SCIENCE CHINA
Technological Sciences

March 2010 Vol.53 No.3: 772–775
doi: 10.1007/s11431-009-0241-y

Influence of modulation ratio on structure and properties of nanoscale ZrB_2/ZrAlN multilayered coatings

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Received December 12, 2008; accepted March 19, 2009

ZrB_2/ZrAlN multilayered coatings with various modulation ratios (t_{ZrB_2}: t_{ZrAlN}) and constant modulation periods were prepared by magnetron sputtering system at room temperature. SEM, XRD, surface profiler and nano-indenter were employed to investigate the influences of t_{ZrB_2}: t_{ZrAlN} on the microstructure and mechanical properties of the coatings. Sharp interfaces and nanoscale multilayered modulation were confirmed by SEM. The multilayer with modulation period of 40 nm and ratio of 3:1 displayed the highest hardness (36.4 GPa) and critical fracture load (76.477 mN) with lower stress. The polycrystalline structure and multilayered modulate structure were directly responsible for the enhanced mechanical properties.

ZrB2/ZrAlN multilayered coating, magnetron sputtering, modulation ratio, nanoscale

Citation: Li D J, Kang Y B, Dong L, et al. Influence of modulation ratio on structure and properties of nanoscale ZrB2/ZrAlN multilayered coatings. Sci China Tech Sci, 2010, 53: 772–775, doi: 10.1007/s11431-009-0241-y

In recent years, owing size-effect of nano-structured materials, there has been an increasing interest in applying proper multilayered coatings which possess superhardness effect to protect cutting tools [1, 2]. Multilayer coatings made of two different kinds of materials such as metal/metal, metal/nitride, oxide/oxide and nitride/nitride stacks have been developed in recent years, and they can provide superior electrical, optical, mechanical and chemical properties as compared to single layer coatings [2–5]. For mechanical applications, the nitride/nitride multilayers, including TiN/AlN, AlN/CrN, CrN/NbN, TiN/NbN, TiN/TaN, TiN/W, TiAlN/CrN_x, and TiN/Ti(C,N) multilayer coatings, are the most common candidates owing to their high hardness, chemical inertness and toughness [6–14]. It is suggested that these nitride/nitride multilayer systems would enhance the hardness of a surface in the as-deposited state, and would exhibit excellent oxidation resistance at elevated temperature. So, these multilayer systems with the stable bilayer structure have the ability to be developed and applied to various kinds of cutting tool protection to enhance their lifetime and efficiency.

In our previous works [15–17], we synthesized ZrN-based multilayered coatings such as ZrN/TiAlN, ZrN/W_2N, and ZrN/W. In this investigation, we worked with ZrB_2/ZrAlN multilayered coatings synthesized by magnetron sputtering. Compared with our previous ZrN-based multilayer systems, both single layers in this multilayer system have high melting temperature and hardness at room temperature firstly. Then, they have different structures (hexagonal for ZrB_2 and face-centered-cubic for ZrAlN), which lower mismatch between the (111) planes of ZrAlN and the (001) planes of ZrB_2 can induce a relatively low energy interface, providing a substantial barrier to dislocation motion. Thirdly, addition of Al to the ZrN to form ZrAlN is expected to improve the resistance to oxidation and hence the high-temperature stability. In this work, we employed magnetron sputtering to synthesize a series of ZrB_2/ZrAlN

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multilayered coatings with various modulation ratios. The influence of modulation ratio on microstructure and mechanical properties of the coatings was discussed.

