

플라즈마 화학증착법에 의해 제조된 $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ 박막의 미세조직 및 기계적 특성에 관한 연구

이동각, 이승훈, 한영훈, 이정중

서울대학교

The Microstructure And The Mechanical Properties Of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ Coatings Deposited By Plasma Enhanced Chemical Vapor Deposition(PECVD)

D. K. Lee, S. H. Lee, Y. H. Han, and J. J. Lee

School of Materials and Engineering, Seoul National University, Shilim, Kwanak,
Seoul 151-742, Korea

Abstract

$(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ has been deposited on high speed steel(HSS) substrate using PECVD from the gas mixture of TiCl_4 , AlCl_3 , NH_3 , H_2 , and Ar. The correlation between the microstructure and the mechanical properties was investigated. $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ showed single phase NaCl-structure up to $X=0.87$, while a mixed phase of NaCl Type (Ti, Al)N and wurtzite structure AlN was observed for $0.87 < X < 1$. The grain size of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ became by degrees as increasing X , which made the hardness of the coating higher by Al addition. When the coating was composed of a mixed phase, however, the hardness decreased abruptly due to the effect of soft AlN phase. The wear volume of the coatings could be obtained as the concentration of the coating was varied, and the relation between the wear volume and hardness or the adhesion strength was discussed.

1. Introduction

TiN, which is widely used as wear-resistant coating, oxidizes rapidly to form rutile TiO_2 at temperature above 500°C . The large difference in the molar volumes between TiO_2 (18.8cm^3) and TiN (11.4cm^3) results in the development of compressive stress in

the oxide layer which spalls and exposes unoxidized nitrides to the further oxidation until the entire nitride layer is consumed¹⁾.

$(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ coatings has been the subject of much attention owing to its improved oxidation resistance at high temperature and cutting performance in drilling and turning operations compared

to TiN^{2-4} . $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ has been deposited mainly by the physical vapor deposition (PVD) techniques⁵⁻¹⁰⁾ such as sputtering, ion plating, and arc process, but recently some works¹¹⁻¹³⁾ on $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ which was deposited by plasma enhanced chemical vapor deposition (PECVD) were successfully performed. By using the PECVD technique, the concentrations of metallic elements in the coatings, i.e. Ti and Al could be easily controlled, and compositionally gradient $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ coatings in which the concentrations of Ti and Al changes gradually, could also be formed without difficulty¹¹⁾.

In this study, we investigated the microstructure of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ dependent on X, and discussed the hardness and wear-resistance of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ related to the microstructure.

2. Experiments.

$(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ coatings were deposited on M2 high-speed steel (HSS) by PECVD using a gas mixture of TiCl_4 , AlCl_3 , NH_3 , H_2 , and Ar. The PECVD equipment used for the deposition is shown in Fig. 1. The gases were supplied through two separate lines to prevent the formation of $\text{TiCl}_4 \cdot n\text{NH}_3$ and NH_4Cl , which could clog the lines. Table 1 represents typical deposition conditions. The flow rates of TiCl_4 and AlCl_3 were controlled by varying both evaporating pressures and the amount of carrier gases, Ar and H_2 . A detailed description of the apparatus and the experimental procedure is presented elsewhere¹¹⁾. The coating thickness was set at approximately $3\mu\text{m}$ for most specimens in order to eliminate the effect of thickness on the mechanical properties.

Compositional ratio of Al in the coatings was measured by energy dispersive spectroscopy

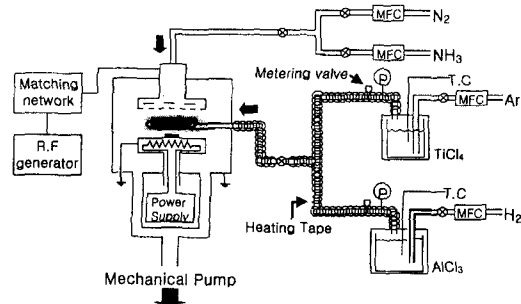


Fig. 1. Schematic diagram of the apparatus used for the deposition of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$.

Table 1. Deposition condition for the $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ coatings.

