Improvement in Adhesion of Sputtered TiB$_2$ Nano-Composite Coatings onto High Speed Steel by a Chromium Interlayer

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This work addresses at the development of the use of interlayer of different materials for TiB$_2$ coatings with increased adhesion to the substrate and retained high hardness. Ti and Cr were deposited on stationary high speed steel and silicon wafer substrates by magnetron sputtering as an interlayer material. The resultant coatings were evaluated with respect to fundamental properties such as structure, coating roughness, hardness, modulus and adhesion. It was found that the adhesion of resultant TiB$_2$ coatings was increased tremendously with Cr interlayer, whilst the hardness was slightly increased.

Keywords: titanium diboride coating, magnetron sputtering, adhesion

1. Introduction

Titanium diboride (TiB$_2$) is a ceramic compound with a hexagonal crystal structure and possessing many interesting physical, mechanical and chemical properties, such as high hardness, good chemical stability and good thermal and electrical conductivity. There have been increasing interests in fabrication of this material in thin film and coating forms for many potential applications, for example to combat wear and corrosion in engineering components and particularly in material processing tools and dies. Among the many coating deposition techniques employed so far, non-reactive sputtering from a TiB$_2$ target is the most widely used for TiB$_2$ coating fabrication. Although the structures and properties of sputter-deposited TiB$_2$ coatings have been studied by many investigators in recent years, the commercialization of sputtered TiB$_2$ coatings has been hindered mainly due to the poor adhesion of the coating to the substrate. Indeed, for the coating systems, adhesion or coating adhesion to substrate is certainly the first attribute that a film must possess before any of its other properties can be exploited or achieved.

To enhance the adhesion of a ceramic coating onto a metallic substrate, it is a common practice that a thin titanium interlayer is used between the coating and the substrate. The roles of the metallic interlayer have been reported to be twofold. Firstly, the titanium interlayer acts as an oxygen-getter to dissolve the native oxide film on the substrate surface. Secondly, the soft interlayer acts as a compliance layer by plastic deformation under mechanical loading to reduce the stresses at the coating-substrate interface region. Similar techniques have been used to enhance the adhesion of TiB$_2$ coating onto steel substrates. However, Berger and Larson addressed that the yield strength and fracture strength of titanium interlayers were insufficient to accommodate the level of stresses generated in TiB$_2$ coatings during deposition and during application. In the present attempt to further improve the adhesion strength of sputtered TiB$_2$ coatings onto high speed steel (HSS) substrates, chromium was used as the interlayer material. It was found that a chromium interlayer can significantly enhance the adhesion of TiB$_2$ coating onto HSS, as compared to that achieved by a titanium interlayer.

In this work, the Ti and Cr interlayer have been investigated in order to overcome the problem of poor coating adhesion and the high residual stress of the TiB$_2$ coating deposited with stationary substrates by magnetron sputtering technique. Highly stressed TiB$_2$ coatings were layered with a ductile Ti and Cr. The Ti/TiB$_2$ and Cr/TiB$_2$ coatings were deposited using magnetron sputtering with Ti and Cr and TiB$_2$ targets. To evaluate the coating roughness and cross-sectional structure, AFM and FESEM were used, respectively. Hardness and coating adhesion were examined by nanoindentation and microscratch test, respectively.

2. Experimental Details

A commercial high speed steel (HSS), SECO WKE45 (Sweden), in fully hardened and tempered condition was chosen as substrates. The specimen’s surface was manually ground and polished. In order to measure the real roughness of coatings, silicon wafer was selected due to its surface smoothness. The HSS and silicon substrates were then ultrasonically cleaned with acetone and ethanol before charging the deposition chamber. The working pressure was 0.65 Pa and working gas was Ar with 20 standard cubic centimeter per minute (sccm) flow rate. The substrates were stationary during deposition and the substrate-target distance was kept constant at 60 mm for TiB$_2$ and 100 mm for Ti and Cr targets, respectively. Substrate temperature was 400°C and both direct current-DC (Ti and Cr) and radio frequency-RF (TiB$_2$) sputtering power were 200 W. Ti and Cr targets were sputtered for 20 min as an interlayer and TiB$_2$ was then sputtered as a top layer for 3 hours.

