JTTEE5 19:635–641
DOI: 10.1007/s11666-010-9469-0
1059-9630/$19.00 © ASM International

Peer Reviewed

Cubic Aluminum Nitride Coating Through Atmospheric Reactive Plasma Nitriding

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(Submitted July 6, 2009; in revised form September 24, 2009)

Aluminum nitride is a promising material for structural and functional applications. Cubic AlN (*c*-AlN) is expected to have higher thermal conductivity due to their high symmetry; however, its fabrication is difficult. In this study, *c*-AlN was synthesized by atmospheric plasma spray process through the reaction between Al feedstock powder and nitrogen plasma. Al powders were supplied to the plasma stream by Ar carrier gas and reacted with surrounding N_2 plasma, then deposit onto substrate. The obtained coatings were *c*-AlN/Al mixture at 150 mm of spray distance, and the nitride content was improved by increasing the spray distance. The coatings almost consist of *c*-AlN at 300 mm of spray distance. The coatings thickness decreased from 100 to 10 µm with increasing spray distance from 150 to 300 mm. Using carrier gas, N_2 enable to fabricate thick *c*-AlN coating with hardness 1020 Hv.

Keywords atmospheric plasma spray, cubic aluminum nitride, reactive nitriding, spray distance and carrier gas

1. Introduction

Group III wide band gap nitride semiconductors are promising candidate materials for optoelectronic devices and electronic packaging applications. Among these materials, aluminum nitride (AlN) has received considerable attention from researchers. Aluminum nitride possesses an excellent combination of properties: a large band gap of 6.2 eV, high-thermal conductivity (up to 320 W/mK for pure single crystal and 180-220 W/mK for sintered compact) and nontoxicity. Moreover, it has good chemical/physical stability at fairy high-temperature regions, high hardness (Hv 1400), high electrical resistivity (10^{13} Ω cm), low-thermal expansion coefficient (similar to silicon and GaAs) and high resistance of molten metals, wear, and corrosion (Ref 1-5). These made AlN as promising materials in several applications; heat sinks, electronic substrates, semiconductor packages, crucibles and vessels for handling corrosive chemicals and molten metals, parts of semiconductor equipment, reaction vessels of etching. It is well known that AlN has a hexagonal (wurtzite) structure and two kinds of cubic structure (rock salt and zinc-blend). Hexagonal AlN (*h*-AlN) is more common and stable at ambient conditions, and it can be fabricated easily by many methods: as powders (Ref 6-8), sintered compacts (Ref 9-12), and thin films (Ref 13-16).

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Cubic aluminum nitride (*c*-AlN) is a metastable structure, an unexplored material whose properties may be quite different from those of *h*-AlN (Ref 17). Cubic AlN (Rock salt) has higher thermal conductivity, electrical resistivity (10^{16} Ω cm) due to their higher symmetry (Ref 18, 19).

Synthesis of *c*-AlN is more difficult than *h*-AlN because it is metastable phase. There is no way to synthesize *c*-AlN directly from hexagonal phase, either static or shock compression over 14 GPa pressure is required to transform hexagonal phase to cubic phase (Ref 20). Its synthetic methods can be classified into three main types: the carbothermal reduction and nitridation (CRN) reaction of alumina (Ref 19, 21, 22), the solvothermal decomposition of $[Al\ (urea)_3]Cl_3$ (Ref 23), and the reaction of $AlCl_3$ with NaN_3 or Li_3N in organic solvents (Ref 24, 25). Recently *c*-AlN coatings were investigated through transformation of *h*-AlN by aerosol deposition (AD) method (Ref 26, 27).

Fabrication of thermal-sprayed AlN coatings will enable cost-effective solutions for a number of applications (Ref 28). However, it was impossible to fabricate AlN thermal spray coatings directly from AlN powder due to thermal decomposition of AlN during spraying. To fabricate AlN coatings by thermal spray some methods were developed: spraying of AlN and Al_2O_3 powder by detonation spray (Ref 28) or low pressure plasma spray (LPPS) (Ref 29), and fabrication of AlN coatings through carbon reduction of Al_2O_3 by plasma spraying was also investigated (Ref 30-32). However, the coatings fabricated by those studies included a few AlN phase.

Reactive plasma nitriding considered to be ideal solution for fabrication AlN coatings and other nitride ceramics such as Fe_4N and Si_3N_4 as shown in our pervious study (Ref 33-36). In which the raw materials Al, Fe, and Si, respectively, react with the surrounding active species in N_2 plasma such as nitrogen ion or atom in the radio frequency (RF) plasma spraying system which was carried out in vacuum ambient.

In this study, c-AlN coating was fabricated through the reaction between Al powder and N_2/H_2 active plasma in atmospheric plasma spray (APS) system. APS system is atmospheric plasma process, reactive plasma system and it is characterized by its high-deposition rate. Improvement of AlN phase in the fabricated coatings, nitriding reaction of Al powders and enhancing the nitriding reaction were investigated.

2. Experimental Procedure

All experiments were carried out by 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 1. Pure aluminum powder (average particle size of 30 μm) was used as feedstock powder. The morphology of the aluminum particles is shown in Fig. 1, the particles are quasi-spherical in shape. Table 2 presents the typical impurities in aluminum powder. The feedstock powder is supplied to the plasma stream with carrier gas of Ar or N_2. Blasted soft steel (SS400) plates were prepared as substrate. The spray distance was changed from 100 to 300 mm. The residual amount of Al in the fabricated coatings was removed by using HCl solution (Ref 3, 37).

