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Multilayered Systems of Nanostructured TiB_2 Thin Films and its Mechanical Properties

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Abstract

This study focuses on the development of single and multilayer TiB_2 coatings with Ti interlayer with the aim of improving the mechanical integrity of the coating-substrate system. The nanostructured TiB_2 thin films and multilayered coatings were deposited on high speed steel substrates by magnetron sputtering. The resultant coating systems were evaluated with respect to microstructure, fractured cross-section and fundamental properties such as cross-sectioned fracture, surface roughness, hardness, modulus and coating adhesion to the substrate. It was found that the adhesion strength of TiB_2 coating to HSS substrate could be significantly enhanced in the multilayer system, and by a proper combination of alternate Ti and TiB_2 layers, an optimal enhancement in adhesion could be achieved. The effects of alternate layers on other structural and property features of the resultant coatings are also discussed in this paper.

Keywords: titanium diboride coating, multilayer, magnetron sputtering, hardness, adhesion

Introduction

Titanium diboride (TiB_2) coatings have been attracting increasing interests from industry due to their outstanding properties such as very high hardness, high chemical stability at high temperatures and good wear resistance.[1-3] Although the structure and properties of sputter-deposited TiB_2 coatings have been studied by many investigators in recent years.[4-7] one drawback of TiB_2 coatings is their poor adhesion to the substrate materials due to the evolution of high compressive residual stresses during deposition. It is well known that it is essential to control compressive stresses which develop during coating growth, since such stresses not only reduce coating adhesion but also limit film thickness. A possible way to obtain lower stress levels could be to utilize multilayer coatings, which involve the combination of the stressed material with a more ductile material in a layered structure.[8]. The use of multilayer coatings offers many advantages when compatible coating layers are chosen, for example, the use of alternate layers of ceramic and ductile materials to improve the toughness and mechanical integrity of the coating-substrate system.[9,10]

In this work, a multilayer system has been proposed in order to overcome the problems of brittleness and high residual stresses of TiB_2 coatings deposited by magnetron sputtering technique. Ultra hard TiB_2 coatings were layered with alternate ductile titanium (Ti). There are two reasons for choosing ductile Ti for a multilayer structure. First, Ti has similar crystal structure, hcp, compared to TiB_2, which shows material compatibility. Second, Ti is mostly used as an interlayer media between two materials owing to its strong adhesion to other materials. This paper presents experimental results on a series Ti/TiB_2 coatings in terms of structure, morphology, and mechanical properties.

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Experimental

In this study, a commercial high speed steel (HSS), SECO WKE45 (Sweden), in fully hardened and tempered condition was chosen as a substrate. The specimen's surface was manually ground and polished. The HSS substrates were then ultrasonically cleaned with acetone and ethanol before charging in the deposition chamber. A planar magnetron sputtering system supplied by the Coaxial Company (UK) was used for depositions. The system consists of a cylindrical chamber with three 3-inch water cooled target holders tilted at approximately 30 degree with respect to the normal of the horizontal substrate holder, which can be heated by graphite heating elements. The substrates were stationary and the substrate-target distance was kept constant at 60 mm and 100 mm for TiB_2 and Ti targets, respectively. All the experiments were conducted at a constant working pressure of 0.65 Pa and at a total gas flow rate (Ar) of 20 standard cubic centimeters per minute (sccm). The substrate temperature was 400ºC for all depositions. A RF power biased to the substrate was used to sputter clean the substrate surface for 90 min for all depositions. Both of DC and RF sputtering was used in this work by using DC power for the Ti target and RF power for the TiB_2 target. The DC and RF power employed in this study was 200 W for all depositions. Four types of TiB_2-based nanostructured coatings have been fabricated. These include:

(1) Conventional two layer Ti-TiB_2 coating, by depositing a thin Ti interfacial layer at the interface followed by a TiB_2 layer on top.
(2) Four layer Ti-TiB_2 coating, by depositing 4 alternate Ti and TiB_2 layers.
(3) Six layer Ti-TiB_2 coating, by depositing 6 alternate Ti and TiB_2 layers.
(4) Twelve layer Ti-TiB_2 coating, by depositing 12 alternate Ti and TiB_2 layers.

The total deposition time for TiB_2 was fixed at 3 hrs in all depositions. Thus, the overall thickness of TiB_2 is similar for all samples. The details of deposition are summarized in Table 1.