1 Experimental details

ZrB_2/ZrAlN multilayers were deposited on Si (100) substrate at a fixed substrate bias of −80 V by magnetron sputtering. The schematic diagram of this system can be found in our previous work [17]. The ZrB_2 and ZrAl disks were used as targets. The target-to-substrate distance was kept at 7 cm. The base pressure of experiment was lower than 2×10^{-4} Pa. Ar and N_2 gas flows were controlled independently using mass-flow controllers. The deposition of multilayers started with the deposition of about 65 nm thick ZrAl buffer layer to increase the coating adhesion. In the process of deposition, ZrB_2 target was operated in RF mode with power of 100 W while the ZrAl was sputtered in DC mode with current of 200 mA. The working pressure was 0.3–0.4 Pa. To obtain different modulation ratios (t_{ZrB_2}:t_{ZrAlN}) with a constant modulation period (Λ) of 40 nm, we controlled the alternate time of substrates exposed to the ZrB_2 and ZrAl sources by a computer-driven shutter, that is, the deposition rates were 6 nm/min for ZrB_2 and 10 nm/min for ZrAl, respectively. The total thickness of about 500 nm with about 12 layers of ZrB_2 and 12 layers of ZrAlN can be measured by an XP-2 profiler.

The cross-section of the sample was examined by the scanning electron microscopy (SEM, Hitachi 4800, Japan). A D/MAX 2500 diffractometer used for crystallinity analysis was operated with Cu Kα radiation at 1.54056Å. The hardness and elastic modulus of the coatings as a continuous function of depth from a single indentation were achieved by continuous stiffness measurement (CSM) technique using a Nano Indenter XP system. This system was also used in scratch , with the maximum load up to 100 mN in order to measure the fracture resistance. Residual stress (σ) generated during the coating growth process was calculated by applying Stoney formula [18] according to the measured curvature using an XP-2 profiler.

$$\sigma=-\frac{E_s t_s^2}{6t_c(1-v_s)R},$$

where E_s, t_s and v_s are respectively elastic modulus, thickness and Poisson ratio of the substrate, t_c is the coating thickness, and R is the radius of curvature of the multiplayer coated substrate.

2 Results and discussion

Figure 1 shows the SEM image for multilayer with Λ=40 nm. It provides direct evidence of the sharp interfaces and nanoscale multilayered modulation. The light and dark colored layers are ZrB_2 and ZrAlN, respectively. It is clear from Figure 1 that the modulation ratio is about 3:1 within each modulation period of 40 nm. All modulation structures are consistent with our design before experiment.

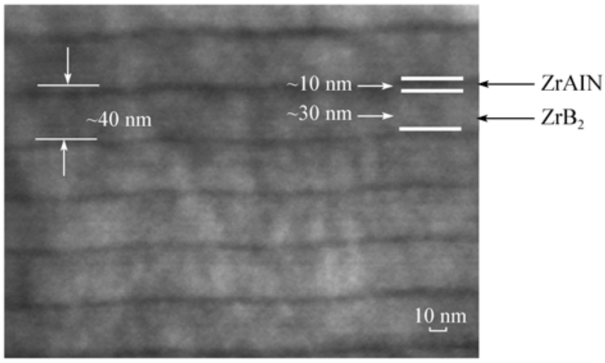

Figure 1 Cross-sectional SEM image of ZrB_2/ZrAlN coating with Λ=40 nm.

Figure 2 shows the low-angle and high-angle XRD patterns of ZrB_2/ZrAlN multilayers with different ratios of t_{ZrB_2}:t_{ZrAlN}. The numerous reflections of low-angle XRD pattern gives an indication of the sharp interfaces between the ZrB_2 and ZrAlN layers and the nature of the nanoscale multilayered structure. The Λ is calculated to be about 40 nm, which is in good agreement with the result of SEM observation. In order to compare with the multilayer case, the patterns of monolithic ZrB_2 and ZrAlN with typical hexagonal and face-centered-cubic structures, respectively are also shown in Figure 2. The strong ZrB_2 (001) and ZrAlN (111) textures with weak shoulder peaks of AlN (100) and Zr (110) can be seen in all multilayer structures. The appearance of Zr (110) peak is due to 65 nm thick ZrAl buffer layer in the multilayer. The full-width at half-maximum of these peaks of multilayers is broader than that of monolithic layer, which indicates smaller grain size in multilayer structure. Besides stronger ZrB_2 (001) texture, a new peak corresponding to ZrB_2 (101) texture appears when t_{ZrB_2}:t_{ZrAlN} =3:1, which may be beneficial to the mechanical properties of multilayer. This is because periodic insertion of ZrAlN into ZrB_2 layers limits the grain size of ZrB_2(001) and forces the appearance of ZrB_2(101). The results above show that the crystallinity of a individual layer in multilayered coatings could be changed by controlling the modulation ratio.

