www.czasopisma.pan.pl PAN www.journals.pan.pl
POLSKA AKADEMIA NAUK

A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 60 2015 Issue 2

DOI: 10.1515/amm-2015-0243

Y. NAKAFUSHI*,♯, K. MATSUDA**, M. NOSE***

MECHANICAL PROPERTIES AND MICROSTRUCTURE OF AlN/SiCN NANOCOMPOSITE COATINGS PREPARED BY R.F.-REACTIVE SPUTTERING METHOD

WŁAŚCIWOŚCI MECHANICZNE I MIKROSTRUKTURA POWŁOK NANOKOMPOZYTOWYCH AlN/SiCN WYTWORZONYCH METODĄ REAKTYWNEGO ROZPYLANIA JONOWEGO RF

FIn this work, AlN/SiCN composite coatings were deposited by r.f.-reactive sputtering method using a facing target-type sputtering (FTS) apparatus with composite targets consisting of Al plate and SiC chips in a gaseous mixture of Ar and N_2, and investigated their mechanical properties and microstructure. The indentation hardness (H_{IT}) of AlN/SiCN coatings prepared from composite targets consisting of 8 ~32 chips of SiC and Al plate showed the maximum value of about 29~32 GPa at a proper nitrogen gas flow rate. X-ray diffraction (XRD) patterns for the AlN/SiCN composite coatings indicated the presence of the only peeks of hexagonal (B4) structured AlN phase. AlN coatings clarified the columnar structure of the cross sectional view TEM observation. On the other hand, microstructure of AlN/SiCN composite coatings changed from columnar to equiaxed structure with increasing SiCN content. HR-TEM observation clarified that the composite coatings consisted of very fine equiaxial grains of B4 structured AlN phase and amorphous phase.

Keywords: AlN, SiCN, XRD, sputtering, TEM

W pracy scharakteryzowano właściwości powłok kompozytowych AlN/SiCN naniesionych metodą reaktywnego rozpylania jonowego RF za pomocą aparatury FTS. Proces rozpylania prowadzono w mieszaninie gazowej Ar i N_2 a jako tarczy użyto kompozytów składających się z płytki Al i wiórów SiC. Następnie zbadano właściwości mechaniczne i mikrostrukturę w/w powłok. Maksymalna twardość powłok AlN/SiCN otrzymanych z tarcz kompozytowych składających się z 8~32 wiórów SiC oraz płytki z Al wynosiła ok. 29~32 GPa przy określonej prędkości przepływu azotu. Analiza dyfrakcji promieniowania rentgenowskiego powłok kompozytowych AlN/SiCN wykazała występowanie refleksów jedynie fazy AlN o strukturze heksagonalnej (B4). Istnienie w powłoce fazy AlN wyjaśniło strukturę kolumnową, którą obserwowano w zdjęciach TEM z przekroju poprzecznego. Jednocześnie, mikrostruktura powłok kompozytowych AlN/SiCN zmieniła się ze struktury kolumnowej w równoosiową wraz ze zwiększeniem się zawartości SiCN. Obserwacje HR-TEM wykazały, że powłoki kompozytowe składały się z drobnych równoosiowych ziaren fazy AlN o strukturze B4 oraz fazy amorficznej.

1. Introduction

Transition metal nitrides such as TiN, ZrN, CrN have been adopted as hard protective coatings of mechanical tools due to their wear and corrosion resistance and high melting point [1]. However, there has been considerable interest in the study of coatings consisting of light elements such as Si, Al, C, N, against a background of the resources problem for rare metals in recent years. AlN coatings are known to possess good high-temperature stability and hardness [2], but to have poor adhesion to metal substrate due to its high covalent character. On the other hand, SiCN coating have near thermal expansion coefficient and Young's modulus to those of steel, in addition to a good high-temperature stability and wear resistance [3]. It was reported that Polimar derived SiAlCN ceramic coatings had much better oxidation resistance than SiCN coatings [4]. However, few amount of research on AlSiCN coatings prepared by r.f.-reactive sputtering has been conducted. To study the effect of SiCN addition to AlN on the microstructure and mechanical properties of the coatings, a series of AlN/SiCN nanocomposite coatings have been deposited by r.f.-reactive sputtering using a facing target-type sputtering (FTS) apparatus.

