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Hardness and Young's Modulus of Titanium Nitride Films Deposited onto Stainless Steel by Ion Beam Assisted Deposition

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Titanium nitride films were deposited on stainless steel by an ion beam assisted deposition technique. Hardness and Young's modulus were measured for the deposited TiN films. They depended weakly substrate temperature although it depended strongly on nitrogen ion energies. This similar relation is because hardness and young modulus reflect the bond strength of atoms consisting matters. The highest hardness was measured on TiN films deposited with the 1 keV nitrogen ion beams regardless of deposition temperatures.

Key words: Titanium nitride, Stainless steel, Hardness, Young's modulus, IBAD

1. Introduction

Stainless steel has high resistance for corrosion although its hardness is not sufficient for application to machinery area [1]. This disadvantage can be improved by sophisticatedly coating the surface of stainless steel with hard thin films such as titanium nitride (TiN). Titanium nitride (TiN) is used as a material in advanced surface protective coating area for steels [2]. Hardness of the matter is a function of lattice energy. The stronger the bond forces between elements, then naturally the harder the matter and the more difficult it is to rupture it. On the other hand, Young's modulus is defined as a ratio of stress and strain for tensile stress acting in one direction with the sides of specimen left free. Thus, they relate through lattice energy.

Physical vapor deposition is a modern material technology for coating steel with hard thin film. Metal species is vaporized and they react with ionized gaseous species to coat stainless steel surfaces with desired compounds. The gaseous species is ionized to ensure a fully dense and well-adhered hard coating on stainless steel surfaces [3]. We had an interest for the fact whether hardness and Young's modulus of deposited TiN films are modified with the large energy deposition.

2. Experimental details

Ion beam assisted deposition (IBAD) used for this experiment was constructed basically from an electron beam evaporator for Ti evaporation and an electron cryotron resonance (ECR) ion source for N ionization. Ionized N particles were accelerated to the energy of 0.5-2.0 keV. The beam intensity was held constant to 0.1 mA/cm^2. The substrate holder was continuously rotated to achieve uniform hard coating. The background pressure was lower than 4 x 10^{-5} Pa. Titanium nitride films were deposited on stainless steel in vacuum of ~ 10^{-2} Pa at substrate temperatures of 400 ~ 770 °C for 60 min. The surfaces of austenite stainless steel SUS304 with a size of 20 x 20 x 0.5 mm were scoured with a 0.3 μm-diamond paste and successively were polished with a puff. The stainless steel was a polycrystal preferred to the <111> direction. The samples were rinsed in alcohol, acetone, and solvent naphtha, and charged into the apparatus immediately after rinsing with deionized water. The thickness of the deposited TiN films was measured using a laser probe roughness tester and was in a range from 1.5 to 2.2 μm. The prepared samples were examined using X-ray diffraction (XRD) with $Cu_{K\alpha}$ excitation radiation in Seeman-Bohlin geometry at an incident angle of 5°. Hardness was measured under unloading in the range from 5 gf to 150 gf at a rate of 0.2 gf/s using a dynamic ultra microhardness tester.

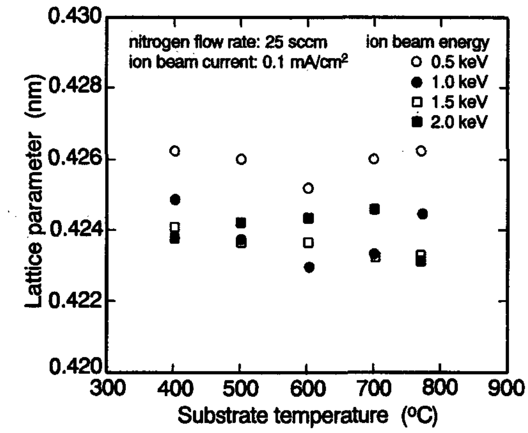

Fig. 1. The dependence of lattice parameters of TiN films on N ion-beam energy and substrate temperature.

3. Experimental results and discussion

Figure 1 shows the dependence of lattice parameters of TiN films on N ion-beam energy and substrate temperature. The deposited TiN films were a polycrystal. The lattice parameters became smaller with increasing substrate temperature, reached minimum at 600°C, and again became larger. The lattice parameters were significantly dependent on N ion-beam energy rather than substrate temperatures. It seems that the substrate temperatures were not high for making a serious change in the lattice parameters. The N ion-beam energy and substrate temperature dependences of the lattice parameter were resulted from the fact that the TiN films have shortened or expanded to the <111> direction. Titanium nitride deposited with N ion-beam energies higher than 1.0 keV had lattice parameters smaller than the standard lattice parameter of 0.42416 nm [4], while that deposited with N ion-beam energies of 0.5 keV had lattice parameters larger than the standard lattice parameter. It is found that irradiation of energetic ion particles leaves larger stress in the deposited films as reported by many people [5].

