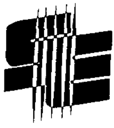

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Deposition of (Ti,Cr,Zr)N-MoS_2 Thin Films by D.C. Magnetron Sputtering

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Abstract

As technology advances, there is a demand for development of hard solid lubricant coating. (Ti,Cr,Zr)N-MoS_2 films were deposited on AISI H13 tool steel substrate by co-deposition of MoS_2 with (Ti,Cr,Zr)N using a D.C. magnetron sputtering process. The influence of the N_2/Ar gas ratio, the amount of MoS_2 in the films and the bias voltage on the mechanical and structural properties of the films were investigated. The highest hardness level was observed at the N_2/Ar gas ratio of 0.3. Hardness of the films did not change much with the increase of the MoS_2 content in the films. As the substrate bias potential was increased, hardness level of the film reached maximum at −150 V. Surface morphology of these films indicated that high hardness was attributed to the fine dome structure

Keywords: Solid lubricant coating, (Ti,Cr,Zr)N-MoS_2 films, Magnetron sputtering

1. Introduction

Development of new coatings have been undertaken actively to replace existing electroplated films and to increase the durability of tools, dies and mechanical parts. Nitrides such TiN, CrN, TiAlN have been studied a lot since the films have high hardness and wear resistance.

Friction and wear degrades the function and the durability of machine parts. Liquid lubricants have been used to decrease the wear of these operating parts. However, liquid lubricants are expensive and pose an environmental concern for disposal. Solid lubricant such as MoS_2[1-4] has been exploited a lot to replace the liquid lubricants. We can pursue two different ways to achieve hard solid lubricated coatings. One way is to deposit a solid lubricated film on the hard films[5]. The other way is to incorporate a solid lubricant in a hard coating[6]. Carrera *et al.*[5] reported CrN/MoS_2 coating. They deposited CrN film first and MoS_2 film was subsequently deposited. Incorporation of MoS_2 in a TiN matrix by D.C magnetron sputtering co-deposition has been studied by Gilmore *et al.*[6]. Previously we reported incorporation of MoS_2 in a CrN matrix[7] and in a (TiCr)N matrix[8] by D.C magnetron sputtering. We extended this work by incorporation of MoS_2 in (TiCrZr)N matrix. The influence of the process parameters on the mechanical and structural properties of (Ti,Cr,Zr)N-MoS_2 thin films was investigated.

2. Experimental Detail

The (Ti,Cr,Zr)N-MoS_2 films were deposited on AISI H13 tool steel (1.5%C, 11.5%Cr. 0.8%Mo, 0.9%V) substrate by an unbalanced D.C. magnetron sputtering system. A schematic diagram of the experimental apparatus is shown in Fig. 1. One sputter source fitted with a titanium target (diameter of 12 mm) and the other with a MoS_2 target (diameter of 76.2 mm) were installed facing each other on each side of the chamber wall. On Ti target, six chromium pellets (diameter of 7 mm) and six zirconium pellets (diameter of 7 mm) were attached alternately. The voltage and current applied to the TiCrZr target and MoS_2 target were

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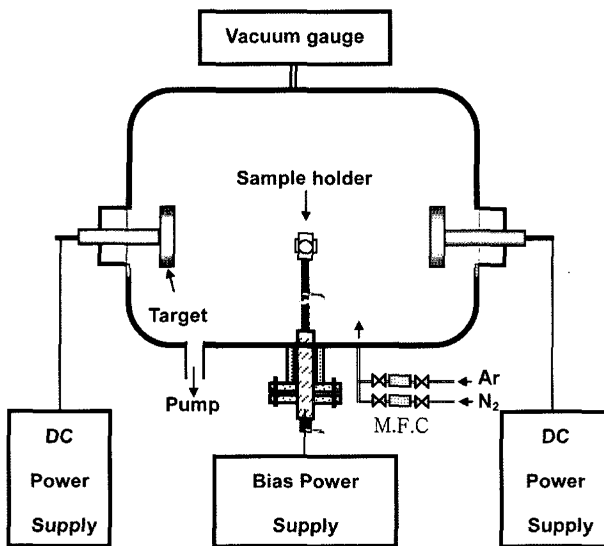

Fig. 1. Schematic diagram of the experimental apparatus.

