

Comparative Study of Effects of Alloying with Cu and TiN Addition in Ni-Matrix on Residual Stress and Microstructure

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AbstractIn this work, the effect of addition of alloying element (Cu) to Ni matrix on the microstructure and residual stress of Ni-TiN nanocomposite thin films has been investigated. These films were processed by magnetron co-sputtering of Ni, Cu and Ti targets using Ar:N₂ = 1:2 at substrate bias of -60 V. The grain size, RMS strain, residual stress as well as surface roughness have been measured, and compared with those of pure nanocrystalline Ni film as well as Ni-TiN nanocomposite thin films. The average grain sizes of Ni, NiCu and TiN have been found to be in the range of 13-14nm, 11-12 nm and 9-10nm, respectively. The residual stress has been found to become more compressive with the increase in Cu concentration in the Ni matrix and addition of TiN in the Ni matrix.

Key words: Magnetron Sputtering; Nanocomposite thin films; Residual stress; Microstructure

I. INTRODUCTION

In recent years, development of nanocomposite thin films has received significant world-wide attention, due to their excellent magnetic, mechanical, optical and physical properties compared to those of bulk materials. Particular attention has been paid to synthesis and characterization of the nanoparticle dispersed composites with either ceramic or metallic matrix. Researchers have noticed significant improvement in strength, when the average particle size or matrix grain size is reduced to nanoscale dimensions. Nanocomposite thin films having nanocrystalline (nc) TiN [1-4], (Ti,M)N (M = Al, Si, Zr, etc.) [5,6], ZrN or CrN [7] as the matrix with its grains being encapsulated by a few layers of amorphous (*a*) Ni for the purpose of controlling grain growth, increasing hardness, toughness and reduction of the compressive residual stress, have been developed as hard and wear resistant coatings for cutting tools. Furthermore, incorporation of the soft

metallic phase in TiN matrix is known to reduce the friction coefficient very significantly [5, 8]. An additional advantage of the TiN film is its metal-like electrical conductivity, besides its high hardness and elastic modulus [9-11]. But the main problem with the nanocomposite thin films is the development of huge amount of residual stress during their deposition. Therefore in the present study, the effect of addition of alloying element (Cu) to Ni matrix on the microstructure and residual stress of Ni-TiN nanocomposite thin films has been studied.

II. EXPERIMENTAL PROCEDURE

2.1 Processing

The nanocomposite films were deposited using a magnetron sputtering system (model KVS-T 4065, Korea Vacuum Tech., Gyeonggi-do, South Korea), equipped with one radio frequency (RF) and two direct current (DC) sources for sputtering. The sputter chamber was evacuated to a base pressure lower than 2×10^{-6} Torr using a rotary vane and turbo-molecular pump. For the purpose of sputtering, Ni and Ti targets with 99.9 % purity were used as raw materials. Furthermore, Ar and N₂ with 99.99 % purity were used as sputtering and reactive gases, respectively. The Ar to N₂ gas ratio was controlled by a throttle valve, whereas the chamber pressure was measured using an MKS Baraton gauge. The nanocomposite thin films were deposited on p-type Si (100) substrates, which were ultrasonically cleaned sequentially with acetone first and then with ethanol or isopropanol. The targets were pre-sputtered for about 5 minutes to remove surface oxides on the target to ensure purity of the films. To maintain the uniformity in the film thickness, the substrates were rotated at 25 rpm for all depositions. The parameters used for deposition of the Ni-TiN films are shown in Table 1.

TABLE 1 MAGNETRON SPUTTERING RELATED PROCESSING PARAMETERS

Processing parameters	Values
Base pressure	2.0x10 ⁻⁶ Torr
Working pressure	30 mTorr
Ar:N ₂	1:2
Ti RF Power	300 W
Ni DC Power	50 W
Cu DC Power	9 W
Substrate temperature	RT
Substrate bias	-60 V
Substrate Rotation Speed	25 rpm
Substrate to Target distance	150 mm