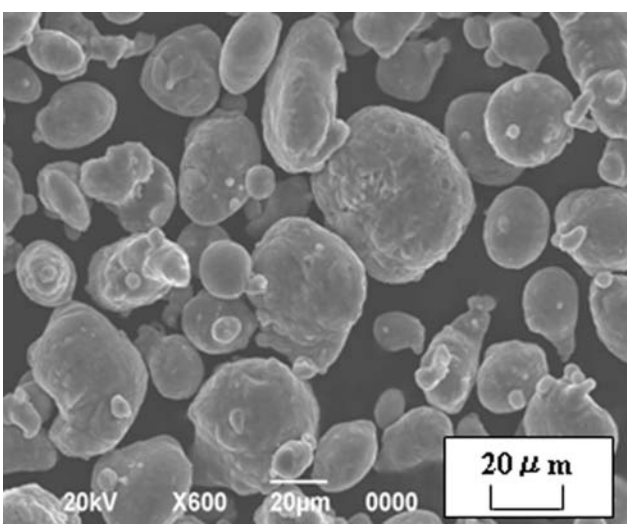

Fig. 1 Morphology of Al powders

Table 1 Typical spray conditions

First gas	N_2
Pressure	330.9 kPa
Flow rate, L/min	100
Second gas	H_2
Pressure	344.7 kPa
Flow rate, L/min	5
Spray distance, mm	100-300
Carrier gas	Ar or N_2
Flow rate, L/min	1
Substrate materials	SS400

The fabricated coatings on blasted SUS 304 substrates were placed in 15 wt.% HCl solutions for 13 h then washed with water and the AlN content in the fabricated coatings was calculated from the weight difference after removing the unreacted Al. Nitriding reaction of Al particles was investigated during flight by particle collection on carbon tape. Nitriding reaction on the substrate was examined by irradiation of N_2 plasma to Al substrate. Substrate temperature was measured on the back surface of the substrate by thermocouple. The existence of AlN in the deposited coating was verified by x-ray diffraction (XRD: RINT-2500, Rigaku) with Cu Kα radiation. Cross section microstructure of the coatings was observed by scanning electron microscope (SEM: JSM-6390, JEOL). The hardness of the coatings was examined by micro-Vickers hardness tester (HMV-1, SHIMADZU).

3. Results and Discussion

3.1 Improvement of Nitride Phase

Figure 2 shows the XRD spectra of the raw material and the fabricated coatings at different spray distance. It indicates that at short spray distance the fabricated coating consists of c-AlN/Al mixture (Fig. 2c). Furthermore, the nitride content in the fabricated coatings enhanced with increasing the spray distance. At spray distance 300 mm, c-AlN-based coating was fabricated as shown in Fig. 2(d). The intensity of the strongest peak is used to identify the formation of c-AlN that the main peak of Al lies around 38° of 2θ value (Fig. 2a) and for c-AlN the main peak lies around 44° of 2θ value (Fig. 2e). Therefore, it is possible to fabricate c-AlN-based coatings in atmospheric conditions by APS method through the reaction between Al feedstock powder and N_2/H_2 plasma. The residual amount of Al in the fabricated coatings was removed by keeping the coatings in 15 wt.% HCl solutions for 13 h and then washing with H_2O. The AlN content was obtained by calculating the weight difference after removing the unreacted Al. The AlN content in the coatings increased gradually from about 50 to 90 wt.% with increasing spray distance from 150 to 300 mm, respectively, as shown in Fig. 3. XRD spectra of the fabricated coatings after removing the residual Al amount at 150 mm spray distance is shown in Fig. 4, it clear that after using 15 wt.% HCl solution for 13 h almost all the residual Al content was remove and only the c-AlN coating remained.

However, the thickness of the fabricated coatings decreased with the spray distance as shown in the cross