Temperature of TiCl_4 vaporizer	0°C
Temperature of AlCl_3 vaporizer	90~130°C
Flow rate of Ar	10 sccm
Flow rate of H_2	100 sccm
Flow rate of NH_3	25 sccm
Substrate temperature	530°C
Deposition pressure	0.5~1 torr
RF power	25 W
Electrode spacing	3 cm
Coating thickness	about 3 μm

(EDS). The surface morphology and thickness of the $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ coatings were investigated using scanning electron microscopy (SEM). To analyze the structure, the transmission electron microscopy (TEM) and X-ray diffraction (XRD) method were used. The hardness of the coating was determined by Knoop micro-indentation tests with a load of 10g. The wear behavior of coatings at room temperature and at high temperature (700°C) was studied unlubricated using a CSEM ball-on-disk type tribometer with silicon carbide ball of 6mm diameter. To consider effects of adhesion strength between coating and substrate, the test performed can be divided into two groups: (1) wear test I in condition that could exclude the effect of adhesion due to small load and short sliding distance; (2)

Table 2. The condition of wear test for $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$

	Ball	Load (N)	Speed (m/s)	Rotation number	Sliding distance (m)
Wear test I	SiC	1N	0.1	4000	125
Wear test II	SiC	2N	0.1	15915	500

wear test II in condition that had to consider the effects of adhesion because the coating was mostly worn. The condition of respective wear test are summarized in Table 2. After the test was completed, the depth profiles of wear track was measured using α -step and then, then wear volume of each sample was calculated.

3. Result and Discussion.

3. 1. Structure.

Fig. 2 shows the XRD patterns of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ dependent on X . Only (200) peak of a NaCl structure could be observed when X is less than 0.87. The peak shifts to higher angles since the lattice parameter decreases when X increases. However, in the $(\text{Ti}_{0.07}\text{Al}_{0.93})\text{N}$, the AlN phase with a wurtzite structure could be observed in addition to the phase of the NaCl structure. Accordingly $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ deposited by PECVD is a single phase of the NaCl structure for $0 < X < 0.87$, a two-phase mixture consisting of the NaCl structure and the wurtzite structure for $0.87 < X < 1$. This result affects the mechanical properties of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ to a great extent as described below.

3. 2. Surface and cross-sectional morphology and microstructure.

Fig. 3 shows the surface and cross-sectional morphologies of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ as to X . The surface morphology of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ has smaller and more round shape than that of TiN which has open po-

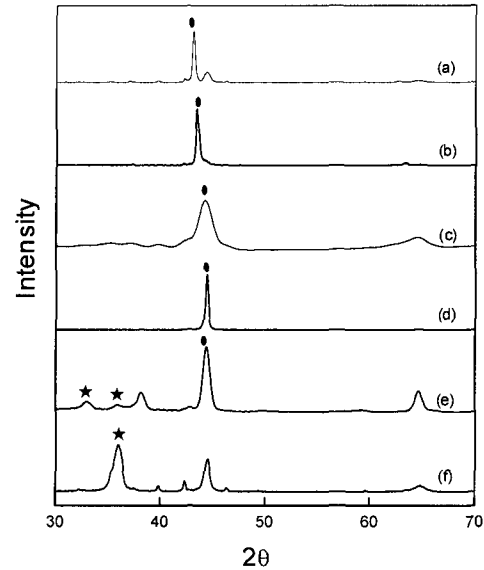
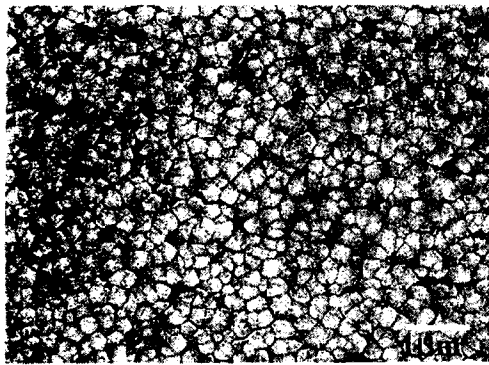