The phase composition of the resulted coatings was examined by Shimadzu X-ray diffractometer with Cu-K_α radiation. The fractured cross-sections of the coatings were imaged using a field emission scanning electron microscope (FESEM), Jeol JSM 6340F. The coating thickness was measured by making a ball-crater on the coating surface using the Calotest machine manufactured by CSEM, Switzerland. The roughness of surfaces was imaged using an atomic force microscopy (AFM).

Table 1: Deposition conditions

Sample	Mode	Conditions
Sample 1	Conventional 2 layers Ti/TiB_2	Ti 20 min + TiB_2 180 min
Sample 2	4 layers Ti/TiB_2	2x(Ti 20 min + TiB_2 90 min)
Sample 3	6 layers Ti/TiB_2	3x(Ti 20 min + TiB_2 60 min)
Sample 4	12 layers Ti/TiB_2	6x(Ti 20 min + TiB_2 30 min)

Nanoindentation test was performed using the NanoTest™ instrument manufactured by Micro Materials Ltd (UK), with a Berkovich diamond indenter. 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[11]. The reported hardness and modulus values were the average of 10 measurements.

The microscratch test was performed using the single-pass scratch mode available in the NanoTest™ device with a Rockwell diamond indenter topped with a conical with spherical end form of 25 μm in radius. The scanned length was scratched by applying a linearly increasing load at 5 mN/s after prescanning the initial 50 μm 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 was obtained. The critical load for coating failure (Lc), commonly used to measure the coating-substrate adhesion strength, was determined by the sudden change in friction force.

Results and Discussion

Structural Characteristics

Figure 1 shows the fractured cross sections of all samples studied in this work, from which the alternate Ti/TiB_2 layered structures can be clearly seen. The total thickness and other structural and property features of each coating are listed in Table 2. Since the total sputtering time for the TiB_2 target is the same for all coatings, it is obvious that with increasing number of alternate layers, the thickness of each individual TiB_2 layer decreases due to the shorter sputtering time for each layer and the total coating thickness increases due to the introduction of more Ti layers. From Figure 1, it can be seen that the conventional TiB_2 coating (sample 1) exhibits a dense and nearly equiaxed grain structure (Figure 1a), whilst the multilayer coatings (samples 2-4) show a columnar structure, which is typical of sputter deposition at relatively low adatom energies and limited mobility[12]. This observation indicates that sufficient time is required for the TiB_2 layer to develop into a dense and equiaxed structure, and interrupting the growth of the TiB_2 layer with a Ti layer obstructs the development of such a structure and favors the columnar growth of TiB_2.

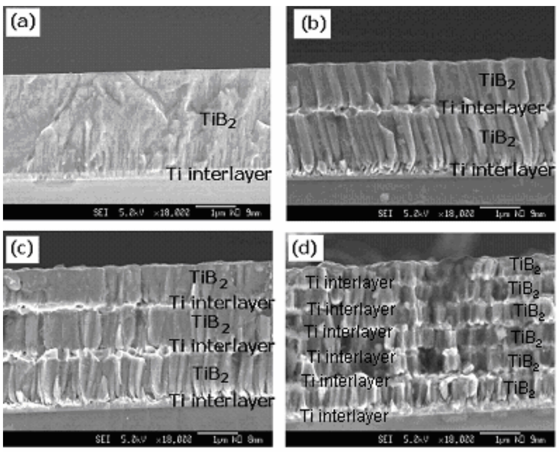


Figure 1. FESEM images showing the fractured cross-section of (a) sample 1, (b) sample 2 and (c) sample 3 and (d) sample 4.

Figure 2 shows the X-ray diffraction patterns recorded for the four coatings listed in Table 2. Each pattern shows several broad reflection peaks corresponding to the hexagonal TiB_2 structure and some minor peaks from the Ti layers. The broadness of the reflected peaks indicates the nanocrystalline nature of the coating structure, as confirmed by FESEM examination (Figure 1). It is interesting to note that the conventional TiB_2 coating (sample 1) exhibits a very strong (001) preferred orientation, and such a fiber texture, to a lesser extent, is retained in the 4-layer coating (sample 2). But the TiB_2 phase is randomly oriented in the 6-layer and the 12-layer coatings. Another interesting observation is that with increasing number of layers, the crystallinity of the TiB_2 phase decreases, as evidenced by the decreased XRD intensity and increased broadness of the reflections peaks. These observations suggest that the TiB_2 layer needs sufficient time (at least 90 min in the case of sample 2) to develop into a well crystallized structure with preferred (001) orientation. The limited growth time of 60 min (sample 3) and 30 min (sample 4) for each individual TiB_2 layer is obviously not enough for the development of the (001) fiber texture. Figure 4 shows the difference in grain structure at surface of samples 1 and 3.