Table 2 Content of impurities in Aluminum powder

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

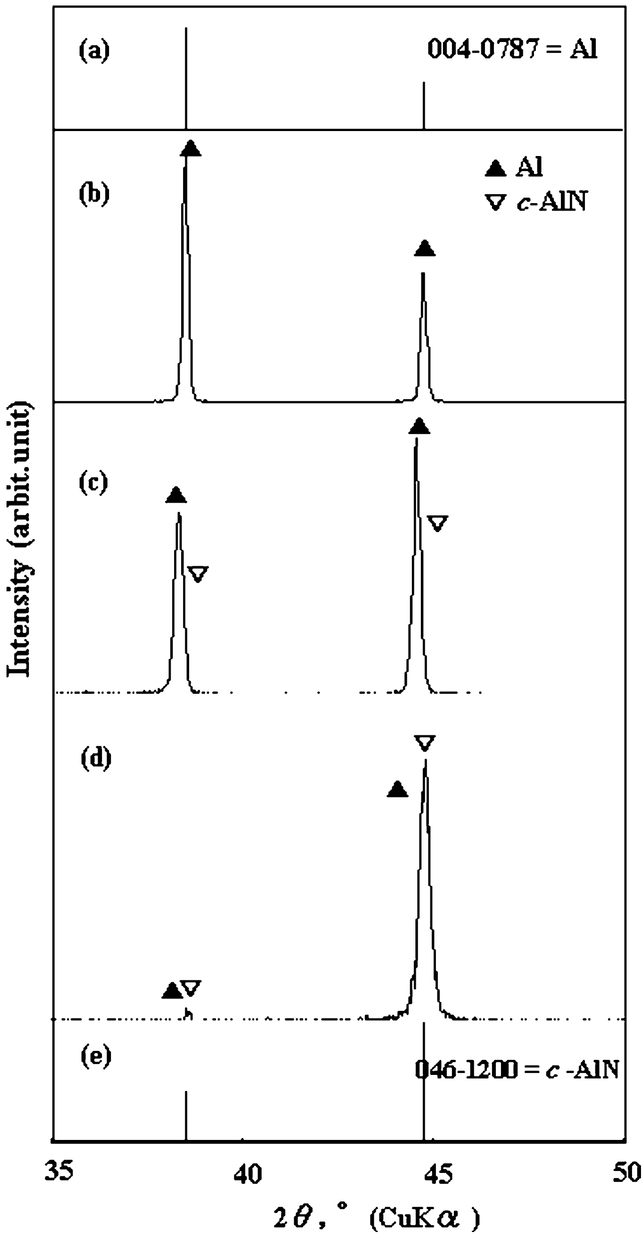

Fig. 2 XRD spectra of (a) standard XRD of Al card no. 004-0787, (b) Al feedstock powder, (c) the fabricated coatings at spray distance 150 mm, (d) the fabricated coatings at spray distance 300 mm, and (e) standard XRD spectra of cubic AlN card no. 046-1200

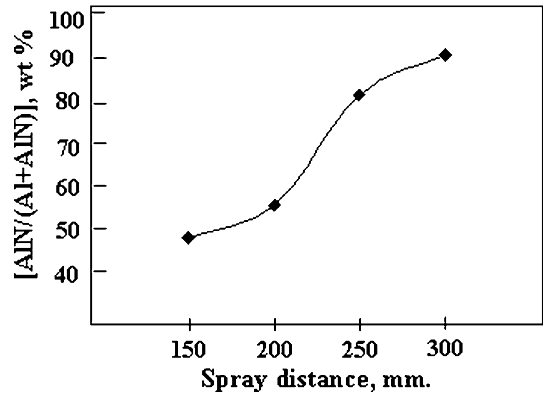

Fig. 3 AlN content in the fabricated coatings at different spray distance

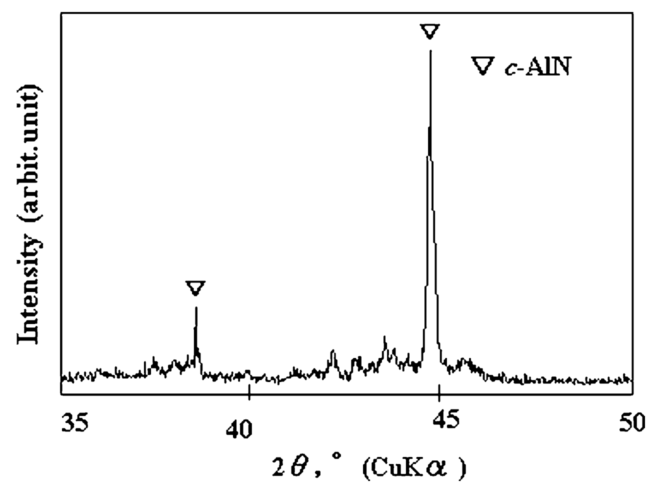

Fig. 4 XRD spectra of the fabricated coatings at 150 mm spray distance after removing the residual Al amount using 15 wt.% HCl solution for 13 h

section microstructures in Fig. 5. The thickness of the fabricated coatings was approximately 100 and 10 μm at spray distance of 150 and 300 mm, respectively. The hardness of the fabricated coating at 150 mm spray distance (*c*-AlN/Al mixture) was about 540 Hv which is much higher than Al, which emphasize the nitriding reaction and formation of AlN phase in the fabricated coating. Therefore, it was possible to fabricate thick *c*-AlN/Al composite coating by APS and with increasing the spray distance the nitride content was enhanced. However, the coating thickness was suppressed.

In our pervious study, reactive plasma nitriding of Al powders in evacuated RF plasma spray system forms *h*-AlN structure. The formation of the meta-stable *c*-AlN structure in the coatings during atmospheric plasma nitriding of Al powder in APS system is directly related to the rapid solidification phenomena in plasma spraying process. As it is well known that in plasma spraying process the powder particles injected into the plasma jet are quickly melt and propelled onto the substrate where they spread upon impact and rapidly solidify (Ref 38-42). Rapid solidification is a relatively recent development in which a two-phase mixture of equilibrium phases in a eutectic alloy could be replaced by an extended solid solution like nonstable phases, a new crystalline phase, or a noncrystalline phase (i.e., metallic glass) simply by quenching with enough rapidity from the liquid state (Ref 43-47). Rapid solidification provide large departures from equilibrium constitution resulting in substantial extensions of solid solubility and formation of new equilibrium crystalline phases and metallic glasses compared