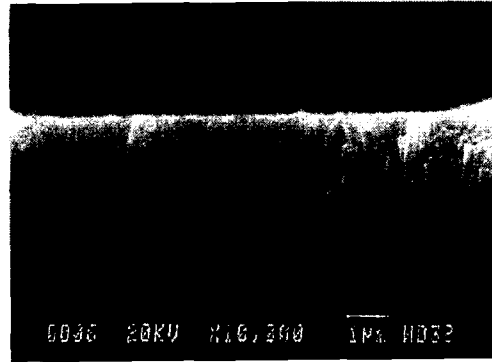
Fig. 2. XRD patterns for $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ with various X .
 (a) TiN (b) $X=0.26$ (c) $X=0.64$
 (d) $X=0.87$ (e) $X=0.93$ (f) AlN
 (● : NaCl structure, ★ : wurtzite structure, unindexed : substrate)

rous cubic shapes. However, it is difficult to tell morphology changes such as grain refinement with only SEM image. $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ was grown into columnar structure with zone I and zone T of Thornton's model¹⁴⁾ regardless of X , so the cross-sectional morphology of the coatings do not show much differences.

Fig. 4 shows the plan-view TEM micrographs of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ as to X . The grain size of TiN is from about 70nm to 100nm, however, as X increases, that of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ becomes smaller by degrees, which reaches to 20nm for that of $(\text{Ti}_{0.07}\text{Al}_{0.93})\text{N}$. The grain of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ is a more dense and more round shape than that of TiN.



(a) TiN



(b) TiN

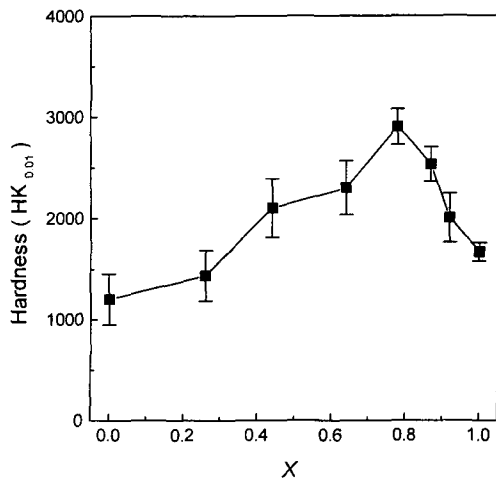
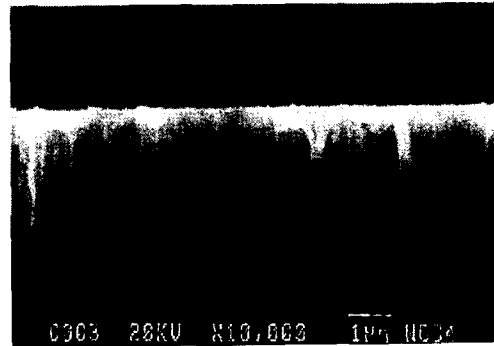
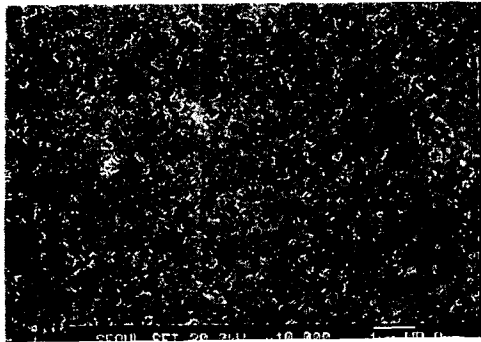
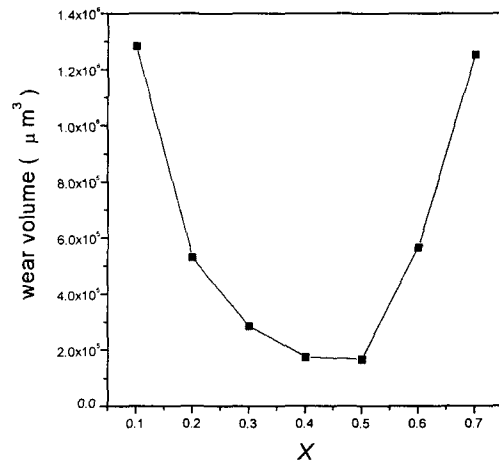


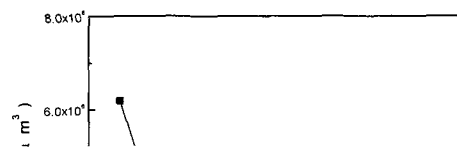
Fig. 5. Knoop micro-hardness of (Ti_{1-x}Al_x)N as a function of Al fraction, X.