2.2 Characterization

The thicknesses of the as-deposited films were measured using a contact-type surface profilometer (Dektak 150 surface profiler, Veeco Instruments, Plainview, NY, USA) equipped with a diamond tip stylus having diameter of 12.5 μm, which was operated with a force of 3 mgf. For this purpose, the thin films were deposited by masking a portion of the substrate, and the stylus was passed across the interface between the masked and as-deposited zones to measure the step height in order to obtain the film thickness. The as-deposited Ni-TiNnanocomposite thin films were characterized using grazing incidence X-ray diffraction (XRD) with the help of a diffractometer (Philips X'Pert PRO Diffractometer, PANalytical, Almelo, The Netherlands) operated with accelerating voltage of 40 kV and current equal to 30 mA. The scans were performed using Cu K_α radiation (wavelength = 0.154 nm), keeping an angle of 1.5° between incident X-rays and specimen plane, while the detector was revolved between 35° and 65° with respect to the specimen at a speed of 0.05°/s. The XRD peaks were also analyzed to estimate the values of both average grain sizes. The grain sizes were estimated by analyzing the GIXRD peaks using the Williamson-Hall relationship [12]. Furthermore, the residual stress in the Ni-TiNnanocomposite thin films was measured with the help of a diffractometer in Bragg Brentano configuration (Bruker D8 Discover, Germany) by the Sin²Ψ technique as described in detail elsewhere [13-16]. The microstructures of nanocomposite thin films were investigated using a field emission scanning electron microscope (FESEM) (Model: Zeiss SUPRA 40, Carl Zeiss SMT GmbH, Oberkochen, Germany) operated at an accelerating voltage of 20 kV. The microstructure was observed using secondary electron (SE) and back scattered electron (BSE) imaging modes using the FESEM. In course of the microstructural studies, chemical analysis was carried out with the help of an energy dispersive x-ray (EDX) microanalyzer. Moreover, EDX maps

were recorded to locate the positions of enrichment of each of the constituent elements.

III. RESULTS

3.1 Chemical composition

The chemical compositions of the matrix in the Ni_{100-x}Cu_x-TiN nanocomposite films as determined by EDX analysis are x = 6, 10, 16, and

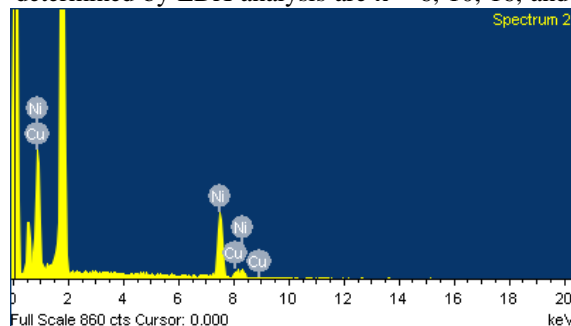


Fig. 1 EDX spectrum of NiCu alloy film.

TABLE 2 THE RATIOS OF NI:CU OBTAINED ON THE BASIS OF EDS ANALYSES AS WELL AS GROWTH RATES OF NI AND CU FILMS.

Cu target power (W)	Ni:Cu ratio on the basic of EDS analysis	Ni:Cu ratio on the basic of growth rate of Ni and Cu films
6	16.7:1	93.5:6.5
9	10.0:1	89.7:10.3
12	6.3:1	83.2:16.8
15	4.8:1	76.6:23.4

3.2 X-ray diffraction analysis

The results of XRD analysis of the NiCu-TiNnanocomposite thin films deposited using Ar to N₂ ratios of 1:2 and substrate bias of -60 V are shown in Fig.2. The XRD peaks from the thin films of Ni and Ni-TiNnanocomposite are included in this figure for the purpose of comparison. A shift in the Ni peak positions towards the lower 2θ angle is suggestive of increase in lattice constant due to the

formation of NiCu₁₀ alloys thin films, as shown in Fig. 2. The values of lattice constant measured from the positions of the XRD peaks shown in Fig. 2 have been plotted against Cu concentration in Fig. 3. The increase in lattice constant with increase in Cu content of the alloy is consistent with the predictions according to the Vegard's law. The average grain sizes of the Ni matrix and TiN calculated using Williamson-Hall relationship [12] are shown in Table 3. These values of grain size are less than those found for pure Ni. On the other hand, the RMS strain found for the NiCu₁₀-TiN nanocomposite film has been found to be significantly higher than the values found for Ni and Ni-TiN nanocomposite film.

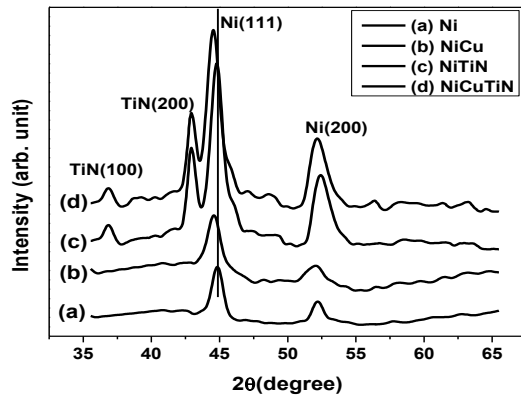


Fig.2. XRD patterns of nanocrystalline (a) Ni, (b) NiCu₁₀, (c) Ni-TiN, and NiCu₁₀-TiN thin films deposited at optimized conditions.