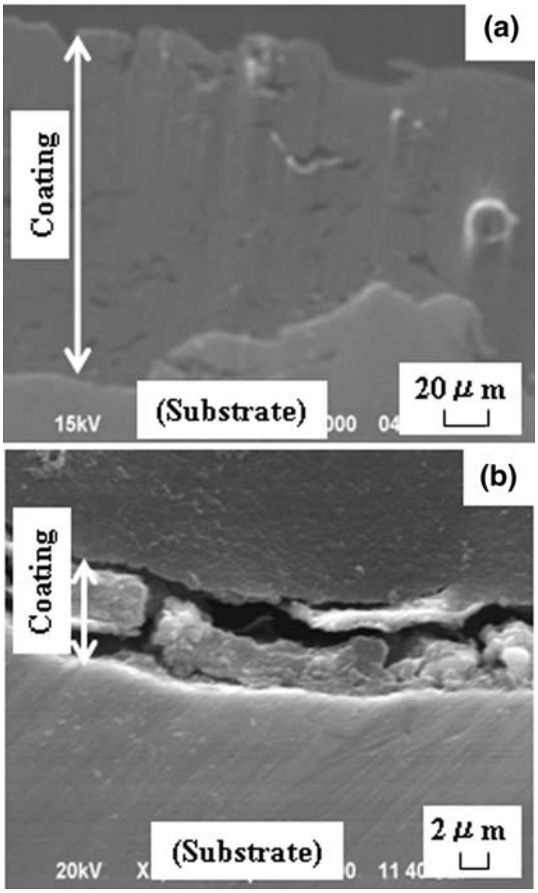

Fig. 5 SEM cross section of the coatings at spray distance (a) 150 and (b) 300 mm

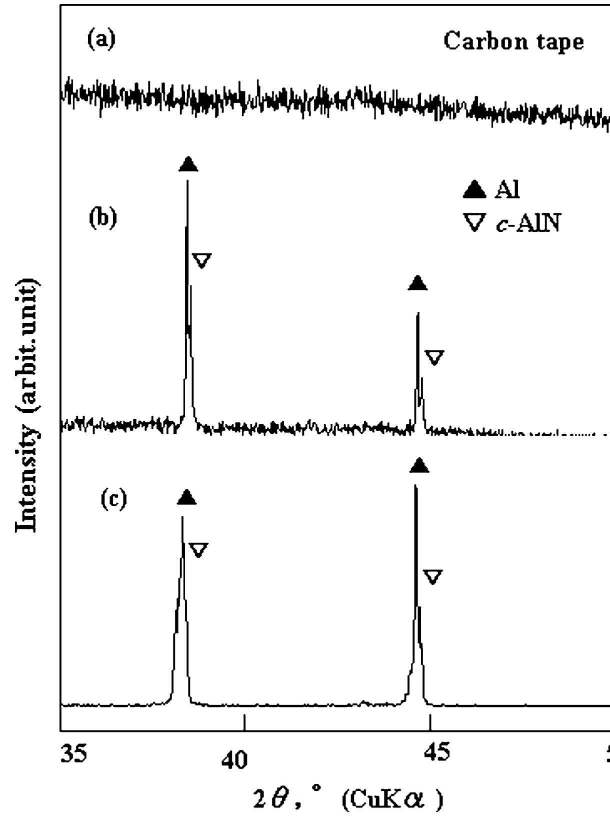

Fig. 6 XRD spectra of (a) carbon tape used for powder collection, (b) collected particles on carbon tape after spraying, and (c) plasma-irradiated Al substrate

with conventional solidification of relatively heavy sections.

Therefore in APS process the reacted sprayed powder particles experience very rapid cooling rates upon impact with the substrate which prevent the crystal growth and formation of the stable *h*-AlN phase. Moreover, the high particle velocity in APS process does not provide enough time for complete crystal growth before impacting on the substrate and rapid cooled.

For complete understanding of APS nitriding system, the nitriding reaction of Al powder was studied.

3.2 Nitriding Reaction of Al Powder

Nitriding reaction of Al powder was investigated during flight and after deposition. During flight, nitridation was investigated by powder collection on carbon tape. It was clear that some of Al particles reacted during flight as shown by XRD spectra of the collected particles after spraying in Fig. 6(b). Figure 7 shows the microstructure of the collected particles in which the egg-shell structure is clear. It was mentioned in the reports of nitriding of Al particles (Ref 33, 34, 48-50) that presence of egg-shell structure is a characteristic feature of formation AlN through the direct nitridation of Al. In which, the nitriding reaction occurs via three steps (Ref 48-50):

- Nitridation at the surface of the particles with the formation of a crystalline nitride shell. Due to the thermal stress of large volume of the molten Al, the Al starts to break the AlN shell to go out. Moreover at this high-temperature conditions, the generation rate of the reaction heat is enough to vaporize the molten Al present inside the shell and this is the beginning of the second step.
- Breakaway of the AlN shell and flow out of molten or vaporized Al core by capillary-like phenomena.
- The diffused Al vapor reacted with the surrounding N_2 through volume nitridation outside the shell with a remaining hole or an empty core.

Therefore, the egg-shell structure which appeared in some of the collected particles emphasizes the nitriding reaction of some Al particles during flight in APS process.

Nitriding reaction after deposition was investigated by irradiation of N_2/H_2 plasma to Al substrate without using powders. XRD spectra showed the formation of *c*-AlN phase on the irradiated Al substrate as shown in Fig. 6(c). It indicates that during APS process some of Al particles reacted after deposition on the substrate surface.