3. 4 .Wear-resistance.

Fig. 6 shows the wear volume of (Ti_{1-x}Al_x)N as



(a) at room temperature



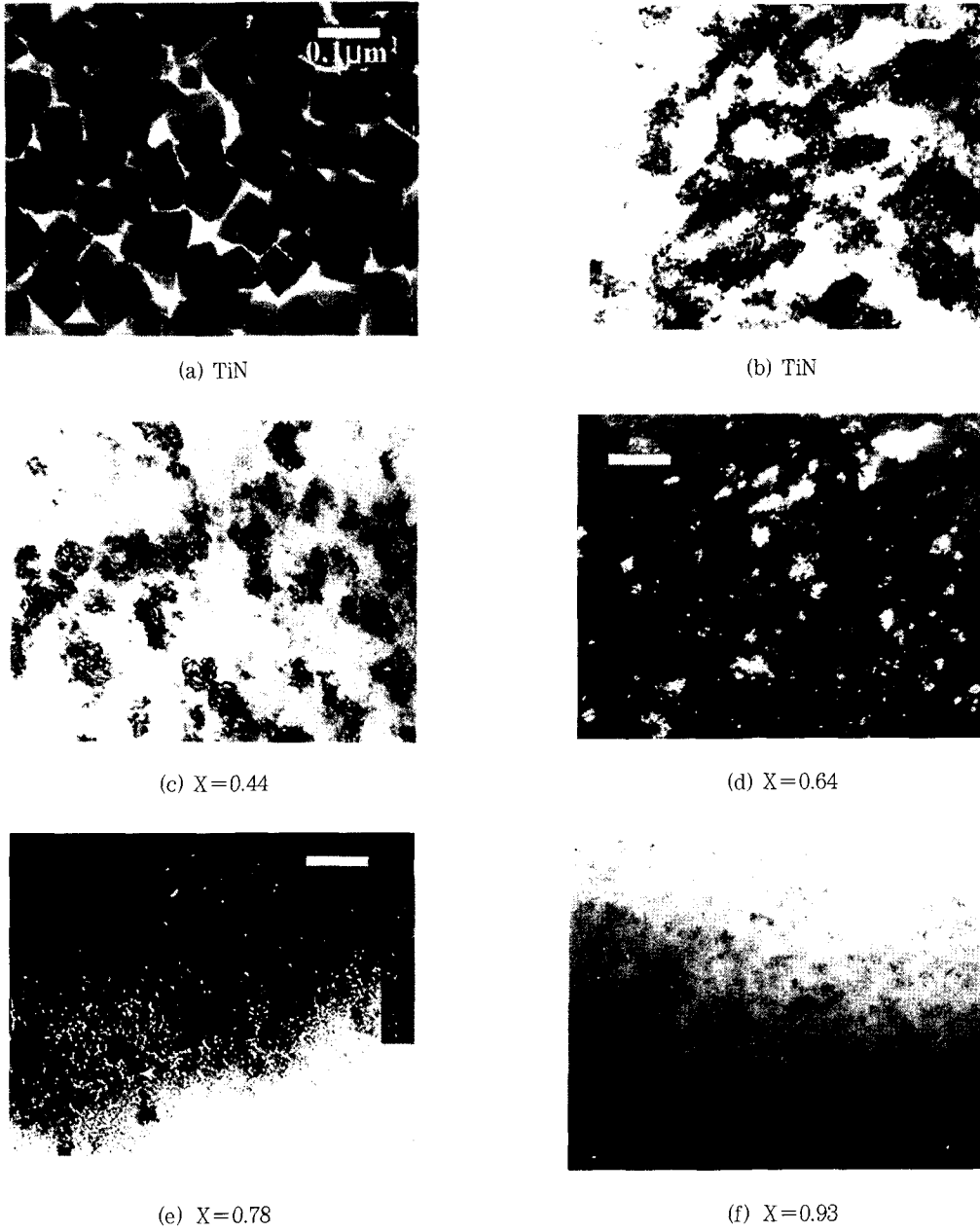


Fig. 4. Plan-view TEM micrographs of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ with various X.