Table 2. Properties of resultant coatings

Samples	Mode	Coating thickness (micron)	Average roughness, Ra (nm)	Hardness (GPa) (at 50 m)	Reduced modulus (GPa)	Critical load Lc (mN)
No.1	2 layers	2.2	2.33	34.3 ± 1.2	329.5 ± 4.2	1,240
No.2	4 layers	2.52	15.49	33.4 ± 0.9	340.2 ± 5.2	1,855
No.3	6layers	3.1	18.18	35.6 ± 2.2	365.4 ± 7.2	1,995
No.4	12 layers	3.42	20.61	20.1 ± 5.9	126.4 ± 23.5	1,650

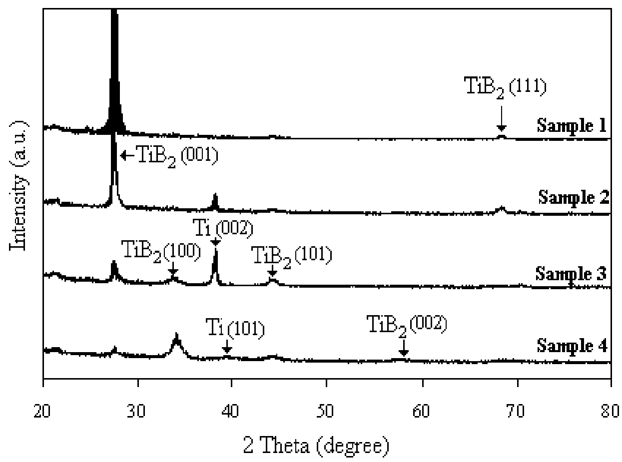
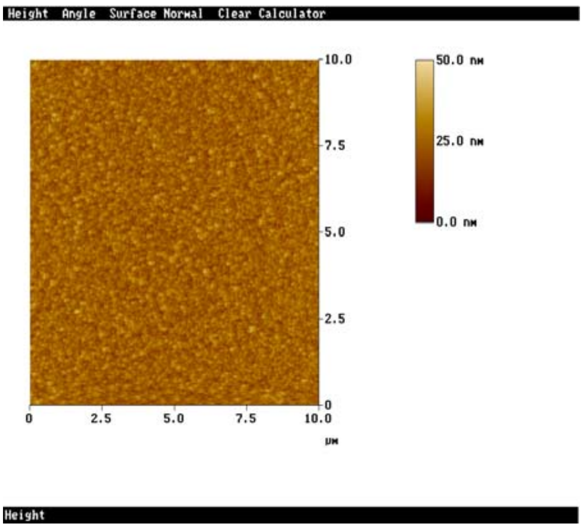


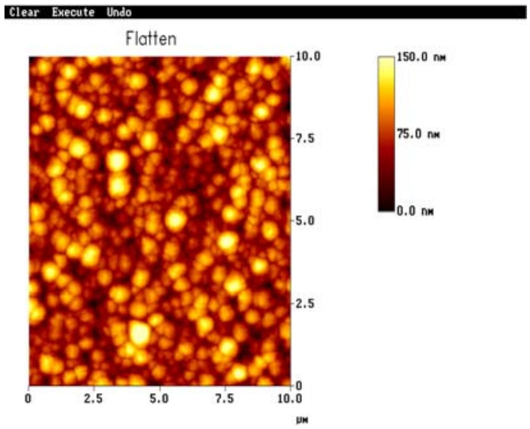
Figure 2. XRD patterns of conventional and multilayer TiB_2 coatings

