitriding reaction and the fabricated coatings would consist of mainly *c*-AlN phase. Moreover, some hexagonal AlN phase appeared in the fabricated coating with an increase in the NH_4Cl content in the mixed powders.

The NH_4Cl additives promoted Al nitriding through changing the reaction pathway, which can be explained. As is well-known in the direct nitriding of Al powders, the molten or semimolten particles react with the surrounding N_2 gas species through a liquid-gas mechanism according to (Ref 16):

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

The nitridation is insignificant below the melting point of Al, but noticeably commences after the melting of Al particles. As Rosenband and Gany explain, the Al particle surface is usually coated by an initial protective oxide film (Ref 15), which prevents good contact with nitrogen gas

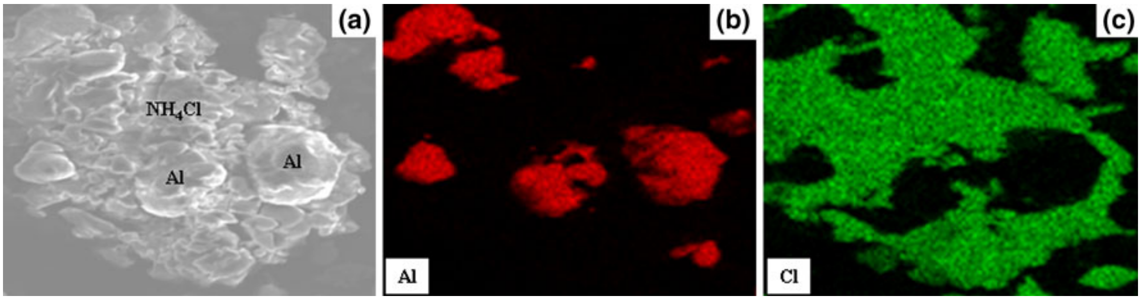

Fig. 3 (a) SEM micrograph of the mixed 50 wt.% NH_4Cl/Al powders. (b) EDX image of Al. (c) EDX image of Cl

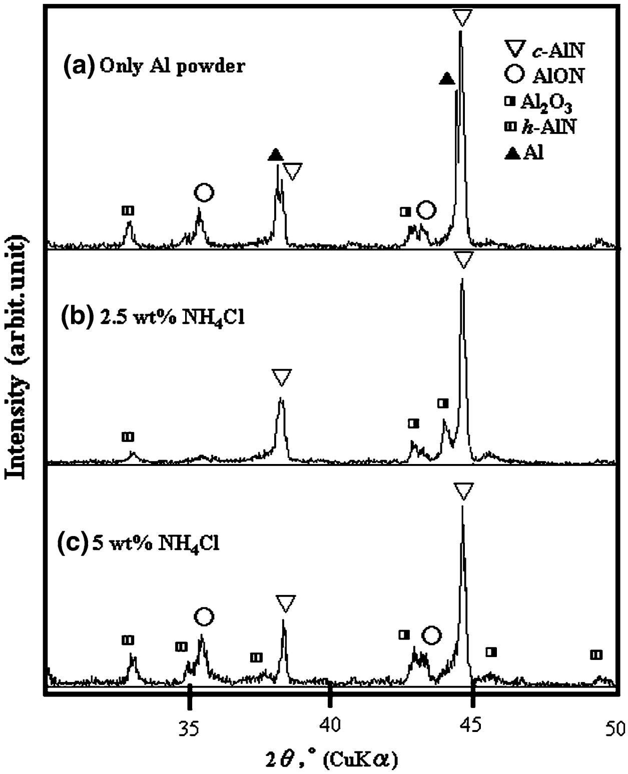

Fig. 4 XRD spectra of the fabricated coatings at spray distance 100 mm: (a) using only Al powder, and after using NH_4Cl additives: (b) 2.5 wt.% and (c) 5 wt.%