420 V, 3 A and 290 V and 0.25 A, respectively. A substrate holder, which could be rotated while applying bias voltage was located at the center of the chamber. The distance from the substrate to the Ti target and MoS_2 target were 95 mm and 200 mm, respectively. The AISI H13 steel specimens were manually ground and polished with 1500-grit SiC papers using a low speed polishing machine and degreased ultrasonically in alcohol. The base pressure achieved by a rotary pump and a diffusion pump before deposition was below 1.33×10^{-4} Pa. Argon gas mixed with nitrogen gas at a predetermined ratio was introduced to chamber to maintain working pressure (0.27 Pa). Before deposition, the substrate was sputter etched with argon plasma at a pressure of 113.32 Pa for 40 min with current of 600 mA. The voltage and current applied as bias potential during the sputter etching was −350 V and 0.6 A.

To determine the effect of nitrogen partial pressure, the N_2/Ar gas ratio of inlet gases was varied from 0.3 to 0.6. By varying the current ratio of MoS_2 to TiCrZr, the influence of MoS_2 content of the film on the structural and mechanical properties of (Ti,Cr,Zr)N-MoS_2 film was investigated.

The phases and chemical composition of the films were determined by an X-ray diffractometer (Rigaku, RAD-3C) and an electron probe microanalyzer (EPMA-1400, Shimadzu). Morphology was observed by a field emission scanning microscope (JEOL, JSM-820). A computer-controlled nanoindentor (MTS, Nanoindentor XP) equipped with Berkovich diamond indentor was used to measure the hardness of the films. The continuous stiffness measurement method was employed.

3. Results and Discussion

The hardness levels of the (Ti,Cr,Zr)N-MoS_2 films deposited at various N_2/Ar gas ratios of inlet gases are shown in Fig. 2. The TiCrZr target current and the MoS_2 target current were kept constant at 3.00 A and 0.25 A, respectively. Although the films did not exhibit high hardness in general, the highest hardness level was observed at the N_2/Ar gas ratio of 0.3 and the hardness decreased with the increase of the N_2/Ar gas ratio. Both nitrogen ions and argon ions are present in the plasma. The energy of argon ions is higher than that of nitrogen ions. Lower ratio of N_2/Ar (N_2/Ar=0.3) implies that the concentration of argon ion in the plasma is high which means higher energy is transferred to the substrate to grow the films. Fig. 3 shows XRD diffractograms of (Ti,Cr,Zr)N-

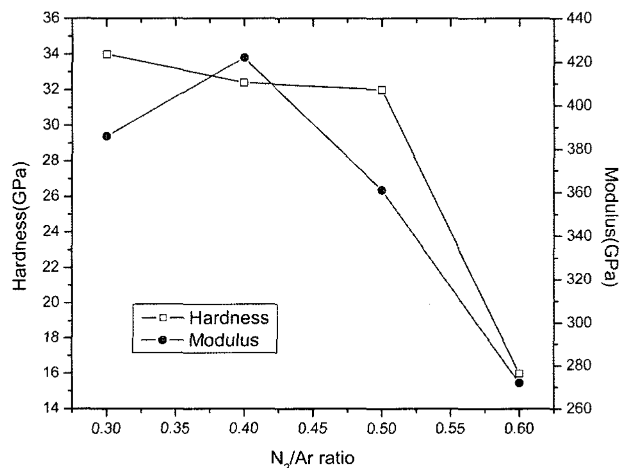

Fig. 2. Hardness of N_2/Ar on (Ti, Cr, Zr)N-MoS_2 films deposited at various N_2/Ar gas ratios.

