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Structural and Mechanical Properties of Fibre Textured Ti-C-N Coatings

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ABSTRACT
Ti-C-N hard coatings were deposited on high speed steel substrates using reactive magnetron sputtering. Surface morphology and cross section micrographs have shown dense columnar microstructure. Compressive stresses were created in the coatings by increasing substrate bias during the deposition at various thicknesses of coatings. Decrease in compressive stress with depth was observed in depth dependent stress study using grazing incidence X-ray diffraction study. Pole figure analysis of the coatings confirmed the strong (111) fibre texture. Mechanical properties of coatings are evaluated using nano indentation. Average hardness and modulus values obtained are 34 GPa and 310 GPa, respectively. Post-mortem analysis of Vickers indented zone shows revealed concentric square cracks.

Key words: Structural, mechanical fiber, coatings

INTRODUCTION
Transition metal carbides and nitrides, especially Ti-C-N coatings are known tribological coatings for increasing the performance of tools owing to their high hardness, thermal stability and chemical inertness (Lengauer, 2000). Most of the commercially available coatings are deposited using arc evaporation or magnetron sputtering technique (Sanchette *et al.*, 2011; Musil and Vlcek, 1999). Generally, high hardness materials have been produced in single phase materials by enhancing residual compressive stresses in materials (Lin *et al.*, 2008). Constant compressive stress throughout the coating and abrupt variation in stresses could result peel-off of coating at lower contact stresses (Moon *et al.*, 2002). Whereas creating compressive stress gradient in coatings gives rise to high damage resistance to coatings even at high contact stresses. Compressive stress-gradient in the coatings makes cracks to bend, thus impeding the cracks penetration into the substrates. Compressive stress on coating's surface imparts high deformation strength by arresting the interfacial cracks that are produced due to thermal stresses (created under operation) (Pender *et al.*, 2001; Fischer and Oettel, 1997). Therefore deposition of coatings with compressive stress gradient is crucial. This can be achieved by tuning substrate bias voltage in sputtering deposition of hard coatings (Fischer and Oettel, 1997).

In this study, we report the deposition of compressive stress gradient coatings through ion bombardment during the growth. Depth profile of stress in the coatings was evaluated by employing Grazing Incidence X-ray Diffraction (GIXRD). Mechanical properties of the coatings were investigated using micro and nanoindenation techniques.

METHODOLOGY

HSS steel samples are degreased and loaded into deposition chamber. Prior to deposition, ion cleaning of the substrate was carried out to remove adsorbed dust from atmosphere. e $TiC_{0.8}N_{0.2}$ coatings were deposited using reactive magnetron sputtering. Ti is sputtered in methane and nitrogen environment at 200°C to obtain films of thickness 4 μm. Compressive stresses in the coatings were varied by increasing negative biasing voltage to the substrate. During the process, up to 1 μm coating -40 V bias was used and from 2-4 μm the biasing gradually increased from -40-120 V. The phase composition of Ti-C-N systems was investigated by GIXRD using Cu K_a characteristic X-ray radiation. Additionally, the GIXRD technique was used to evaluate depth profile of stresses in coating. The orientation alignment of the thin film on HSS substrates was characterized by X-ray diffraction measurements (Cu K_a characteristic X-ray radiation) with a four-circle goniometer. Using an Eulerian cradle, the pole figures were measured at a fixed detector position of $2O_{hkl}$ by rotating the deposited film around α- axis normal (azimuth angle ϕ) and parallel (polar angle Ψ) to the substrate. Step widths of the azimuth and polar angles were 3°.

Mechanical properties of the films were investigated using a nanoindenter (Triboindenter of Hysitron, Minneapolis, USA) with low load and high load transducer. The machine continuously monitors and records the applied load, P and displacement, h, of the indenter into sample surface. Force and displacement resolutions were 100 nN and 1 nm, respectively. Berkovich (three sided pyramidal) diamond indenter with a tip radius of ~100 and ~500 nm was used to indent the films with loading and unloading rates of 0.8 and 3 mN sec^{-1}, respectively. The 3 sec of hold time at peak load was maintained. A minimum of ten indentations were performed. To avoid the overlapping of plastic zones of two neighbouring indentations, a distance of 10 times the diagonal length of the indentation was maintained between two indentations. Surface fracture mode in the coating was studied using CSM micro indenter where Vickers indenter with tip radius of 2 μm was used. Post-micro indented surface micrographs were captured using scanning electron microscope.