and inhibits the nitridation. When a metal melts, the initial protective oxide film is broken as a result of a tensile stress of increased volume. Nitrogen reacts intensely with liquid metallic particles, and the nitriding reaction occurs via three steps as clarified in more detail in our previous studies (Ref 10, 11): nitridation at the surface of the particles with the formation of a crystalline AlN shell, breakaway or flow out 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), the Al particles melted, followed by coalescing to a ball-like form due to the surface tension. The nitridation occurs at the surfaces of these molten Al particles, forming nitride layers or shells surrounding the molten Al. Without NH_4Cl additives, once the reaction starts, the temperature increases rapidly; the direct nitridation of metallic Al is a typical exothermic reaction, as shown in Eq 1 (the heat evolved sustains the reaction so that no extra energy is required except the small amount used for initiating the reaction). However, with adding NH_4Cl powders to the starting Al powders, NH_4Cl sublimates and dissociate into HCl and NH_3 vapor according to:

$$NH_4Cl_{(s,g)} \rightarrow HCl_{(g)} + NH_{3(g)} \qquad \text{(Eq 2)}$$

The evolved gases from the sublimation or decomposition of NH_4Cl can prevent the Al particles coalescing after melting. Furthermore, the sublimation and dissociation of NH_4Cl are endothermic reaction and produce several gaseous species. These reactions absorb sufficient heat from the sample and distribute the direct nitridation of Al particles with N_2 gas, which decreases the reaction temperature. This will change the nitriding reaction to a mild one with no explosive mode and with relatively low heating rates (Ref 15). These various gaseous species ($HCl_{(g)}$, $NH_{3(g)}$, and $N_{(g)}$) diffuse through the pores and the cracks into the molten particles. The nitridation proceeds via spontaneous vapor-phase chlorination-nitridation sequences similar to the reported data (Ref 16). Thus, the gaseous HCl is very active and spontaneously reacts with molten Al to produce $AlCl_3$ vapors, which are nitrided by a gas-gas reaction (as shown in spontaneous reactions):

$$Al_{(l)} + 3HCl_{(g)} \rightarrow AlCl_{3(g)} + 3/2H_{2(g)} \qquad \text{(Eq 3)}$$

$$AlCl_{3(g)} + 1/2N_{2(g)} + 3/2H_{2(g)} \rightarrow AlN_{(s)} + 3HCl_{(g)} \qquad \text{(Eq 4)}$$

Therefore, addition of NH_4Cl to the starting Al powders promoted the formation of AlN and reached complete nitridation in the reactive plasma spray process. The NH_4Cl plays a critical role because it produces HCl gas, which can be considered a key intermediate product, acting as a catalyst. Thus, HCl promotes the vaporization of the molten aluminum cores into volatile aluminum chloride ($AlCl_3$) species and facilitates the nitridation progress through a sequence of spontaneous chlorination and nitridation intermediate reactions. Therefore, addition of NH_4Cl to the starting Al powders promoted the formation of AlN coatings in reactive plasma spray process by offering a different reaction pathway than