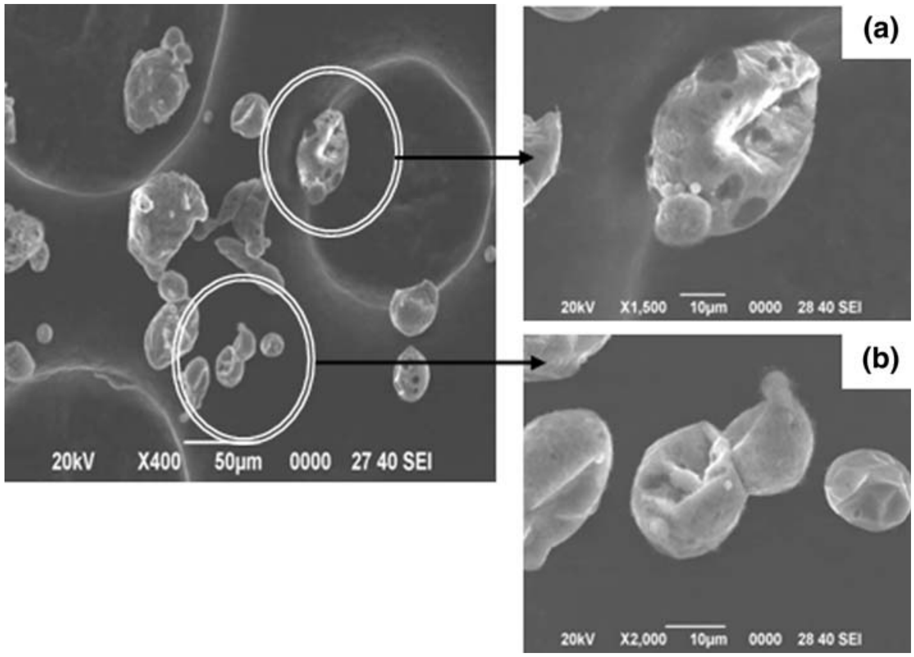

Fig. 7 SEM of the collected particles, (a) and (b) show the AlN egg-shell structure

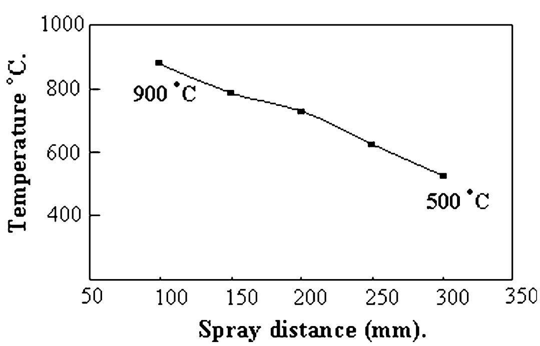

Fig. 8 Substrate temperature back side measurement

To understand the reaction after deposition, the substrate temperature was measured from the back side at different spray distance as shown in Fig. 8. It indicates at short spray distance (100-150 mm) the substrate is directly touched and heated by the plasma jet therefore the temperature is enough to melt or semi-melt aluminum particles to react with N_2 in the plasma. However with increasing the spray distance, the substrate become far from the plasma stream and the jet does not touch or heat it directly, therefore the temperature is not enough for the reaction.

Hereby, nitriding reaction of Al particles in APS occurs during flight and after deposition on the substrate, and controlling the spray distance is the key point to control both nitride content and coating thickness.

– The nitride content increased with the spray distance due to increase the flight time of Al particles in the N_2 plasma, which provides longer time for the particles to start reaction with N_2 plasma during flight and complete its reaction after deposition on the substrate.
– On the other hand, with increasing the spray distance the sprayed particles deviated from the substrate, and the particles temperature decreased which reduced its deposition efficiency and suppressed the coating thickness. It was also considered that the particles which completely reacted during flight could not deposit on the substrate, thus molten or semi-molten particles are required for particles deposition in thermal spray process and AlN particles do not have the molten phase.

Therefore in APS process, some of Al particles started the reaction during flight and others started after deposition on the substrate by N_2 plasma irradiation. Then, the partially reacted Al particles (molten or semi-molten phase) deposited on the substrate will complete the reaction through N_2 plasma irradiation and rapidly cooled and solidify on the substrate to fabricate *c*-AlN structure.

3.3 Enhancing the Nitriding Reaction

By using N_2 carrier gas, it was possible to fabricate films mainly consist of *c*-AlN phase at 100 mm of spray distance, XRD spectrum of the fabricated coating is shown in Fig. 9. The coating consisted of completely *c*-AlN; however, the coating included oxide (Al_2O_3 and Al_5O_6N) phases. It indicates that the N_2 gas as the carrier gas enhanced the nitriding reaction of the sprayed particles during flight in the plasma and the partially reacted Al particles deposited and completed its reaction on the substrate. Also during particles collection, the amount of nitride particles are higher compared to using carrier gas Ar.