RESULTS AND DISCUSSION

Variation of (111) peak intensity of Ti-C-N coatings with grazing angle (incident angle, α) from 0.5 to 9° is shown in Fig. 1. For all the incident angles, (111) peak intensity remains high and during the growth strain energy minimization is predominant. Pole figure diagram of (111) peak is presented in Fig. 2 and it indicates the formation of fibre texture. Generally, for NaCl type Transitional Metal Carbonitride (TMCN) systems, texture evolves in (111) and (200) direction during the growth. Texture selection is governed by surface or strain energy minimization. For instance, in NaCl type TMCN system, strain energy minimization occurs in (111) plane whereas surface energy minimization in (200) (Zhao *et al.*, 1997; Carel *et al.*, 1996). Residual stresses in the coating were evaluated using non-symmetric X-diffraction method (d-Sin^2 Ψ) method (Ma *et al.*, 2002). Obtained compressive residual stress in the coatings and its variation with grazing angle is plotted in Fig. 3. Compressive stress reduced with increasing the grazing angle. Reduction in the compressive stress with depth is attributed to reduction in low energy ion bombardment at lower thickness. Origin of compressive stress in the coating is due to atomic penning effect (D'Heurle and Harper, 1989). Enhancing the compressive stress on top surface produces higher hardness than the subsurface. Gradient in the hardness and modulus makes the cracks to bend thus hindering them to reach the substrate.

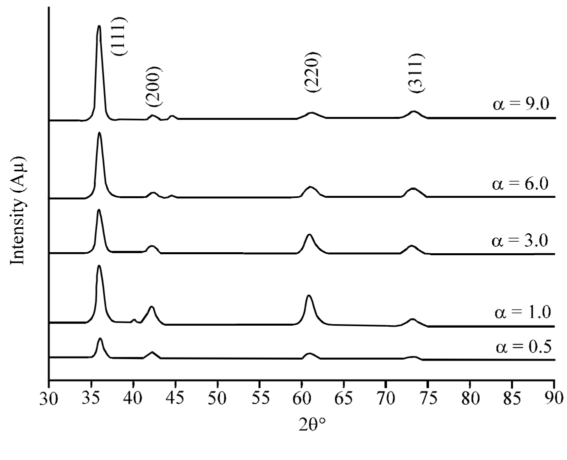

Fig. 1: Variation of (111) peak intensity with different grazing angle incidence

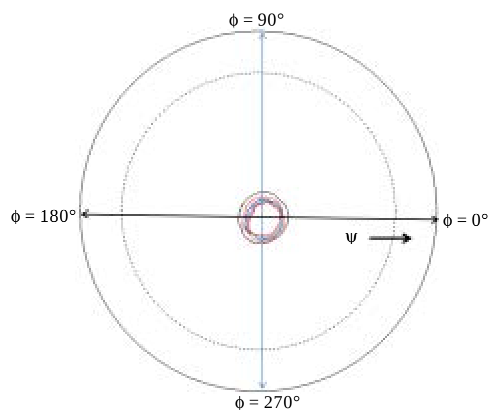

Fig. 2: Representative fibre texture (111) pole figure for Ti-C-N coating

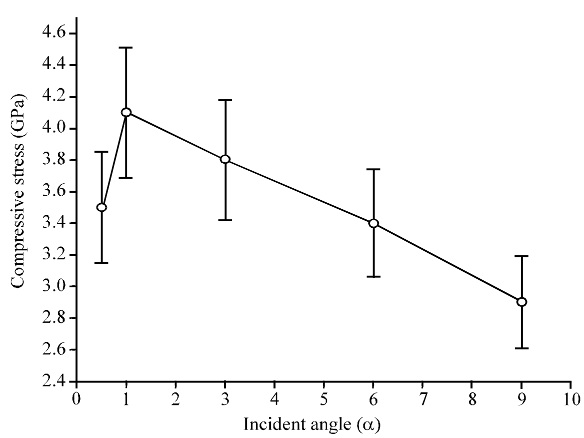

Fig. 3: Variation of compressive residual stress with grazing incident angle

Table 1: Variation of hardness for different peak load

Peak load (mN)	Hardness (GPa)	Reduced modulus (GPa)
10	38	328
50	34	320
100	32	310
200	26	280