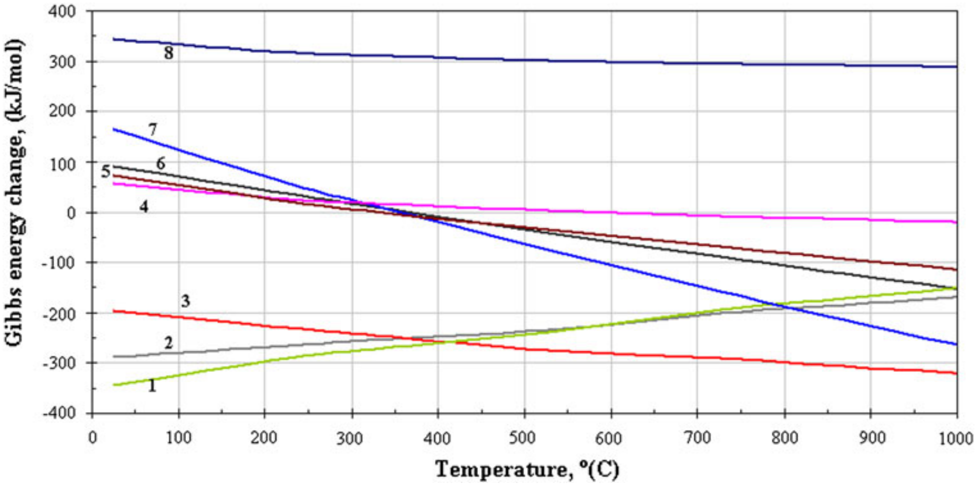

Fig. 5 Gibbs energy changes of possible intermediate reactions: (1) $Al + 3HCl = AlCl_3 + 3/2H_2$. (2) $Al + 1/2N_2 = AlN$. (3) $Al + NH_4Cl + 1/2N_2 = AlN + NH_3 + HCl$. (4) $AlCl_3 + 1/2N_2 + 3/2H_2 = AlN + 3HCl$. (5) $AlCl_3 + NH_3 = AlN + 3HCl$. (6) $NH_4Cl = NH_3 + HCl$. (7) $AlCl_3 + NH_4Cl = AlN + 4HCl$. (8) $AlCl_3 + 1/2N_2 = AlN + 3/2Cl_2$

the direct nitridation mechanism. This different nitridation proceeds via spontaneous chlorination-nitridation sequences (vapor-phase nitridation). The nitriding reaction can be explained: After supplying the powders to the plasma jet, a thin AlN shell is formed on the Al particle surface. Then, various gaseous species such as $HCl_{(g)}$, $NH_{3(g)}$, and $N_{2(g)}$ slowly infiltrate through the shell into the molten Al core. The molten Al core is spontaneously halogenated to $AlCl_{3(g)}$ and then nitrided to AlN through the gaseous phase as shown in Eq 4.

The values of Gibbs energy change of the encountered intermediate reactions, calculated from JANAF thermochemical data (Ref 23) are given in Fig. 5. The thermodynamic calculations confirmed the postulated growth mechanism through intermediate reactions and species, which suggests that the nitridation of Al particles occurred through a spontaneous vapor-phase chlorination-nitridation sequences.

Regarding the NH_3 gases evolved from the NH_4Cl decomposition, it may promote the nitriding reaction in two possible ways. It may react directly with the $AlCl_3$ gases under such high-temperature conditions as reported by Wang et al. (Ref 24), in an $AlCl_3$-NH_3-N_2 system, according to:

$$AlCl_{3(g)} + NH_{3(g)} \rightarrow AlN_{(s)} + 3HCl_{(g)} \quad \text{(Eq 5)}$$

Moreover, as reported by Qiu and Gao (Ref 14), the NH_3 also may decompose and dissociate at the surface of Al particles:

$$NH_{3(g)} \rightarrow N_{(g)} + 3H_{(g)} \quad \text{(Eq 6)}$$

Followed by the reaction between the reactive nitrogen radicals and the liquid Al by diffusion into Al particles:

$$Al_{(l)} + N_{(g)} \rightarrow AlN_{(s)} \quad \text{(Eq 7)}$$

The reactive H radicals promoted the decomposition of NH_3:

$$NH_{3(g)} + 3H_{(g)} \rightarrow N_{(s)} + 3HCl_{(g)} \quad \text{(Eq 8)}$$

In which the complete reaction can be expressed as:

$$Al_{(l)} + 2NH_{3(g)} \rightarrow AlN_{(s)} + 1/2\ N_{2(g)} + 3H_{2(g)} \quad \text{(Eq 9)}$$

However, the decomposition of the ammonia to produce hydrogen may change the heat transfer behavior significantly, and further study will be conducted.

Figure 6(a) and (b) show the cross-section microstructure of the fabricated coatings with using 2.5 and 5 wt.% NH_4Cl additions. It indicates that the coating was about 350 and 300 μm thick at 2.5 and 5 wt.% NH_4Cl additions, respectively, with homogeneous dense structure. The fabricated coating does not contain any NH_4Cl feedstock material as confirmed by the EDX results of a high-magnification part as shown in Fig. 6(d). However, the fabricated coating contains some acicular phases that were confirmed to be of iron (Fe) from the substrate surface as shown in Fig. 6(f). Therefore, it was possible to fabricate thick AlN based coating through the reactive plasma nitriding of Al particles and using NH_4Cl additives.

Hereby, addition of NH_4Cl powders to Al powders in the reactive atmospheric plasma process is promising method to avoid coagulation and improve the nitriding reaction of the Al particles at short spray distance to fabricate thick AlN coatings. Thus, NH_4Cl acts as a catalyst, nitrogen source, and diluent agent. To optimize the NH_4Cl/Al mixing ratio for reactive plasma spray process, the NH_4Cl content was increased up to 60 wt.%.