reaches to $1600\text{HK}_{0.01}$ for AlN. This sudden decrease of micro-hardness results from the crystal structure change to a mixture phase of NaCl structure and wurtzite structure which has a low hard-

ness as described above. The increase of hardness is thought to result from solid solution hardening effects as generally known.

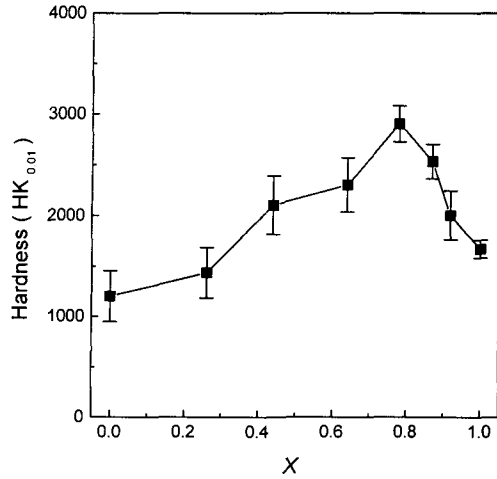
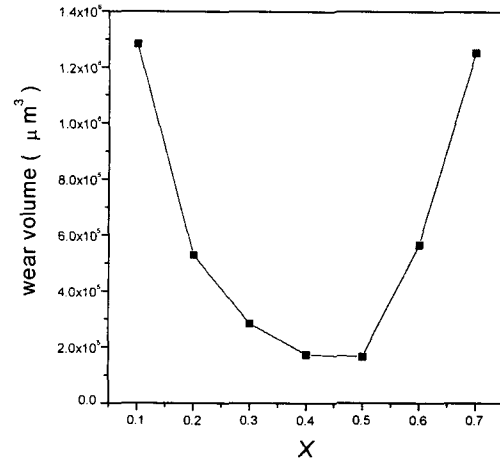


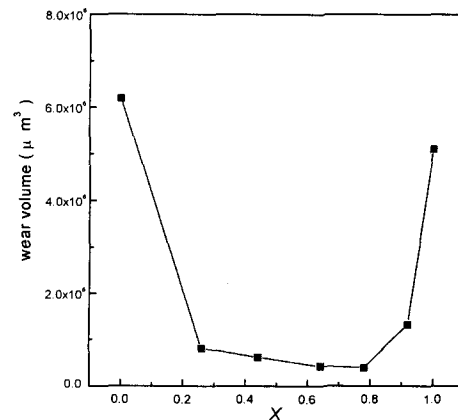
Fig. 5. Knop micro-hardness of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ as a function of Al fraction, X .

3. 4 .Wear-resistance.

Fig. 6 shows the wear volume of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ as a function of X for wear test I at room temperature and at 700°C . The wear volume of the coating decreased continuously as increasing X , but it increased abruptly when the wurtzite AlN phase appeared at $X > 0.87$ irrespective of temperature. This result is a good agreement with the result of hardness measurement. In consequence, in the early stage of wear coating, wear is fully dependent on the hardness of the coating. At 700°C , the wear volume of TiN was much larger than that of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ or AlN, though there was little difference between the wear volume of TiN and that of AlN at room temperature. This is thought to result from the oxide layer. At 700°C , the oxide layer is formed on the top of the coating due to the oxidation. Al_2O_3 which is formed by AlN has higher hardness than AlN and there is no difference between the molar volume of AlN and that of Al_2O_3 . But, the hardness of TiO_2 is lower than that of TiN and the difference of the molar volume of TiN and TiO_2 is large.