2. Experimental Procedure

AlN/SiCN nanocomposite coatings were deposited with the Facing Target-type Sputtering (FTS) apparatus; Osaka Vacuum Co., Ltd., FTS-R2 using the r.f. power supply and composite targets consisting of rectangular plate (160 mm×100 mm×10 mm) of Al (99.7%) and SiC (99.5%) chips (10 mm×10 mm×2 mm) in a mixture of Ar and N_2, both

* SCHOOL OF SCIENCE AND ENGINEERING FOR EDUCATION, UNIVERSITY OF TOYAMA, 3190 GOFUKU, TOYAMA 930-8555, JAPAN
** GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR RESEARCH, UNIVERSITY OF TOYAMA, 3190 GOFUKU, TOYAMA 930-8555, JAPAN
*** FACULTY OF ART AND DESIGN, UNIVERSITY OF TOYAMA, 180 FUTAGAMI-MACHI, TAKAOKA 933-8588, JAPAN
♯ Corresponding author: ikenolab@eng.u-toyama.ac.jp

of 99.9999% purity. Mirror polished silicon wafers of 25 mm square and high-speed steel (HSS) of 23 mm square were used as substrates. The system was evacuated to a vacuum better than 2×10^{-4} Pa prior to deposition. We fixed Ar gas flow rate at 10 sccm and controlled N_2 gas flow rate in the range of 0 to 17 sccm. The r.f. input power (13.56 MHz) was fixed at about 1 kW. The substrates were heated up to 250°C without applying negative bias voltage during deposition.

The indentation hardness was measured by a nanoindentation system (Fisher scope, H100C-XYp). The crystal structure of coatings was identified by the X-ray diffractometer (Philips X'pert system) using a Cu-Kα radiation with θ-2θ or grazing angle mode (GAXRD). The microstructure was investigated by TEM (TOPCON EM-002B, JEOL JEM4010HT, respectively. Cross-sectional TEM specimens were prepared by the FIB (Focus Ion Beam) technique.

3. Results and discussion

Figure 1 shows variation of indentation hardness (H_{IT}) and young's modulus (E^*) of AlN/SiCN coatings with N_2 gas flow rate; AlN/SiCN coatings were fabricated from composite target having 8, 16 or 32 SiC chips. H_{IT} of AlN/SiCN composite coatings deposited from the composite target having 8 chips of SiC increases from 21 GPa with increasing N_2 gas flow rate 3 sccm to 17 sccm reaching to the maximum hardness of 32 GPa in the range of 15 sccm to 17 sccm of N_2 flow rate. H_{IT} of AlN/SiCN composite coatings deposited from the composite target with 16 chips of SiC shows maximum value about 32 GPa at 5 sccm of N_2 gas flow rate and then decreases when N_2 flow rate increases from 5 to 10 sccm. But it increases slightly with increasing the N_2 flow rate up to 17 sccm. H_{IT} of AlN/SiCN composite coatings deposited from the composite target having 32 chips of SiC shows maximum value about 26 GPa at 3 sccm of N_2 gas flow rate. The H_{IT} decreases abruptly to about 18 GPa at 4 sccm of N_2 gas flow rate, and keeps the value in the range of 18 GPa to 20 GPa up to 17 sccm of N_2 flow rate. In Fig.1, down-pointing arrow indicates the maximum hardness of each series of AlN/SiCN composite coatings. As can be seen in the figure, N_2 flow rate providing the maximum hardness of AlN/SiCN composite coating shifted to lower N_2 gas flow rate with increasing numbers of SiC chips. E^* values show similar tendency with H_{IT}.

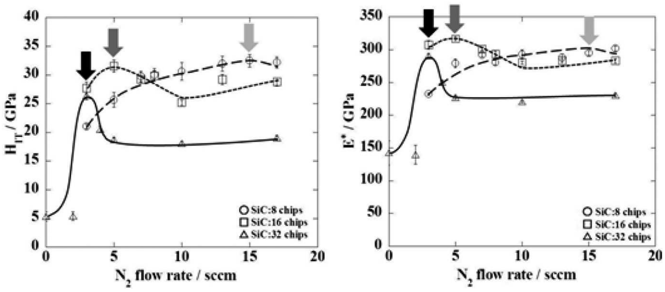

Fig. 1. (a) Variation of indentation hardness (H_{IT}) and Young's modulus (E^*) of AlN/SiCN coatings with N_2 flow rate

Figure 2 shows X-ray diffraction (XRD) pattern of AlN/SiCN composite coating on (a) thin film method and (b) -2 method. The XRD patterns for the AlN/SiCN composite coatings indicated the presence of the only peeks of B4 structured AlN phase.