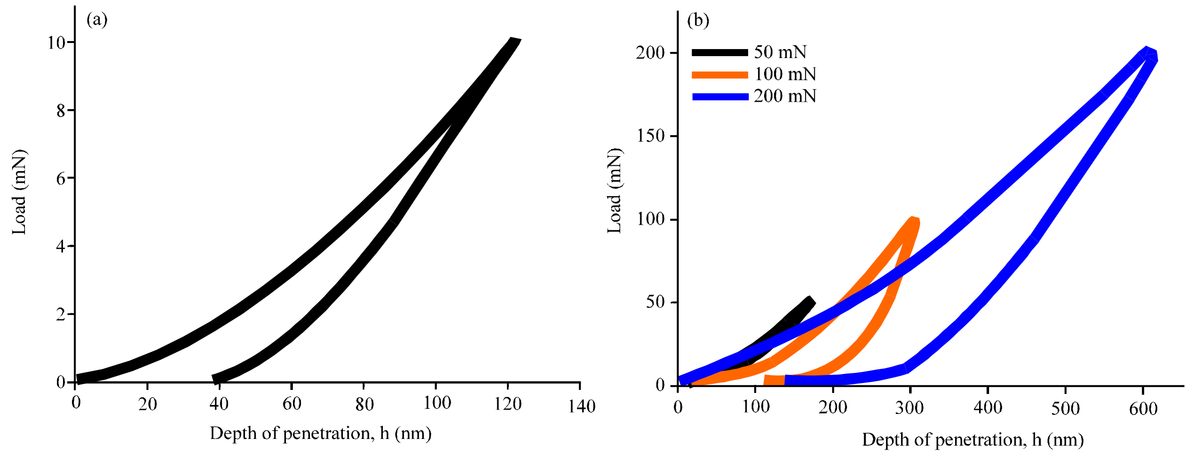

Fig. 4(a-b): Representative load, P-displacement, h curves, for Berkovich indenter, (a) Low load (10 mN) and (b) At different high loads

Representative P-h curves of $TiC_{0.8}$ $N_{0.2}$ thin films deposited with different compositions are shown in Fig. 4a and b. Maximum penetration depth of the indenter, h_{max}, (at peak loads of 10, 50 and 100 mN) is less than 10% of the film thickness which rules out the substrate's influence on the observed mechanical response. In case of 200 mN peak load, h_{max} is more than 10% film thickness and reduction in hardness was observed. The mechanical parameters such as hardness, H and modulus, E were calculated by fitting the P-h unloading curve using Oliver-Pharr method (Oliver and Pharr, 1992). H and E values of the film for different peak load were tabulated in Table 1. For low loads (<10 mN) hardness is high as compared to that of high loads and measurement is also surface sensitive. High hardness could be attributed to the dense columnar microstructure and high residual stresses at surface of the coatings. Dense microstructure resulted because of higher bias voltage of top surface during the growth. Hardness is reduced with increasing the depth, which due to reduction in compressive stresses and substrate effects.

Surface fracture of the coatings was investigated with Vickers micro indenter; Fig. 5 shows representative P-h curves for 150 and 200 mN. Vickers hardness and reduced modulus were calculated by fitting the unloading curve of the 150 mN P-h curve using Oliver-Pharr method. Vickers hardness and modulus of the film is 4040 HV and 320 GPa, respectively. At higher loads (>200 mN) and higher loading rates (400 mN min^{-1}), pop-in was observed which is shown in Fig. 5. The pop-in could be inter-columnar shear or cracks generation during loading. Inter-columnar shear is the common fracture mode in columnar grown polycrystalline ceramic films. At lower loads surface damage was found to be less and it is depicted in Fig. 6a. Severe surface fracture was with increasing the load as shown in Fig. 6b, c. Surface fracture of coatings showed concentric square cracks with steps under Vickers indenter. Generation of concentric square