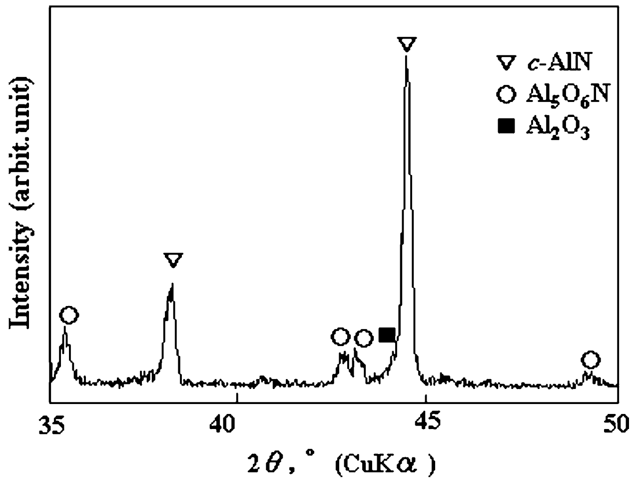

Fig. 9 XRD spectra of the coating at 100 mm using N_2 carrier gas (1 L/min)

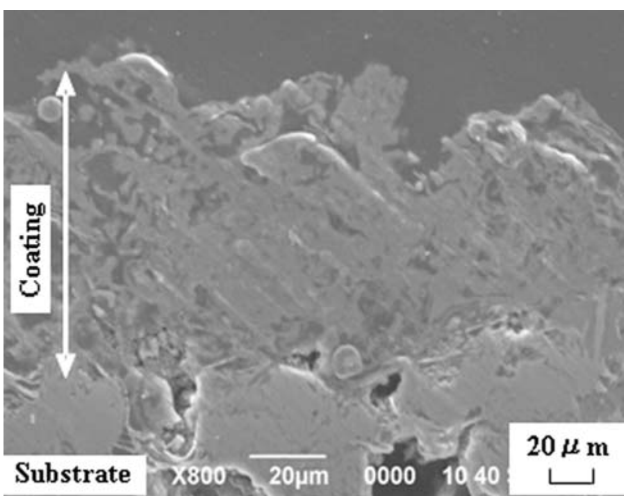

Fig. 10 SEM cross section of the coating fabricated at 100 mm using carrier gas N_2

The thickness of *c*-AlN coating was improved after using N_2 carrier gas, the thickness was about 80 μm at spray distance 100 mm as shown in Fig. 10. The hardness of the fabricated coating was about 1020 Hv, which is similar as the hardness of sintered AlN bulk. It means that the metal Al particles were almost completely transformed into AlN coating. Therefore, it was possible to fabricate thick *c*-AlN coating with high hardness by using N_2 for carrier gas.

4. Conclusion

Cubic AlN was fabricated by APS technique through reaction between Al powder and active N_2/H_2 plasma. The result of this study can be summarized as follow:

– Cubic AlN phase formed due to rapid solidification upon impact with the substrate which prevents the crystal growth and formation of the stable *h*-AlN phase and the high particle velocity in APS system assist to avoid the complete crystal growth before solidifying on the substrate.
– Cubic AlN content improved with increasing the spray distance.
– Nitriding reaction of Al particles during flight enhanced with increase of spray distance.
– Increasing the spray distance decreased the deposition efficiency of sprayed particles and suppressed the coating thickness due to decreasing the particle velocity and completing nitriding reaction during flight.
– Carrier gas species affect to the nitriding reaction of the sprayed particles.
– Thick *c*-AlN based coating with high hardness was successfully fabricated with using N_2 as powder carrier gas.

References

1. H.O. Pierson, *Handbook of Refractory Carbides and Nitrides*, Noyes Publications, NJ, USA, 1996, p 237-239
2. A.W. Wemer, *Carbide, Nitride and Boride Materials Synthesis and Processing*, Chapman & Hall, London, 1997, p 6-68
3. A.W. Weimer, G.A. Cochran, G.A. Eisman, J.P. Henley, B.D. Hook, L.K. Mills, T.A. Guiton, A.K. Knudsen, N.R. Nicholas, J.E. Volmering, and W.G. Moore, Rapid Process for Manufacturing Aluminum Nitride Powder, *J. Am. Ceram. Soc.*, 1994, **77**(3), p 3-18
4. S. Nakamura, The Roles of Structural Imperfections in InGaN-Based Blue Light-Emitting Diodes and Laser Diodes, *Science*, 1998, **281**, p 956-961
5. N. Ichinose and H. Kuwabara, *Nitride Ceramics*, Nikkan-Kogyo-Shinbunsha, Tokyo, 1998 (in Japanese)
6. Y. Qiu and L. Gao, Nitridation Reaction of Aluminum Powder in Flowing Ammonia, *J. Eur. Ceram. Soc*, 2003, **23**, p 2015-2022
7. T. Sakurai, O. Yamada, and Y. Miyamoto, Combustion Synthesis of Fine AlN Powder and Its Reaction Control, *Mater. Sci. Eng. A*, 2006, **415**, p 40-44
8. S.-L. Chung, W.-L. Yu, and C.-N. Lin, A Self-Propagating High-Temperature Synthesis Method for Synthesis of AlN Powder, *J. Mater. Res.*, 1999, **14**(5), p 1928-1933
9. Z.Y. Fu, J.F. Liu, H. Wang, D.H. He, and Q.J. Zhang, Spark Plasma Sintering of Aluminium Nitride Transparent Ceramics, *Mater. Sci. Technol*, 2004, **20**, p 1097-1099
10. T. Shirakami, K. Urabe, H. Nakano, T. Meguro, K. Komeya, and N.H. Kim, Microstructural Evolution during Sintering of Aluminum Nitride Ceramics Doped with Alumina and Yttria, *J. Am. Ceram. Soc.*, 2001, **84**(3), p 631-635
11. K. Komeya and H. Inoue, The Effects of Particle Size of AlN and Composition on Sintering with Nitriding Reaction of the System AlN-Al, *J. Jpn. Soc. Powder Powder Metall.*, 1970, **17**(3), p 108-115
12. D.D. Marchant and T.E. Nemecek, Aluminum Nitride: Preparation, Processing and Properties, *Adv. Ceram.*, 1989, **26**, p 19-54
13. S. Winsztal, B. Wnuk, H. Majewska-Minor, and T. Niemyski, Aluminium Nitride Thin Films and Their Properties, *Thin Solid Films*, 1976, **32**, p 251-254
14. V. Mortet, A. Vasin, P.-Y. Jouan, O. Elmazria, and M.-A. Djouadi, Aluminium Nitride Films Deposition by Reactive Triode Sputtering for Surface Acoustic Wave Device Applications, *Surf. Coat. Technol.*, 2003, **176**, p 88-92
15. A. Mahmood, N. Rakov, and M. Xiao, Influence of Deposition Conditions on Optical Properties of Aluminum Nitride (AlN) Thin Films Prepared by DC-Reactive Magnetron Sputtering, *Mater. Lett.*, 2003, **57**, p 1925-1933