The roughness of surfaces and fractured cross-sections of the coatings were imaged using an atomic force microscopy...
(AFM), Digital Instrument, and a field emission scanning electron microscope (FESEM), Jeol JSM 6340F, respectively. The coating thickness was measured by making a ball-crater on the coating surface using the Calotest machine manufactured by CSEM. A stainless steel ball of 25.4 mm diameter was used for cratering with a speed of 500 rpm for 240 s and all coating thicknesses are summarized in Table 1.

Nanoindentation test was performed using the NanoTest™ instrument (Micro Materials Limited, UK), with a Berkovich diamond indenter of 0.5 micron in radius. All experiments were performed at a constant loading and unloading rate of 0.05 mN/s. In order to assess the intrinsic mechanical properties of the coatings i.e. hardness and modulus, all specimens were tested at 50 nm penetration depth to avoid any possible effect from the substrate during the indentation process. The unloading curves were used to derive the hardness and reduced modulus values by the analytical technique developed by Oliver and Pharr. The reported hardness and modulus values are the average of 10 indentation measurements.

The microscratch test was performed using the single-pass microscratch mode available in the NanoTest™ device with a diamond indenter topped with a conical with spherical end form of 25 \( \mu \text{m} \) in radius. The scanned length was scratched by applying a linearly increasing load at 5 mN/s after prescanning the initial 50 \( \mu \text{m} \) distance under a small initial load of 0.25 mN. During scratching, the friction force on the indenter and the surface profile along the full length of the scratched track were measured continually, such that a friction force versus scratching distance (or load) curve during-scratch profile were obtained. The critical load for coating failure (Lc), commonly used to measure of the coating-substrate adhesion strength, was determined by the sudden change in friction force, which also led to a sudden change in the profile.

3. Results and Discussion

From Table 1, Ball Crater reveals the coating thickness in each layer for both samples. It can be seen that the thickness of both samples are almost in the same range because the deposition rate of Ti and Cr is almost the same. Since both thicknesses are in the same range, the effect of coating thickness for experimental microscratch test could be minimized or possibly eliminated.

3.1 Structural characteristics

X-ray diffraction analysis (Fig. 1) shows that both TiB\(_2\) coatings (with Cr or Ti interlayer) have a similar hexagonal crystal structure, with strong (001) preferred orientation. This is a desired texture since TiB\(_2\) coatings with the basal plane (001) parallel to the surface is known to possess the highest hardness as compared to TiB\(_2\) coatings with other orientations.

From Fig. 2, AFM reveals the coating roughness examined on silicon substrate. Silicon wafer was used as substrate...
material due to the beginning smoothness with the average roughness (Ra) of about 0.15–0.20 nm. Surface morphological examination also revealed that the two TiB$_2$ coatings (with Ti and Cr interlayer) have a similar topographic feature, which is characterized by the densely populated conical projections. This is typical of sputter-deposited coatings. The surface of both resultant coatings deposited on silicon substrate was found to be smooth and homogenous, with Ra at the nano-scale size. Figure 2(b) shows that sample 2 with Cr interlayer has Ra of 2.7 nm, which is less than sample 1 with Ti interlayer having Ra of 3.2 nm. Since sample 2 (Cr interlayer) has a smoother surface roughness than sample 1 (Ti interlayer), it may show the less friction used during scratch process as investigated later.

Figure 3(b) shows the typical fractured cross-sectional morphology of the TiB$_2$ coating with a Cr interlayer. It can be seen that the Cr interlayer exhibits a columnar growth mode, whilst the TiB$_2$ coating has a dense and nearly equiaxed structure. Similar morphological features have also been observed for the TiB$_2$ coating with a conventional Ti interlayer as shown in Fig. 3(a). The dense structure of TiB$_2$ layer can be explained by the effect of stationary substrate, which lies in the energy of the sputtered species arriving the substrate surface. It is known that the energy of the sputtered species decreases with increasing substrate-target distance due to increased collisions between the sputtered species and the gas molecules in the sputtering atmosphere. The energy of the sputtered species arriving the stationary substrates is thus higher than that arriving the rotating substrates, and this would lead to increased adatom mobility and development of a denser structure in the coating.