Figure 3 indicates the regularity of hardness and elastic modulus fluctuation versus the modulation ratio for the multilayer. The multilayer with t_{ZrB_2}:t_{ZrAlN} =3:1 exhibits the highest hardness (36.4 GPa) in all monolithic and multilayered coatings. The trend of elastic modulus change is similar to the hardness. The nature of the nanoscale multilayered modulation and interfaces is critical to the hardness increase, because sharp ZrB_2/ ZrAlN interfaces can produce barriers to dislocation glide and columnar grain growth across layers. Besides, different modulation ratios induce different single

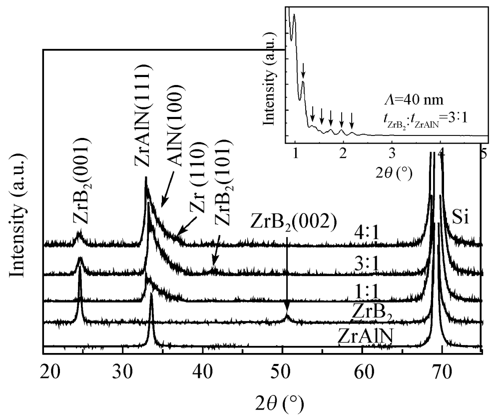

Figure 2 Low-angle and high-angle and XRD patterns for ZrB_2/ZrAlN multilayers with different modulation ratios.

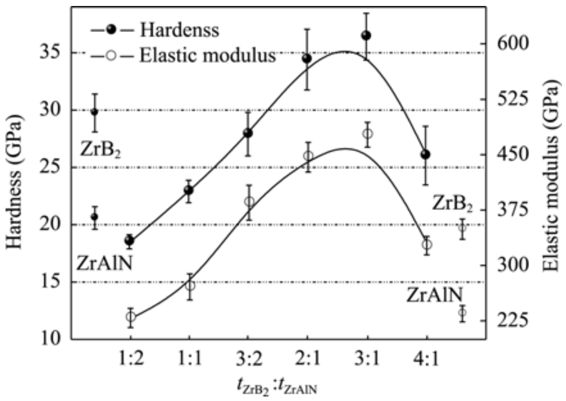

Figure 3 Hardness and elastic modulus of ZrAlN/ZrB_2 multilayers *vs.* t_{ZrB_2}:t_{ZrAlN}.

layer crystal structures, leading a strong mixture of ZrB_2 (001) and ZrAlN (111) textures and the appearance of ZrB_2 (101), which is another reason for the hardness increase. In addition, the alternating stress field caused by different modulation ratios maybe also contributes to the hardness increase. So, a proper modulation ratio can produce synergetic strain-optimization effects on mechanical properties of the multilayers.

Commonly, high hardness is accompanied with high residual stress which leads to the coating crack easily. In our case, for instance, monolithic ZrB_2 layer trends to crack when its thickness becomes thick due to its higher residual stress (–4.17 GPa). However, multilayered structure causes a decrease in the residual stress, as seen in Figure 4. Almost all multilayers exhibit lower residual stresses than the value of monolithic ZrB_2 coatings, which reflects the trend of residual stress reducing. We believe that periodic insertion of ZrAlN into ZrB_2 layers suppresses ZrB_2 grain growth, which releases stress built in the ZrB_2 layers.

Table 1 shows the results of scratch test reflecting the fracture resistance of the coatings. The critical load L_c which can characterize the adhesion strength of the coating is the normal load corresponding to the point in which coating appears an abrupt break. All ZrB_2/ZrAlN multilayered coatings exhibit higher L_c than monolithic ZrAlN and ZrB_2 layers. The multilayer with t_{ZrB_2}: t_{ZrAlN} =3:1 exhibits the highest L_c of 76.477 mN, which indicates its best fracture resistance.