16. Q.S. Paduano, D.W. Weyburne, J. Jasinski, and Z. Liliental-Weber, Effect of Initial Process Conditions on the Structural Properties of AlN Films, *J. Crys. Growth*, 2004, **261**, p 259-265
17. S. Strite and H. Morkoç, GaN, AlN, and InN: A Review, *J. Vac. Sci. Technol. B*, 1992, **10**(4), p 1237-1266
18. I. Petrov, E. Mojab, R.C. Powell, J.E. Greene, L. Hultman, and J.-E. Sundgren, Synthesis of Metastable Epitaxial Zinc-Blende-Structure AlN by Solid-State Reaction, *Appl. Phys. Lett.*, 1992, **60**(20), p 2491-2493
19. J. Wang, W.L. Wang, P.D. Ding, Y.X. Yang, L. Fang, J. Esteve, and M.C. Polo, Synthesis of Cubic Aluminum Nitride by Carbothermal Nitridation Reaction, *Diam. Relat. Mater.*, 1999, **8**, p 1342-1344
20. T. Mashimo, M. Uchino, A. Nakamura, T. Kobayashi, E. Takasawa, T. Sekine, Y. Noguchi, H. Hikosaka, K. Fukuoka, and Y. Syono, Yield Properties, Phase Transition, and Equation of State of Aluminum Nitride (AlN) Under Shock Compression up to 150 GPa, *J. Appl. Phys.*, 1999, **86**(12), p 6710-6716
21. J. Kuang, C. Zhang, X. Zhou, Q. Liu, and C. Ye, Formation and Characterization of Cubic AlN Crystalline in a Carbothermal Reduction Reaction, *Mater. Lett.*, 2005, **59**, p 2006-2010
22. H.U. Joo, S. Chae, and W. Jung, Is It Possible to Synthesize Cubic Aluminum Nitride by the Carbothermal Reduction and Nitridation Method?, *Diam. Relat. Mater.*, 2008, **17**, p 352-355
23. K. Sardar, M. Dan, B. Schwenzer, and C.N.R. Rao, A Simple Single-Source Precursor Route to the Nanostructures of AlN, GaN and InN, *J. Mater. Chem.*, 2005, **15**, p 2175-2177
24. X.P. Hao, M.Y. Yu, D.L. Cui, X.G. Xu, Y.J. Bai, Q.L. Wang, and M.H. Jiang, Synthesize AlN Nanocrystals in Organic Solvent at Atmospheric Pressure, *J. Cryst. Growth*, 2002, **242**, p 229-232
25. L. Li, X. Hao, N. Yu, D. Cui, X. Xu, and M. Jiang, Low-Temperature Solvent Thermal Synthesis of Cubic AlN, *J. Cryst. Growth*, 2003, **258**, p 268-271
26. A. Iwata, J. Akedo, and M. Lebedev, Cubic Aluminum Nitride Transformed Under Reduced Pressure Using Aerosol Deposition Method, *J. Am. Ceram. Soc.*, 2005, **88**(4), p 1067-1069
27. A. Iwata and J. Akedo, Hexagonal to Cubic Crystal Structure Transformation During Aerosol Deposition of Aluminum Nitride, *J. Crys. Growth*, 2005, **275**, p e1269-e1273
28. L.R. Krishna, D. Sen, Y.S. Rao, G.V.N. Rao, and G. Sundararajan, Thermal Spray Coating of Aluminum Nitride Utilizing the Detonation Spray Technique, *J. Mater. Res.*, 2002, **17**(10), p 2514-2523
29. L.H. Cao, K.A. Khor, L. Fu, and F. Boey, Plasma Spray Processing of Al_2O_3/AlN Composite Powders, *J. Mater. Process. Technol.*, 1999, **89-90**, p 392-398
30. F. Kassabji, F. Tourenne, A. Derradji, and P. Fauchais, Aluminum and Aluminum Nitride Deposition by Low Pressure Nitrogen Arc Plasma Spraying, *Proc. 10th Int. Therm. Spray Conf.*, Vol 80, 1983, p 82-84
31. A. Ohmori, M. Wakamatsu, and K. Kamada, Synthesis of Al_2O_3-AlN Coating by Low Pressure Plasma Spraying and Nitriding, *Trans. JWRI*, 1993, **22**(2), p 227-232
32. K.A. Khor, F.Y.C. Boey, X.L. Zhao, and L.H. Cao, Aluminium Nitride by Plasma Spraying of an Al_2O_3-C-Sm_2O_3 System, *Mater. Sci. Eng. A*, 2001, **300**, p 203-210
33. M. Yamada, T. Yasui, M. Fukumoto, and K. Takahashi, Nitridation of Aluminum Particles and Formation Process of Aluminum Nitride Coatings by Reactive RF Plasma Spraying, *Thin Solid Films*, 2007, **515**(9), p 4166-4171