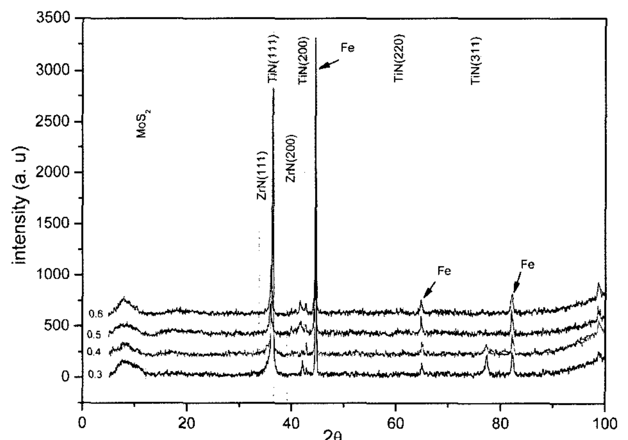

Fig. 3. XRD diffractograms of (Ti, Cr, Zr)N-MoS_2 films deposited at various N_2/Ar gas ratios.

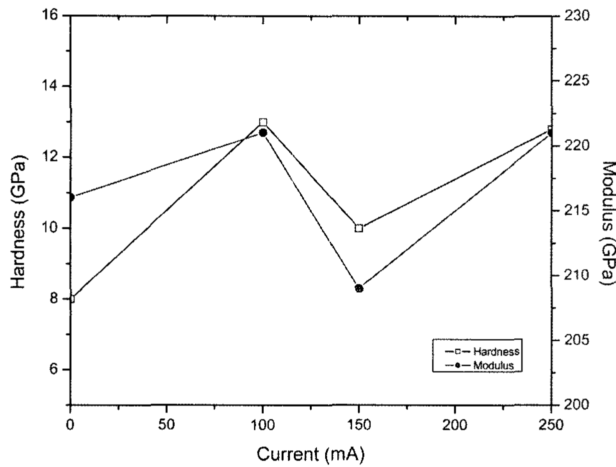

Fig. 4. Hardness of (Ti, Cr, Zr)N-MoS_2 films deposited at various MoS_2 currents (P 0.27 Pa, TiCrZr current 3 A, Bias 0 V, N_2/Ar 0.3).

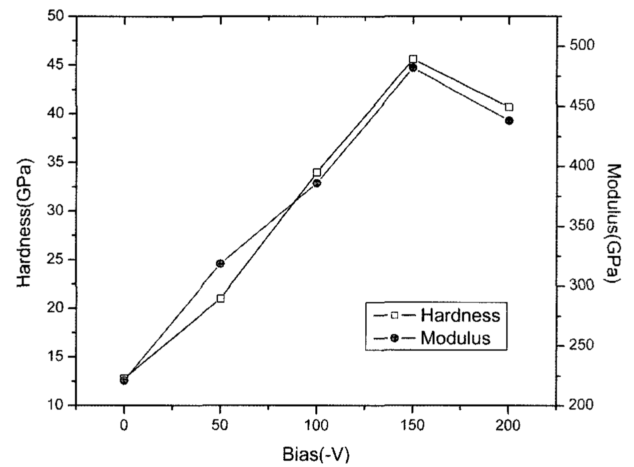

Fig. 6. Hardness of (Ti, Cr, Zr)N-MoS_2 films deposited at various bias voltage (P 0.27 Pa, TiCrZr current 3 A, MoS_2 current 0.25 A, N_2/Ar 0.3).

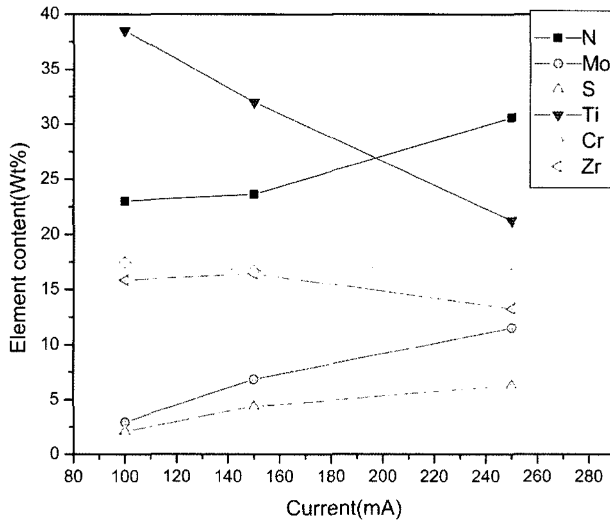

Fig. 5. EPMA analysis of (Ti, Cr, Zr)N-MoS_2 films at various MoS_2 currents.