Hardness for a sample consisting of a thin film with a hardness of H_f and a thickness of δ and a substrate with a hardness of H_s and a thickness d can be approximated by an equation of $(H_m - H_s) \fallingdotseq (2k\delta H_f)/D$ [6]. Here, D is (δ + d), H_m is the measured hardness and k is 0.13/GPa (on assumption that hardness is proportional to abrasive wear resistance with 0.13/GPa). The relationship between H_m and 1/D was measured by varying the set-testing load of the tester. Figure 2 shows the dependence of hardness H_f on substrate temperature and N ion-beam energy. The hardness for the deposited TiN films increased with increasing N ion-beam energy, reached maximum at 1 keV, and then decreased. The obtained hardness was in the range from 300 to 530 GPa larger than about 170 GPa for bulk TiN [7]. The similar

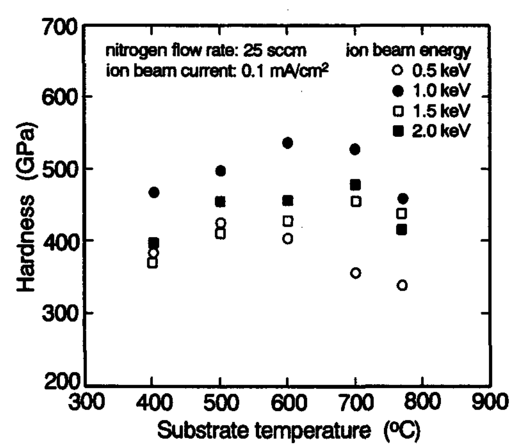

Fig. 2. The dependence of hardness H_f for TiN films on substrate temperature and N ion-beam energy.

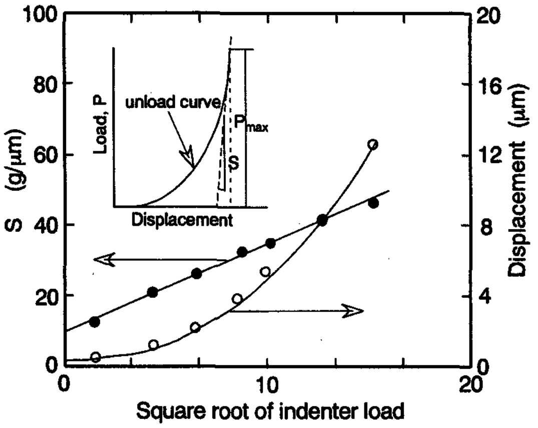

Fig. 3. Determination of S and A. The insert shows a load-displacement curve.

large hardness is well seen for TiN films deposited using technique assisted by energetic ion-beams because stress was induced into the TiN films by collision of energetic N particles during deposition [7]. On the other hand, the hardness for the deposited TiN films increased gradually with increasing substrate temperature, reached maximum at 600°C, and decreased. A decrease in hardness started to occur at a substrate temperature of 700°C, corresponding to the formation of compounds such as $C_7H_6N_4$ and $C_2H_5N_5$, CrFe in stainless steel starts [5].

The investigators used instrumented microhardness testing machines to obtain a load-displacement curve as shown schematically in the insert in Fig. 3. Here, P_{max} is the prefixed load and S is the slope of a line tangent to the load-displacement curve at P_{max}. The indentation load-displacement data was then analyzed according to the following equation [8]: $S = (\Delta W/\Delta d) = (2/\sqrt{\pi})E_r\sqrt{A}$. Here, $S = (\Delta W/\Delta d)$ is the experimentally measured stiffness of the upper portion of the unloading data, A is the projected area of the elastic contact, and E_r is the reduced modulus defined as $1/\{[(1-v^2)/E] + [(1-v_i^2)/E_i]\}$ where v and E are Poission's ratio and Young's modulus for the specimen and v_I and E_i are the same parameters for the indenter. In this experiment, the hardness of the thin TiN films was obtained on the assumption that hardness is proportional to abrasive wear resistance [5]. In order to obtain Young's modulus of the thin TiN films, the values of S and A are obtained by extrapolating measured data to a very light testing load as shown in Fig. 3. In this case that the diamond indenter is thrusting with contact with stainless steel as substrate and abrasively contact with the thin TiN film, the young's modulus is approximated as the equation $1/E_r = (1 - v_f^2)/E_f + (1 - v_s^2)/E_s + (1 - v_d^2)/E_d$, where the suffixes, f, s, and i are for the thin film, the substrate, and the indenter, respectively. The Young's modulus for the thin film is obtained from the indentation load-displacement curve on the assumption that hardness is proportional to abrasive wear resistance [5].