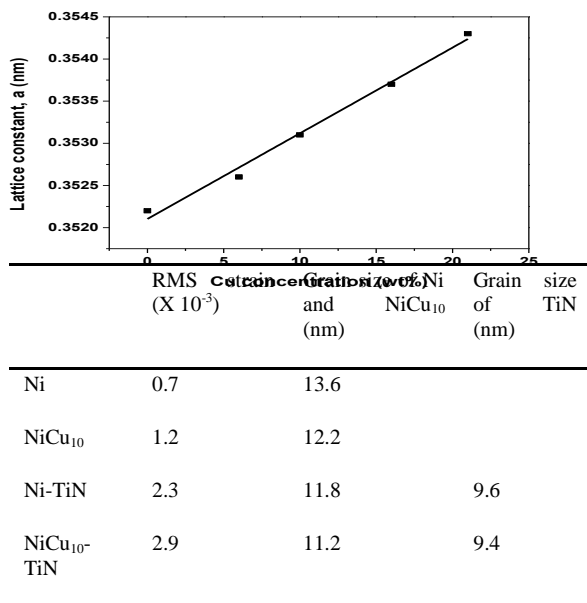


Fig.3. Variation of lattice constant with Cu concentration.

TABLE 3GRAIN SIZE AND RMS STRAIN OBTAINED FOR NiCu₁₀.

3.3 Residual stress

The values of principal normal residual stress (σ_1 and σ_2) in Ni, Ni-TiN and NiCu₁₀-TiN thin films as determined using the $\text{Sin}^2\psi$ technique, are shown in Table 3. Examination of the data presented in the Table 4, indicates that the average residual stress of the nanocrystalline nickel films is tensile, and this stress becomes on either addition of TiN as reinforcement or on alloying of the matrix.

Table 4 The comparison of average residual stress of Ni, Ni-TiN and NiCu₁₀-TiN thin films deposited at optimized condition.

Sample	Residual stress (GPa)	
	σ_1	σ_2
Ni	0.43	0.31
NiCu ₁₀	-0.62	-0.23
Ni-TiN	-1.53	-0.56
NiCu ₁₀ -TiN	-1.82	-0.91

3.4 Microstructure and surface roughness

The typical FESEM micrographs depicting the microstructure of Ni, NiCu₁₀, Ni-TiN, and NiCu₁₀-TiN nanocomposite films deposited using Ar:N₂ = 1:2 at substrate bias of -60 V are shown in Fig.4(a), (b), (c) and (d), respectively. A careful observation of this image shows the formation the clusters of grains, and also microstructure of composite films are appear to be finer and smother compare to pure Ni film. The plots of surface roughness obtained by AFM studies on of Ni, NiCu₁₀, Ni-TiN and NiCu₁₀-TiN nanocomposite films deposited using Ar:N₂ = 1:2 at substrate bias of -60 V is shown in Fig. 5. Examination of the results in this figure indicates that the surface roughness values of the nanocompositethin films are smaller than the pure Ni film.