34. M. Fukumoto, M. Yamada, T. Yasui, and K. Takahashi, Fabrication of Aluminum Nitride Coating by Reactive RF Plasma Spray Process, *Proc. International Thermal Spray Conference (ITSC)*, 2004, CD
35. M. Yamada, Y. Kouzaki, T. Yasui, and M. Fukumoto, Fabrication of Iron Nitride Coatings by Reactive RF Plasma Spraying, *Surf. Coat. Technol.*, 2006, **201**, p 1745-1751
36. M. Yamada, T. Inamoto, M. Fukumoto, and T. Yasui, Fabrication of Silicon Nitride Thick Coatings by Reactive RF Plasma Spraying, *Mater. Trans.*, 2004, **45**, p 3304-3308
37. C. Lin and S. Chung, Combustion Synthesis of Aluminum Nitride Powder Using Additives, *J. Mater. Res.*, 2001, **16**(8), p 2200-2208
38. S. Sampath, X.Y. Jiang, J. Matejicek, A.C. Leger, and A. Vardelle, Substrate Temperature Effects on Splat Formation, Microstructure Development and Properties of Plasma Sprayed Coatings. Part I: Case Study for Partially Stabilized Zirconia, *Mater. Sci. Eng. A*, 1999, **272**, p 181-188
39. S. Sampath and X. Jiang, Splat Formation and Microstructure Development During Plasma Spraying: Deposition Temperature Effects, *Mater. Sci. Eng. A*, 2001, **304-306**, p 144-150
40. H.R. Salimijazi, L. Pershin, T.W. Coyle, J. Mostaghimi, S. Chandra, Y.C. Lau, L. Rosenzweig, and E. Moran, Effect of Droplet Characteristics and Substrate Surface Topography on the Final Morphology of Plasma-Sprayed Zirconia Single Splats, *J. Therm. Spray Technol.*, 2007, **16**(2), p 291-299
41. H. Zhang, X.Y. Wang, L.L. Zheng, and S. Sampath, Numerical Simulation of Nucleation, Solidification, and Microstructure Formation in Thermal Spraying, *Int. J. Heat Mass Trans.*, 2004, **47**, p 2191-2203
42. T. Chraska and A.H. King, Transmission Electron Microscopy Study of Rapid Solidification of Plasma Sprayed Zirconia. Part I. First Splat Solidification, *Thin Solid Films*, 2001, **397**, p 30-39
43. P. Duwez, R.H. Willen, and W. Klement, Continuous Series of Metastable Solid Solutions in Silver-Copper Alloys, *J. Appl. Phys.*, 1960, **31**, p 1136-1137
44. R.A. Rodriguez-Diaz, L. Banos, O. Novelo, C. Flores, J. Colin, J. Arenas-Alatorre, and J.A. Juarez-Islas, Microstructural Characterization of $Fe_{40}Al_{15}Cr$ (% at.) Intermetallic Alloy Produced by Rapid Solidification, *Acta Microsc.*, 2009, **18**(2), p 169-173
45. D.J. Tilly, J.P.A. Lofvander, and C.G. Levi, Solidification Paths and Carbide Morphologies in Melt Processed $MoSi_2$-SiC In Situ Composites, *Metall. Mater. Trans.*, 1996, **28A**, p 1889-1900
46. M.J. Kramer, H. Mecco, K.W. Dennis, E. Vargonova, R.W. McCallum, and R.E. Napolitano, Rapid Solidification and Metallic Glass Formation—Experimental and Theoretical Limits, *J. Non-Cryst. Solids*, 2007, **353**, p 3633-3639
47. J. Kong, Z. Ye, and F. Lv, Non-Equilibrium Solidification Character of $Zr_{56.2}Ti_{13.8}Nb_{5.0}Cu_{6.9}Ni_{5.6}Be_{12.5}$ Bulk Metallic Glass Composites Containing Ductile Dendrite Phase, *J. Alloys Comp.*, 2009, **478**, p 202-205
48. I. Kimura, K. Ichiya, M. Ishii, N. Hotta, and T. Kitamura, Synthesis of Fine AlN Powder by a Floating Nitridation Technique Using an N_2/NH_3 Gas Mixture, *J. Mater. Sci. Lett.*, 1989, **8**, p 303-304
49. T. Fujii, K. Yoshida, K. Suzuki, and S. Ito, Direct Nitriding of Large Grains of Aluminum with 2 mm Size, *Solid State Ionics*, 2001, **141-142**, p 593-598
50. M. Radwan and Y. Miyamoto, Growth of Quasi-Aligned AlN Nanofibers by Nitriding Combustion Synthesis, *J. Am. Ceram. Soc.*, 2007, **90**(8), p 2347-2351