Figure 7 shows the XRD spectra of the fabricated coatings using NH_4Cl additives from 10 to 40 wt.%. It is clear that all of the fabricated coatings mainly consist of cubic AlN phase with some hexagonal phase and some oxides. The formation of the hexagonal AlN phase in the fabricated coating with increasing NH_4Cl content in the feedstock mixture is attributed to easy nitriding of some particles through vapor-phase and complete crystal

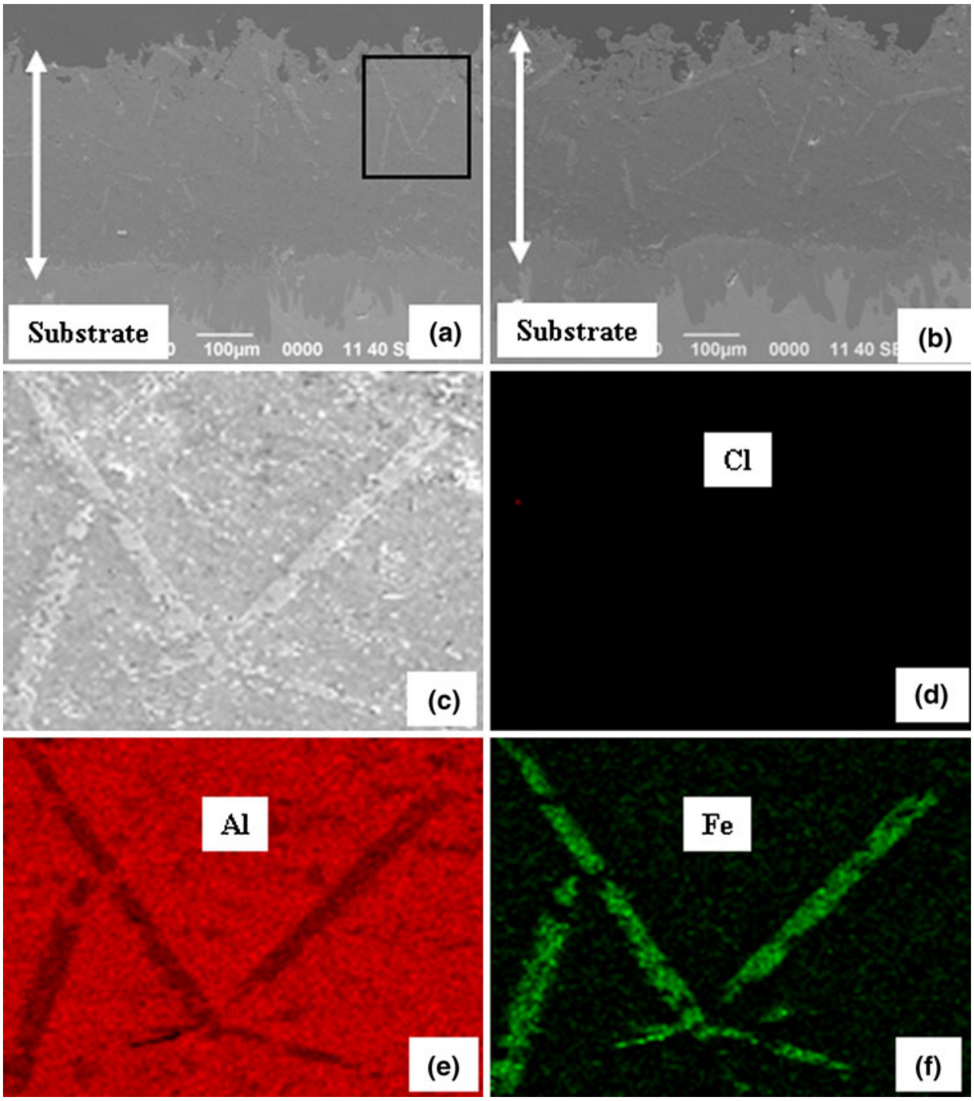

Fig. 6 SEM cross section of the fabricated coating at spray distance of 100 mm after using NH_4Cl additives: (a) 2.5 wt.% and (b) 5 wt.%, (c) high magnification of the squared part in (a), (d) EDX image of Cl, (e) EDX image of Al, and (f) EDX image of Fe

growth from cubic AlN phase to the hexagonal phase. However, with increasing the NH_4Cl ratio to 10, 20, 30, and 40 wt.% the coating thickness decreased as shown in Fig. 8. Suppressing the coating thickness with increasing the NH_4Cl content is attributed to the complete nitriding of some particles (formation of AlN) during flight that prevented its deposition and decreasing the coatings thickness. Also the coatings had porous structures, which attributed to increasing the amount of evolved gases from the sublimation or decomposition of NH_4Cl particles with increasing its ratio.