Figure 4 shows the dependence of Young's modulus on N ion energy and substrate temperature for deposited TiN films. The $(1 - v_f^2)/E_f$ values were calculated using $v_s = 0.28$ and $E_s = 172$ GPa for stainless steel [9] and $v_d = 0.07$ and $E_d = 1141$ GPa for diamond indenter [10]. Moreover, the Poisson's ratio of 0.25 was used for the deposited TiN films [11]. The obtained Young's modulus was smaller than 400 GPa for bulk TiN [11], and depended strongly on both of N ion energy and substrate temperature. The small Young's modulus is due to the

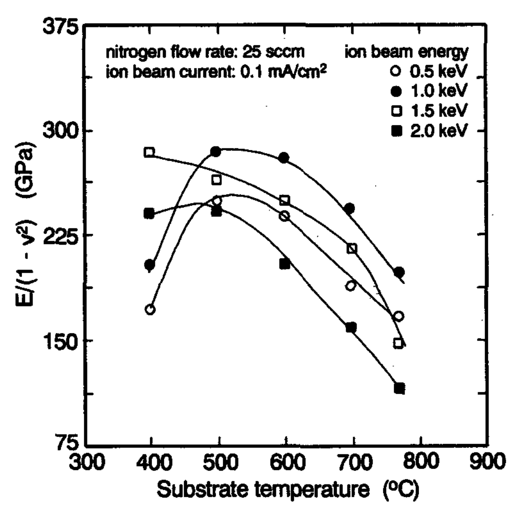

Fig. 4. Young's modulus for deposited TiN films.

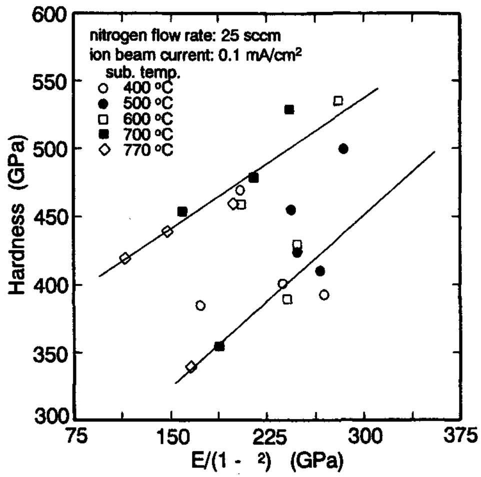

Fig. 5. Hardness as a function of Young's modulus.

measurement technique of the abrasive wear resistance. The Young's modulus decreased with increasing substrate temperature, and the maximum Young's modulus was measured on the TiN films prepared with the N ion-beam energy of 1.0 keV except 400 °C.

Hardness depended on Young's modulus as shown in Fig. 5. On TiN films deposited with the N ion-beam energy of 0.5 keV, more plots of hardness and Young's modulus fell on the lower straight line in Fig. 5. On the other hand, those for TiN films deposited with the N ion-beam energies above 1.0 keV fell on the upper straight line.This suggests that a rise of substrate temperature accompanies relax deposited kinetic energy. Thus, it seems that hardness of deposited TiN films is determined with competition between energy relaxation and energy acquisition. Furthermore, hardness was significantly influenced with radiation damages produced in the TiN films.

4. Conclusion

Hardness and Young's modulus were measured for the deposited TiN films by the IBAD technique. The lattice parameters became smaller as the Young's modulus increased. However, the lattice parameters for TiN films deposited with the N ion-beam energy of 0.5 keV were larger than that for TiN films deposited above 1.0 keV irrespective of the same Young's modulus. The energy with N ions irradiated on the TiN films is required to exceed a threshold value for contributing to shortening bond length. The threshold ion-beam energy is found to be 1.0 keV. Hardness of deposited TiN films is determined with competition between energy relaxation and energy deposition. Furthermore, hardness was significantly influenced with radiation damages produced in the TiN films since hardness depended on nitrogen ion beam energy.

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