Surface Roughness

Figure 3 shows typical AFM images taken from the conventional TiB_2 coating (sample 1) and multilayer coating (sample 3). The coating surface is densely populated with conical projections of varying sizes. Such a surface topography is typical of sputter deposited coatings. The density and sizes of the conical projections vary with the number of multilayers in the coating. As can be seen from Figure 3, the size of individual projections is much larger on the multilayer coating than on the conventional two layer coating. This is also reflected in the measured average roughness (Ra) values summarized in Table 2. The relationship between the number of coating layers and the average surface roughness is more clearly shown in Figure 5. It can be seen that surface roughness increases considerably with increasing number of layers. Such an increase is more dramatic when the number of layers is increased from 2 to 4, and becomes more gradual with further increased layers to 6 and 12. The increased surface roughness on multilayer coatings is most likely due to the increased number of Ti layers which promotes the development of a columnar structure as discussed in the previous section. A coating with columnar structure is likely to have a rougher surface than a coating with dense and equiaxed structure due to the characteristic columnar growth mode.[12]

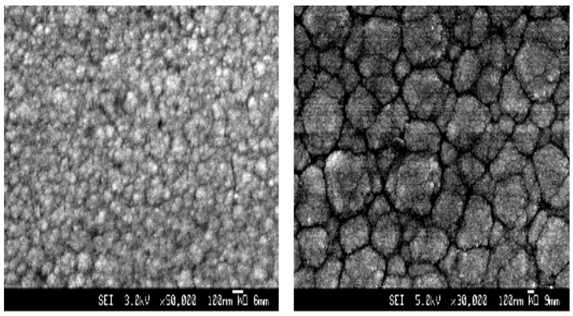


(a) Sample 1



(b) Sample 3

Figure 3. AFM images showing the surface topography of (a) sample 1 and (b) sample 3.



(a) Sample 1 (b) Sample 2

Figure 4. Morphology of Samples 1 and 3: Different grain structure

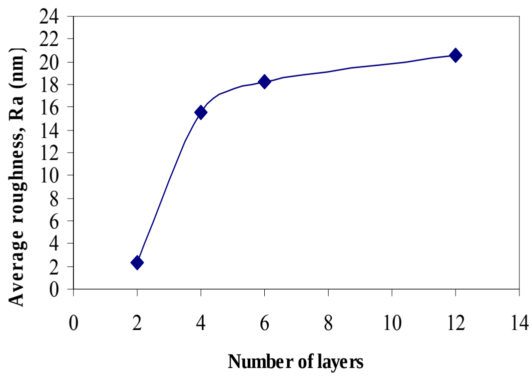


Figure 5. The relationship between average surface roughness and the number of alternate coating layers.

Hardness Test

The hardness and reduced modulus values measured by nanoindentation of all samples are summarized in Table 2. It can be seen that all samples measured at 50 nm depth show high hardness (above 30 GPa) and reduced modulus (above 300 GPa) except for sample 4 with 12 alternate layers. The relatively low hardness of this coating is due to the small thickness of the top TiB_2 layer and thus the effect of underlying soft Ti interlayer. This indicates that the thickness of top TiB_2 layer mainly determines the measured hardness value at 50 nm indentation depth. Indeed, the other three samples with a top TiB_2 layer thicker than 500 nm possess similar hardness of around 35 GPa. Attempts have been made to measure the hardness and modulus at different penetration depths varying from 100 nm to 1000 nm (Figure 6). It was found that at a penetration depth of less than 100 nm, the measured hardness was very high for the coatings in sample 1, 2 and 3. But only sample 1, which has the thickest top TiB_2 layer, shows stable hardness up to an indentation depth of 300 nm. For samples 2 and 3, the hardness dropped significantly at a depth above 100 nm obviously due to the contribution of the soft Ti layers. This was followed by another abrupt drop at a depth of 400 nm, obviously due to the effect of the substrate.

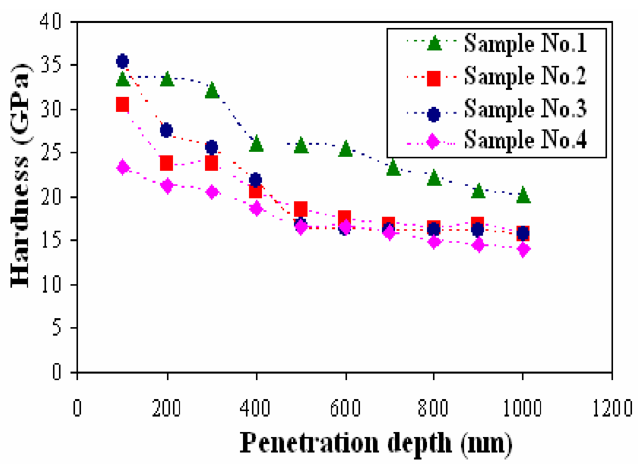


Figure 6. Hardness as a function of depth.