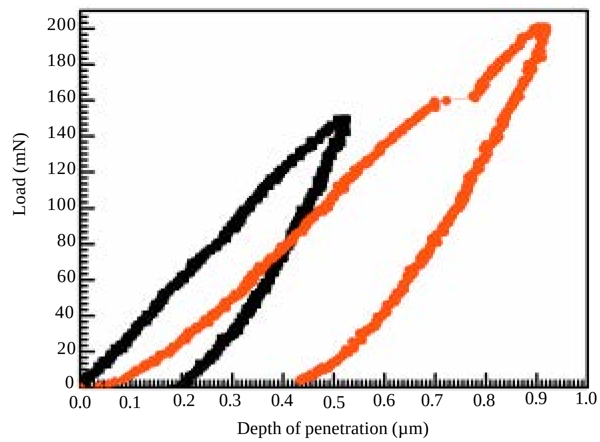

Fig. 5: Representative load, P-displacement, h curves, for Vickers's indenter

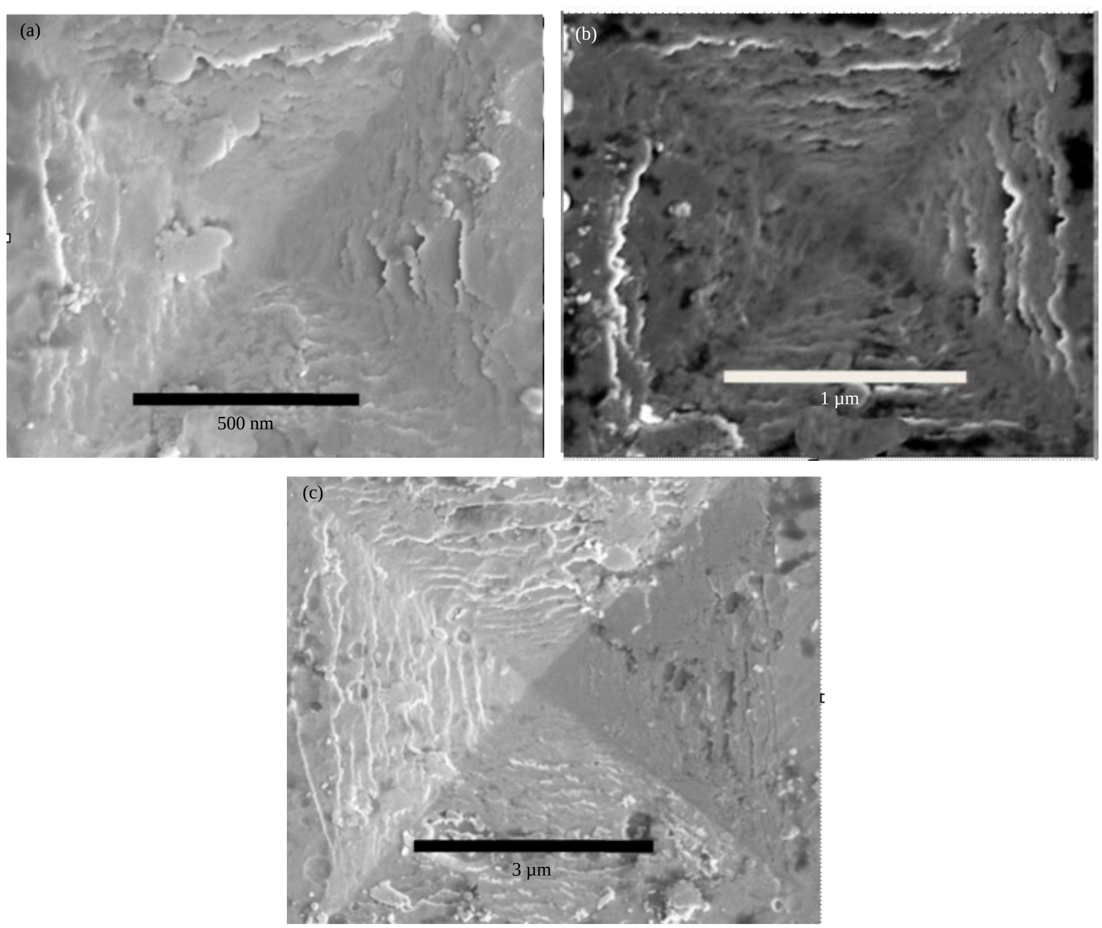

Fig. 6(a-c): Electron microscope images of damaged coating surface for different loads, (a) 500 mN, (b) 800 mN and (c) 2N with steps could be due to inter columnar shear and same type steps could be created on underlying ductile HSS substrate (Ma *et al.*, 2005). Inter columnar shear can be overcome by further tuning the process parameters. Critical stress required for inter columnar shear is highly dependent on residual compressive stress and inter columnar friction (Bhowmick *et al.*, 2005).

CONCLUSION

$TiC_{0.8}$ $N_{0.2}$ coatings were deposited using reactive magnetron sputtering. Compressive stress gradient was evaluated using GIXD and it is matching with process control. Average hardness and modulus of the coatings were found to be 34 GPa and 310 GPa, respectively. Fractography analysis showed the concentric square cracks under the Vickers indenter and attributed to inter columnar fracture. Optimum compressive stress on top of coatings and compressive stresses gradient in the coatings are optimized.

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