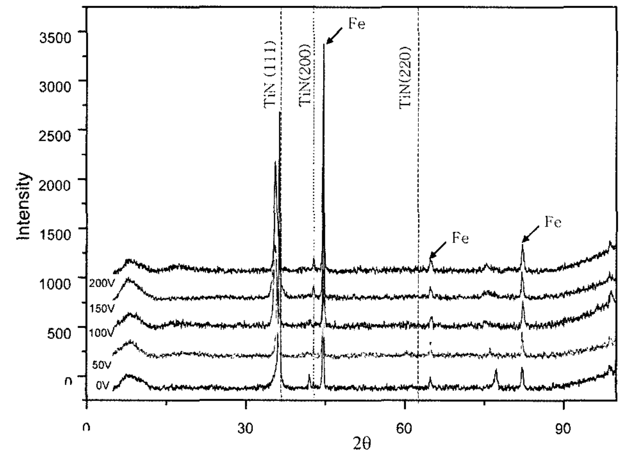

Fig. 7. XRD diffractograms of (Ti, Cr, Zr)N-MoS_2 films deposited at various bias voltage.

MoS_2 films deposited with various N_2/Ar gas ratio. At the ratio of $N_2/Ar = 0.3$, the intensity of preferred XRD peak was stronger which means more crystalline metal nitrides are formed resulting in the increase of the hardness of the films. The intensity of preferred XRD peaks decreased with further increase of the N_2/Ar gas ratio.

MoS_2 content in the composite film was varied by applying different currents to the MoS_2 target. Hardness of the (Ti,Cr,Zr)N-MoS_2 films deposited with various MoS_2 current is shown in Fig. 4. Hardness of the film fluctuated between 8 GPa to 13 GPa. EPMA analysis of (Ti,Cr,Zr)N-MoS_2 films deposited with various MoS_2 currents is shown in Fig. 5. Ti and Zr decreased whereas N, Mo and S increased with the increase of MoS_2 current.

(Ti,Cr,Zr)N-MoS_2 films were deposited with the change of the bias voltage up to −200 V. The hardness of these films was shown in Fig. 6. Hardness of the films increased with the increase of bias voltage reaching 45 GPa at −150 V. Further increase of the bias voltage decreased the hardness of the films. According to Hall-Petch theory, the hardness of materials increases with the decrease of the grain size. This model is valid within the grain size of about several ten to several hundred nanometers. Fig. 7 shows XRD diffractograms of (Ti,Cr,Zr)N-MoS_2 films deposited at various bias voltage. The approximate grain size calculated from XRD peaks by the Scherrer's formula is about 10 nm (grain size of the film deposited at −150 V) and 32 nm (grain size of the film deposited at 0 V). The dependence of hardness and broadening peak on bias voltage is shown in Fig. 8. The bias voltage of −150 V gave the most broadened peak

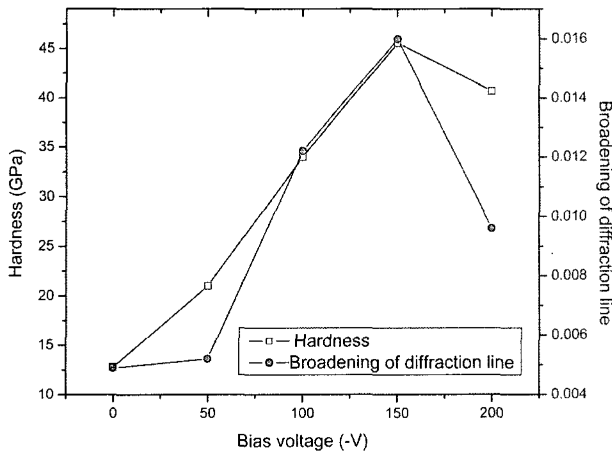

Fig. 8. Hardness and broadening XRD peaks of (Ti, Cr, Zr)N-MoS_2 films deposited at various bias voltage.

and exhibited the highest hardness.