(a) at room temperature



(b) at 700°C

Fig. 6. Wear volume of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ as a function of X for the wear test I.

Therefore, the oxidation from TiN to TiO_2 is thought to promote the delamination and coating wear. However, $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ has much higher wear-resistance than TiN or AlN, because of its higher hardness and higher oxidation resistance.

Fig. 7 shows the result of wear test II at room temperature. Different from the result of wear test I, the wear volume of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ increases with X increasing. This result has a correlation with adhesion strength. The adhesion strength of $(\text{Ti}_{1-x}\text{Al}_x)$

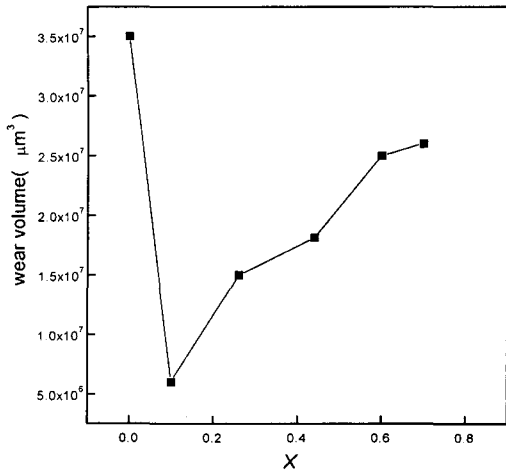
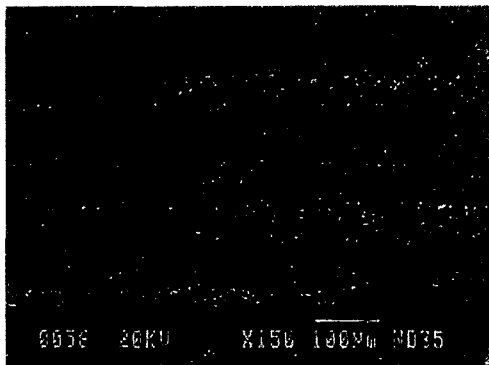
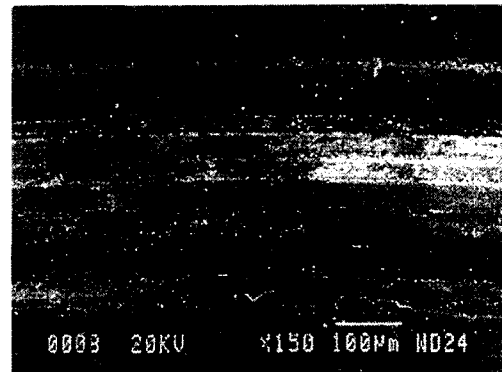


Fig. 7. Wear volume of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ as a function of X for the wear test II at room temperature.

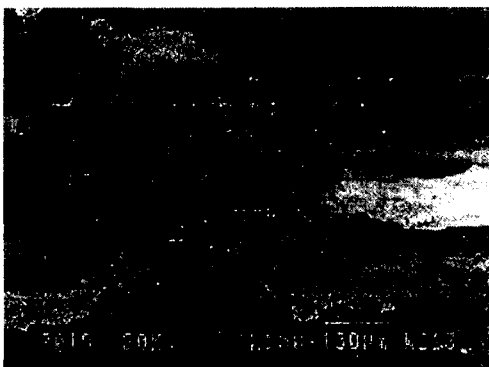
N deposited by PECVD has been reported to decrease abruptly when $X > 0.15^{11)}$. So, as can be observed in Fig. 8, the difference in the track shows dependent on adhesion strength. When the adhesion strength is high enough such as $(\text{Ti}_{0.9}\text{Al}_{0.1})\text{N}$, the coating hardly peels off in the track edge, so there is few delaminated debris. When coating has a weak adhesion strength such as $(\text{Ti}_{0.3}\text{Al}_{0.7})\text{N}$, coating easily peels off in the track edge, and as wear proceeds, debris is easily delaminated from coating. Accordingly coating wear is accelerated and the wear track exposes the substrate here and there. But, in case of TiN, because of low hardness, it has poor wear-resistance compared with $(\text{Ti}_{0.9}$