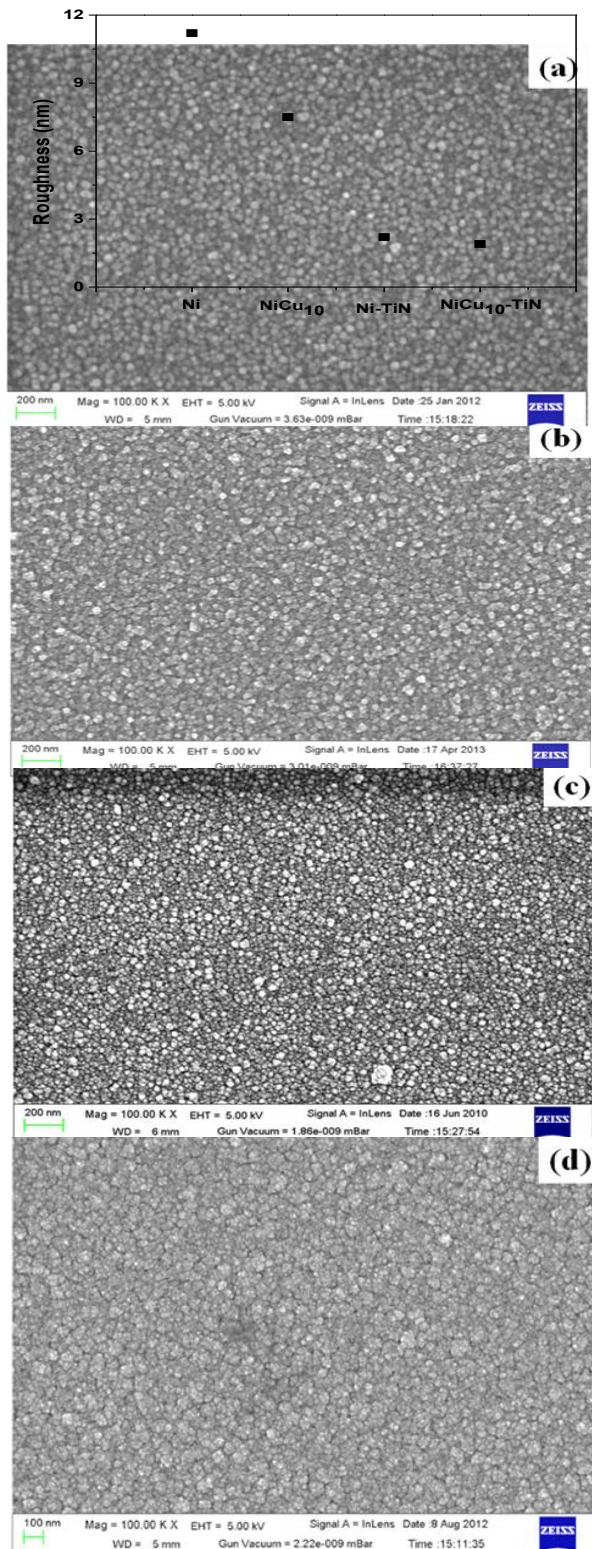


Fig. 4. FESEM micrograph depicting the microstructure of : (a) Ni, (b) NiCu₁₀, (c) Ni-TiN, and NiCu₁₀-TiN nanocomposite films deposited using Ar:N₂ = 1:2 at substrate bias of -60 V.

Fig. 5. Plots depicting the variation of surface roughness as measured by AFM, of Ni, NiCu₁₀, Ni-TiN and NiCu₁₀-TiN nanocomposite films deposited using Ar:N₂ = 1:2 at substrate bias of -60 V.

IV. DISCUSSION

The values of lattice constant measured from the positions of the {111} XRD peaks shown in Fig. 2(b) have been plotted against Cu concentration in Fig. 3. The results in this figure indicate that the lattice constant (a_0) increases with Cu content (C_{Cu}) of the Ni-Cu alloy films following a linear relationship obtained by regressional analysis:

$$a_0 = 0.3521 + 1.0162 * C_{Cu}(\text{at}\%) \quad (1)$$

where C_{Cu} is the concentration of Cu. The linear relationship between a_0 and C_{Cu} with $R^2 = 0.98$ as illustrated in Fig. 7.19 is consistent with the predictions of the Vegard's law. The observed increase in lattice constant of Ni-Cu alloy with increase in Cu concentration may be attributed to higher atomic radius of Cu (≈ 0.128 nm) than that of Ni (≈ 0.124 nm).

The compressive character of residual stress observed on alloying of Ni with Cu may be attributed to greater size of the latter type of atoms, which in turn lead to increase in the lattice constant and therefore the unit cell volume. Moreover, additional amount of shot peening caused by the bombardment of the neutral atoms sputtered from the Cu target could be also responsible for the compressive nature of stress. Higher RMS strain on alloying with Cu could be attributed to the increase in the amount of average variation of atomic position from their original positions in Ni lattice because of higher atomic radius of the former type of atoms. Examination of the results in Fig. 4 indicates that the surface roughness decreases in the following order: Ni > Ni₉₀Cu₁₀ > Ni-TiN > Ni₉₀Cu₁₀-TiN. It is interesting to note that the surface roughness of the Ni₉₀Cu₁₀ alloy and Ni-TiN nanocomposite films is lower than that of Ni by $\approx 33\%$ and $\approx 80\%$, respectively. This trend may be attributed to lower growth rates of both alloy and nanocomposite films compared to that of pure Ni. As discussed in the earlier chapters, lower growth rate enables redistribution of the adatoms leading to a more uniform growth and decrease in surface

roughness. Decrease in surface roughness may also be attributed to decrease in the Ni content of the films on alloying with Cu or TiN addition.