Surface morphology of films deposited at various bias voltages was shown in Fig. 9. Dome structure was not developed without applying bias voltage. Coarse dome structure was developed at –50 V. Dome structure became fine with the increase of bias voltage resulting in the increase of the hardness. At –200 V, dome structure collapsed exhibiting the decrease of the hardness of the films. Similar phenomena relating the dome structure with the hardness was observed previously in the deposition of NbN thin films[9] and TaN thin films[10]. The formation of dome structure on the surface of the thin films can be influenced by various factors such as pressure, deposition temperature, atomic nitrogen concentration on the growth surface and chemical activity of metal species and so on. Further work is needed to delineate the mechanism of dome formation on the film surface.

4. Conclusion

(Ti,Cr,Zr)N-MoS_2 films were deposited on AISI H13 tool steel using an unbalanced D.C. magnetron sputtering system. The highest hardness level was observed at the N_2/Ar gas ratio of 0.3. Hardness of the films did not change much with the increase of the MoS_2 content in the films. As the substrate bias

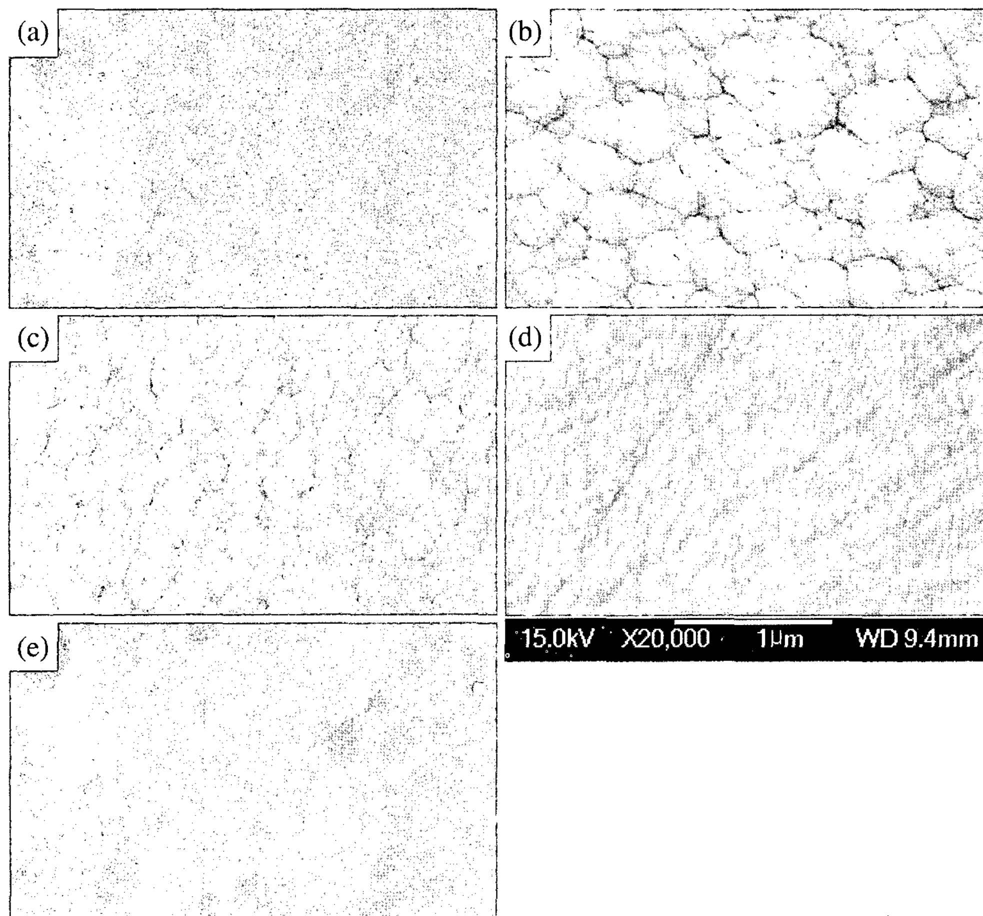

Fig. 9. Surface morphology of (Ti, Cr, Zr)N-MoS_2 films at various bias voltage. (a) 0 V, (b) –50 V, (c) –100 V, (d) –150 V, (e) –200 V.

potential was increased, hardness level of the film increased reaching a maximum value at -150 V and then decreased. Surface morphology of these films indicated that high hardness was attributed to the fine dome structure.

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