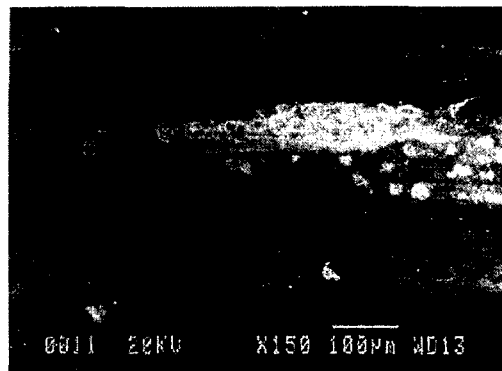
(a) TiN



(b) X=0.1



(c) X=0.44



(d) X=0.7

Fig. 8. Wear track of $(\text{Ti}_{1-x}\text{Al}_x)\text{N}$ with various X for the wear test I at room temperature.

$Al_{0.1}$)N though high adhesion strength. Therefore, high hardness and good adhesion is necessary for wear-resistant coatings and is being studied now.

4. Conclusion.

$(Ti_{1-x}Al_x)N$ deposited by PECVD method showed a single phase NaCl structure in the concentration range of $0 \leq X \leq 0.87$ and a mixed phase of NaCl-type $(Ti,Al)N$ and wurtzite structure AlN in the concentration range of $0.87 < X < 1.0$. The grain size of $(Ti_{1-x}Al_x)N$ reached to $2500 \sim 3000HK_{0.01}$ at the range of $0.78 < X < 0.87$ and then decreased abruptly due to the effect of soft AlN phase. The early stage of the wear test, the wear volume of $(Ti_{1-x}Al_x)N$ reached minimum at the range of $0.7 < X < 0.87$ in the same tendency as micro-hardness change. With going on the wear test, however, the delaminated debris of the coating promoted the coating wear. Consequently, when the coating is worn out and substrate is exposed, the wear volume of $(Ti_{1-x}Al_x)N$ coatings reached minimum at $X=0.1$, and then increased again with increasing X . This phenomena resulted from the poor adhesion strength when $X > 0.15$.

5. Acknowledgement.

The authors wish to acknowledge the financial support of the Center for Iron & Steel Research made in the program year of 1998.

Reference

1. J. Desmaison, P. Lefort, and M. Billy : Oxid. Met 13 (1979) 203.
2. J. R. Roos, J. P. Celis, E. Vancoille, H. Veltrop, S. Boelens, F. Jungblut, J. Ebberink, and H. Homberg : Thin solid Films 193/194 (1990) 547.
3. H. Randhawa, P. C. Johnson and R. Cunningham : J. Vac. Sci. Technol. A6 (1998) 2136.
4. W. D. Munz : J. Vac. Technol. A4 (1986) 2695.
5. O. Knotek, W. D. Munz, and T. Leyendecker : J. Vac. Sci. Technol. A5 (1987) 2173.
6. J. R. Roos, J. P. Celis, E. Vancoille, H. Veltrop, S. Boelens, F. Jungblut, J. Ebberink, and H. Homberg : Thin. Solid Films 193/194 (1990) 547.
7. H. Randhawa, P. C. Johnson, and R. Cunningham : J. Vac. Sci. Technol. A6 (1988) 2136.
8. H. Ichmura and A. Kawana : J. Mater. Res. 8 (1993) 1093.
9. D. McIntyre, J. E. Greene, G. Hakansson, J. E. Sundgren, and W. D. Munz : J. Appl. Phys. 67 (1990) 1524.
10. T. Ikeda and H. Satoh : Thin Solid Films 195 (1991) 99.
11. S. H. Lee, H. J. Ryoo, and J. J. Lee : J. Vac. Sci. Technol. A12 (1994) 1602.
12. S. H. Lee and J. J. Lee : J. Vac. Sci. Technol. A13 (1995) 2030.
13. S. H. Lee, B. J. Kim, H. H. Kim, and J. J. Lee : J. Appl. Phys. 80 (1996) 1469.
14. J. A. Thornton : J. Vac. Sci. Technol. 11 (1974) 666.