Coating-Substrate Adhesion

Figure 7 shows the scratch friction force curves recorded for all samples. Each friction curve was 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 the initiation of coating failure, as confirmed by microscopic examination (Figure 8), and thus corresponds to the critical load for coating adhesive failure (L_C). Clearly, the multilayer Ti/TiB_2 coatings (samples 2, 3 and 4) possess much higher critical loads than the conventional two-layer coating (sample 1) as shown in Table 1 and Figure 6. The critical load initially increases with increasing number of layers, reaching a maximum with the 6-layer coating, and then decreases with further increase in number of layers to 12. Clearly, there exists an optimum combination of alternate layers that gives the optimal enhancement in coating adhesion.

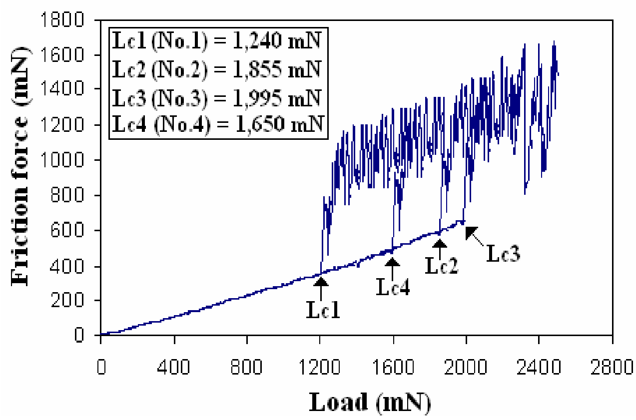


Figure 7. Friction force curves of deposited TiB2 coatings under linearly increasing load.

Microscopic examination and EDS elemental mapping (Figure 8) revealed that compressive spallation was the dominant coating failure mode in all samples. However, after the critical load (L_C) for each coating, the damaged area was larger on the conventional two-layer coating (sample 1) than on the multilayer Ti/TiB_2 coatings. As can be seen from Figure 8, some parts of the multilayer Ti/TiB_2 coating (sample 3) still remain in the scratch track, whilst the conventional two-layer coating (sample 1) has been completely removed from the track. In order to further confirm the failure mode of the coatings, EDS elemental mapping of the scratch tracks was acquired (Figure 7 (b) and (d)). It is noted that coating failure is of the adhesive type and occurred at the interface between the titanium interlayer and the HSS substrate since no titanium was detected within the track after failure of the coating.

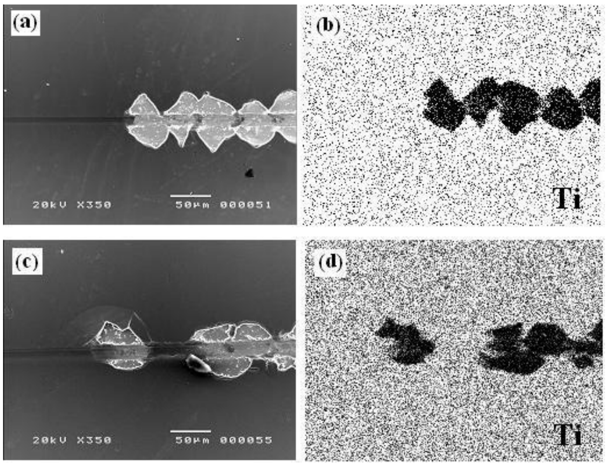


Figure 8. SEM images of the damage region and EDS elemental mapping of Ti on sample 1 (a) and (b) and on sample 3 (c) and (d).

Conclusions

From the experimental results, it can be concluded that under the present deposition conditions, magnetron sputtering of Ti and TiB^2 can be used to produce multilayer coatings with increased coating adhesion and relatively high hardness. There exists an optimum combination of alternate layers that gives the optimal enhancement in coating adhesion. In the present case, the 6-layer coating gives the best results in terms of coating hardness and adhesion strength. In addition, the development of a multilayer Ti/TiB_2 structure significantly affects the structure, texture, morphology and surface roughness of the coating.

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