V. CONCLUSIONS

A comparative study has been carried out on microstructure and residual stress of the nanocrystalline films of pure Ni and Ni₉₀Cu₁₀ alloy, as well as Ni-TiN and Ni₉₀Cu₁₀-TiN nanocomposites. Alloying of Ni with Cu was carried out by co-sputtering of Ni and Cu targets as DC sources, whereas Ti target was used as RF source. All the sputtering experiments were carried out using Ar:N₂ = 1:2 at ambient temperature using substrate bias of -60V. The nanocrystalline Ni thin films have been found to possess tensile residual stress, which is transformed to compressive on alloying with copper and/or TiN addition.

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REFERENCES

- [1] M. Misina J. Musiland S. Kadlec, "Composite TiN-Ni thin films deposited by reactive magnetron sputter ion-plating", Surf. Coat. Technol. Vol.110,pp.168-172,1998.
- [2] A. Akbari, J.P. Riviere, C. Templier and E.L. Bourhis, "Structural and mechanical properties of IBAD deposited nanocomposite Ti-Ni-N coatings", Surf. Coat. Technol. Vol.200,pp. 6298-6302, 2006.
- [3] A. Akbari, J.P. Riviere, C. Templier, E.L. Bourhis and G. Abadias, "Hardness and residual stresses in TiN-Ni nanocomposite coatings deposited by reactive dual ion beam sputtering", Rev. Adv. Mater. Sci. Vol.15,pp.111-117, 2007.
- [4] S. Zhang, D. Sun, Y. Fu, Y.T. Pei and J.Th.M. De Hosson, "Ni-toughened nc-TiN/a-SiNx nanocomposite thin films", Surf. Coat. Technol. Vol.200,pp. 1530-1534,2005.
- [5] Z.G. Li, S. Miyake, M. Kumagai, H. Saito and Y. Muramatsu, "Hard nanocomposite Ti-Cu-N films prepared by d.c.reactive magnetron co-sputtering", Surf. Coat. Technol. Vol.183,pp. 62-68, 2004.
- [6] A. Akbari, C. Templier, M.F. Beaufort, D. Eyidi and J.P. Riviere, "Hard and tough nanocomposite TiN-Ni coatings deposited by reactive ion beam assisted deposition", Surf. Coat. Technol. Vol.206(5), pp.972-975, 2011.
- [7] P. Karvankova, H.D. Mannling, C. Eggs and S. Veprek, "Thermal stability of ZrN-Ni and CrN-Ni superhard nanocomposite coatings", Surf. Coat. Technol. Vol.146-147, pp.280-285, 2001.
- [8] J. Musil and J. Vlcek, "Magnetron sputtering of hard nanocomposite coatings and their properties", Surf. Coat. Technol. Vol.142-144 pp.557-566, 2001.
- [9] P. Patsalas, C. Gravalidis and S. Logothetidis, "Surface kinetics and subplantation phenomena affecting the texture, morphology, stress, and growth evolution of titanium nitride films", J. Appl. Phys. Vol.96(11), pp.6234-6246,2004.
- [10] G. Abadias, "Stress and preferred orientation in nitride-based PVD coatings", Surf. Coat. Technol. Vol. 202, pp.2223-2235, 2008.
- [11] A. Misra and M. Nastasi, "Limits of residual stress in Cr films sputter deposited on biased substrates", Appl. Phys. Lett. Vol.75, pp.3123-3125, 1999.
- [12] G.K. Williamson and W.H. Hall, "X-ray line broadening from filed aluminium and wolfram", Acta Metall. Vol.1(1), pp.22-31, 1953.
- [13] M. Kumar, S. Mishra and R. Mitra, "Effect of Ar:N₂ ratio on structure and properties of Ni-TiN nanocomposite thin films processed by reactive RF/DC magnetron sputtering", Surf. Coat. Technol. Vol. 228, pp.100-114, 2013.
- [14] M. Kumar and R. Mitra, "Effect of substrate bias on microstructure and properties of Ni-TiN nanocomposite thin films deposited by reactive magnetron co-sputtering", Surf. Coat. Technol. Vol.251,pp.239-246, 2014.
- [15] M. Kumar and R. Mitra, "Effect of substrate temperature and annealing on structure, stress and properties of reactively co-sputtered Ni-TiN nanocomposite thin films", Thin Solid Films Vol.624, pp.70-82, 2017.
- [16] B.D. Cullity, Elements of X-ray diffraction, Second Edition, Addison-Wesley Publishing Company, Inc., Reading, MA, 1978, Chap. 9, p. 281, 447.