### 3.2 Hardness and coating-substrate adhesion

The above structural analyses demonstrate that the change in the interlayer material between Cr and Ti does not significantly affect the structure and morphology of the subsequent TiB$_2$ coating. However, the interlayer considerably affects the mechanical properties and integrity of the coating.

Figure 4 shows typical nanoindentation load-unload curves recorded for the two coating systems. The average hardness and reduced modulus derived from 10 measurements for each coating are summarized in Table 1. It can be seen that the use of a Cr interlayer results in higher hardness and smaller reduced modulus of the TiB$_2$ coating. These are also reflected in the load-unload curves shown in Fig. 4, which shows that the TiB$_2$ coating with a Cr interlayer exhibits greater resistance to indentation and larger elastic recovery during the unloading stage. The increased hardness of the TiB$_2$ coating may be related to the higher strength of
the Cr interlayer as compared to that of the Ti interlayer. Indeed, nanoindentation tests of the interlayers on separate samples without subsequent deposition of TiB$_2$ coatings, reveal that the Cr interlayer has a hardness of 4.5 GPa, as compared to the Ti interlayer which has a hardness of as low as 2.5 GPa. Furthermore, it is noted that with Cr interlayer (sample 2) the hardness slightly increases which is about 6% increment (Table 1).

Figure 5 shows the typical scratch friction force curves using single pass scratch mode recorded of both samples. Each friction curve is characterized by an initial smooth region which increases with increasing load, followed by a region with large fluctuation. The critical load at the transition between these two regions coincides with that measured by the surface profile and microscopic examination (Fig. 6), and thus corresponds to the critical load for coating adhesive failure. Clearly, the Cr/TiB$_2$ coating (sample 2) possess much higher critical loads than those on the Ti/TiB$_2$ coating (sample 1) as shown the $L_C$ values in Table 1.

Microscopic examination and energy dispersive spectroscopy (EDS) X-ray elemental mapping reveal that compressive spallation is the dominant adhesive failure mode in both coatings, with coating debonding at the interlayer-substrate interface (Fig. 6). It thus appears that the adhesion of the interlayer onto the HSS substrate plays the most important role in determining the mechanical integrity of the coating-substrate system. However, after the critical load ($L_C$) for each coating, the damaged area is larger on the Ti/TiB$_2$ coating (sample 1) than Cr/TiB$_2$ coating (sample 2), because some parts of the coating of Cr/TiB$_2$ coating still remain at the side of the scratch track (arrow), as can be clearly seen in Fig. 6(d). The enhanced coating adhesion with a Cr interlayer could therefore be derived from not only the higher strength of the interlayer, but also the better structural match between Cr and the HSS substrate, both having body centered cubic (BCC) structure as compared to Ti which has a hexagonal close packed (HCP) structure.

In order to further confirm the failure mode of the coatings, EDS elemental mapping of the scratch tracks was acquired. Figure 6 also shows the mapping images for both samples. It is noted that coating failure is of the adhesive type and occurred at the interface between all titanium layer/interlayer and the HSS substrate since no titanium (from TiB$_2$) was detected within the track after failure of the coating.

4. Conclusions

In summary, this work demonstrate that changing the interlayer material from HCP-Ti to BCC-Cr does not significantly affect the structure and morphology of the subsequent TiB$_2$ coating, but results in higher hardness of the interlayer and the TiB$_2$ coating. More importantly, the adhesion of the TiB$_2$ coating to the HSS steel substrate can be significantly enhanced by the Cr interlayer. Such an enhancement could be explained by the increased interlayer strength and the better structural match between the BCC interlayer and the BCC HSS substrate.

REFERENCES