Furthermore, with increasing the NH_4Cl content to 50 wt.% and more, not all Al particles transformed to AlN as shown in Fig. 9. This reduction of the conversion extent of Al to AlN at higher content of NH_4Cl is attributed to the retardation of nitrogen supply to the Al surface by the gaseous products, resulting from the sublimation and dissociation of NH_4Cl as reported in Ref 15. It became clear that control of the NH_4Cl content is very important to control the coating thickness and microstructure.

Hereby, *c*-AlN based coatings were fabricated by atmospheric reactive plasma spray process through the plasma nitriding of Al/NH_4Cl mixed powders in N_2/H_2 plasma. The NH_4Cl powder plays an important role in controlling the nitriding process and coating structure. Addition of NH_4Cl powders to the Al feedstock is promising method to accelerate the nitriding process and fabricate AlN thick coatings.

4. Conclusion

Aluminum nitride coating was fabricated by the reactive atmospheric plasma spraying of Al/NH_4Cl mixed powders into N_2/H_2 plasma. The NH_4Cl powder plays

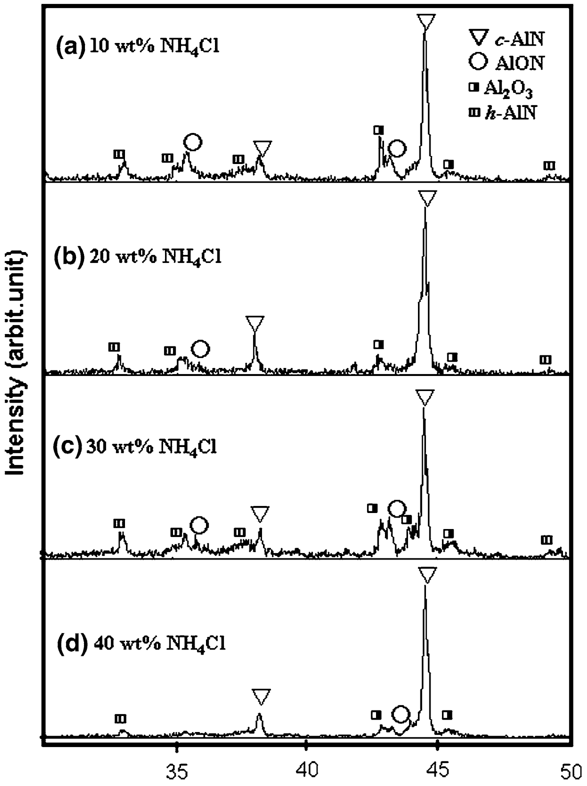

Fig. 7 XRD spectra of the fabricated coatings at spray distance 100 mm after using NH_4Cl additives: (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%, and (d) 40 wt.%