Figure 5 shows the cross sectional profiles of the coatings at a load of 20 mN. The scratch width, residual depth Rd and pile up height in the figure can indicate the destruction degree and plastic recovery ability of the coatings during scratch. It is clear that the multilayer shows a lower pile up height, scratch width, and Rd, as compared with monolithic ZrB_2 and ZrAlN layers. This result proves the enhanced

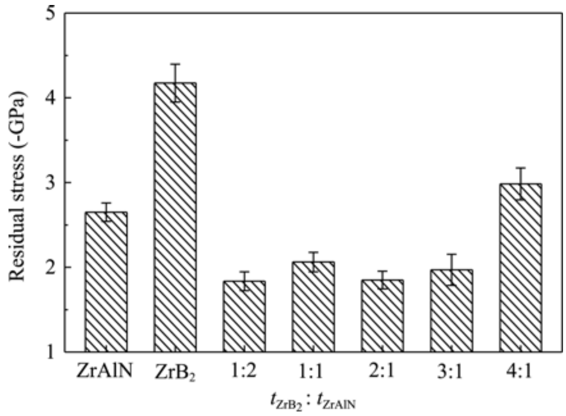

Figure 4 Residual stress of ZrB_2/ZrAlN multilayered coatings *vs.* t_{ZrB_2}: t_{ZrAlN}.

Table 1 Critical load of monolithic ZrAlN, ZrB_2 and ZrB_2/ZrAlN multilayered coatings in scratch test

Coating	t_{ZrB_2}: t_{ZrAlN}	Critical load (mN)
ZrB_2		50.178
ZrAlN		45.178
ZrB_2/ZrAlN	1:1	59.345
ZrB_2/ZrAlN	3:1	76.477
ZrB_2/ZrAlN	4:1	61.691

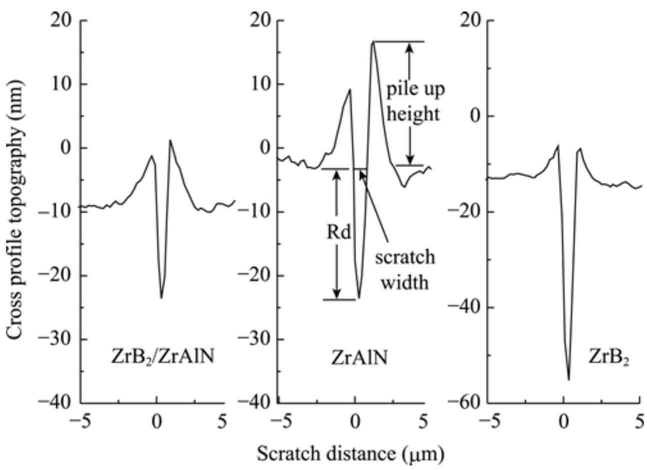

Figure 5 Cross sectional profiles of the ZrB_2/ZrAlN, ZrAlN and ZrB_2 coatings at a load of 20 mN.

fracture resistance and its higher plastic recovery ability.

3 Conclusion

ZrB_2/ZrAlN multilayered coatings were synthesized with different modulation ratios by a magnetron sputtering system. The influence of multilayered modulation structure on the structural and mechanical properties of multilayer is a key factor in its practical applications. This work proves that our deposition parameters can produce nanoscale ZrB_2/ZrAlN multilayers with sharp interfaces. At the optimal modulation ratio of 3:1 the multilayer shows the highest hardness, fracture resistance, and lower compressive stress.

This work was supported by the National Natural Science Foundation of China (Grant No. 50872094), the International Collaboration Project of Tianjin Science and Technology Plan (Grant No. 07ZCGHHZ01500) and Key Project of Applied Basic and Advanced Technology Research Plan of Tianjin"Design and Synthesis of Superhard" Nanomuliti Layers with Boride Layers (2010)".

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