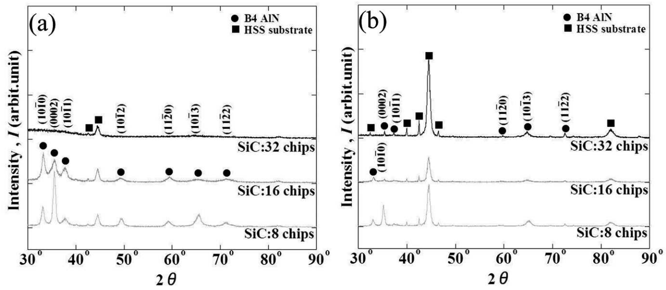

Fig. 2. X-ray diffraction (XRD) pattern of AlN/SiCN composite coating on (a) thin film method and (b) – 2 method

Figure 3 shows the cross-sectional TEM micrographs of AlN/SiCN composite coating (a) 8 chips, (b) 16 chips and (c) 32 chips of SiC was used to examine further the results obtained by XRD. Cross sectional view TEM observation of

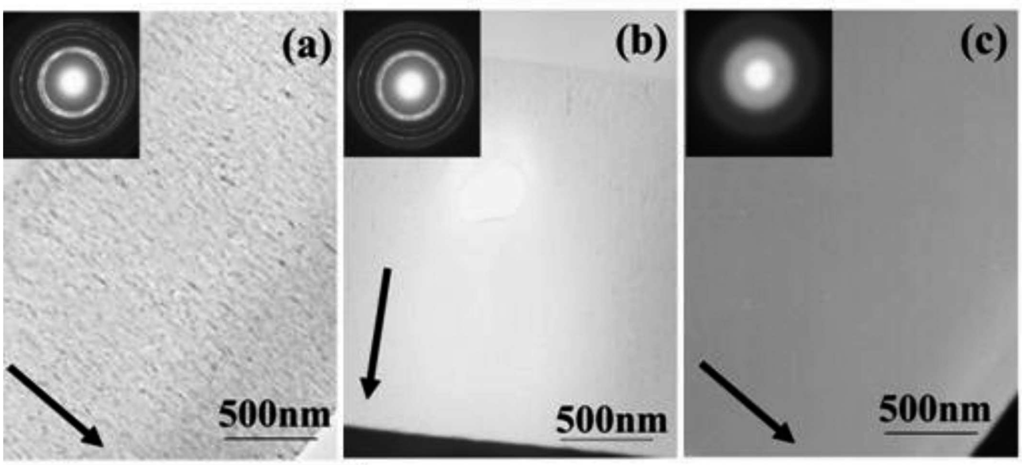

Fig. 3. Cross-sectional TEM and SAED images of AlN/SiCN composite coating deposited at 5 sccm of N_2 flow rate using (a) 8 chips, (b) 16 chips, and (c) 32 chips of SiC

Fig. 3a and 3b clarified that the AlN/SiCN coatings consisted of very fine equiaxial grains, and selected area electron diffraction (SAED) analysis implied that the coatings consist of very fine grains of B4 structured AlN and amorphous SiCN phase. Fig. 3c shows that the coating consisted amorphous structure.

4. Conclusions

To examine the effect of SiCN addition on the microstructure and mechanical properties of AlN coatings, a series of AlN/SiCN coatings have been prepared by r.f. reactive sputtering of composite targets consisting of Al plate and SiC chips in the Facing Target-types Sputtering (FTS) system. The indentation hardness of AlN/SiCN coatings prepared from composite targets consisting of 8~32 chips of SiC and Al plate showed the maximum value of about 32 GPa at proper nitrogen gas flow rate. The results of XRD analysis indicate that the presence of the only peeks of B4 structured AlN phase on AlN/SiCN composite coatings. TEM observation and SAED pattern indicated that the AlN/SiCN coatings (8 chips and 16 chips) consist of very fine equiaxial grains of B4 structured AlN phase.

REFERENCES

[1] D. Valerini, M.A. Signore, L. Tapfer, E. Piscopiello, U. Galietti, A. Rizzo, Thin Solid Films. **538**, 42 (2013).
[2] A.C. Galca, G.E. Stain, L.M. Trinca, C.C. Negrila, L.C. Nistor, Thin Solid Films. **524**, 328 (2012).
[3] C. Pusch, H. Hoche, C. Berger, R. Riedel, E. Lonescu, A. Klein, Surf. Coat. Technol. **205**, S119 (2011).
[4] Y. Wang, Y. Fan, L. Zhang, W. Zhang, L. An, Scripta Materialia. **55**, 295 (2006).

Received: 20 February 2014.