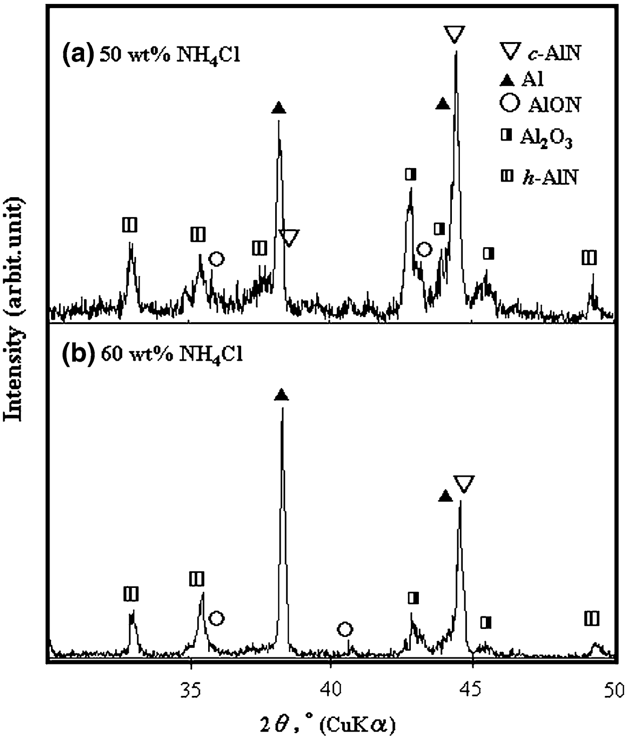

Fig. 9 XRD spectra of the fabricated coatings at spray distance 100 mm after using NH_4Cl additives: (a) 50 wt.% and (b) 60 wt.%

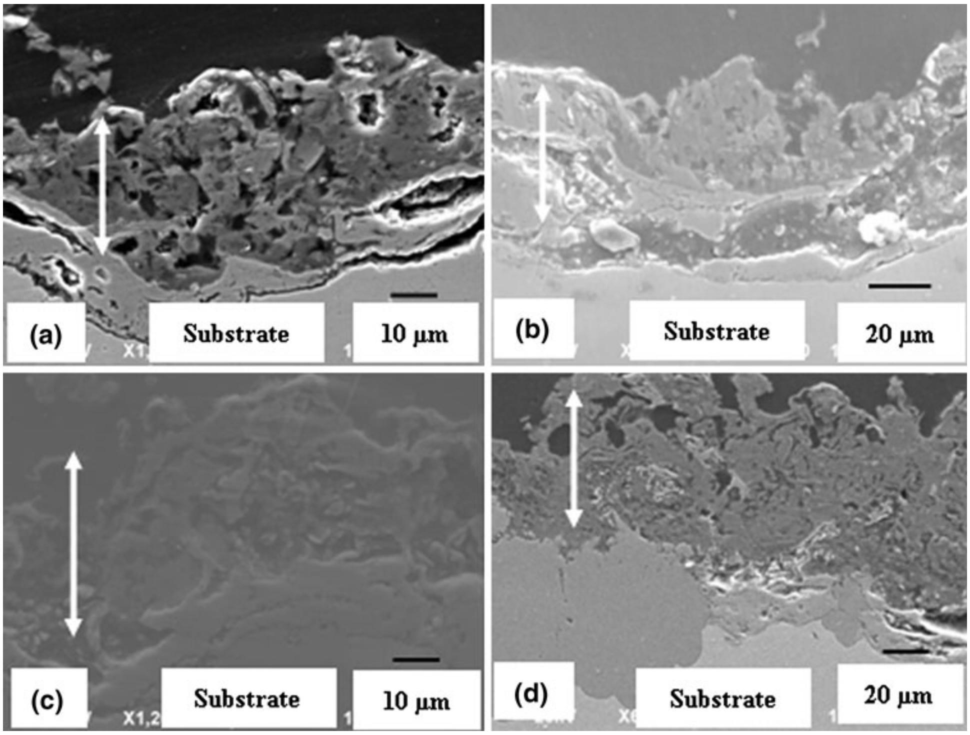

Fig. 8 SEM cross section of the fabricated coatings at spray distance 100 mm after using NH_4Cl additives: (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%, and (d) 40 wt.%

an important role in the nitriding process and the coating microstructure. The results of this study can be summarized:

- Addition of ammonium chloride to the aluminum powder prevented Al aggregation and noticeably enhanced the nitriding reaction.
- Thick and dense AlN coating (more than 300 μm thickness) was successfully fabricated with a small (2.5-5 wt.%) addition of NH_4Cl powders.
- Addition of NH_4Cl promoted the formation of AlN phase in the reactive plasma spray process through changing the reaction pathway of the Al powders from a direct nitridation mechanism (liquid-gas nitridation) to nitridation via a spontaneous chlorination-nitridation sequences (vapor-phase nitridation).
- Increasing the NH_4Cl content in the feedstock powders up to 40 wt.% is not suitable to fabricate dense and thick AlN coatings.
- More than 40 wt.% of NH_4Cl content in the mixed powders prevents the completing nitriding of all aluminum particles.

Acknowledgments

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