Preparation and advanced structural analysis of novel types of hard multicomponent layers

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Abstract:

Preparation of thin films with exceptional mechanical properties is one of the most important tasks of modern material science and engineering industry. Typical representants of hard coatings are ceramic thin films based on binary / ternary transition metal nitrides (Transition Metal - TM). Representatives of this group are e.g. Al-Ti-N, Ti-N, Cr-Al-N prepared by the means of physical vapor deposition. From the view of structure, these films are mostly prepared as cubic solid solutions with high values of indentation hardness (≈ 30 GPa) and high values of Youngs modulus (≈ 400 GPa). However, the application of these films is limited by their inferior temperature stability, oxidation resistance and their properties may not be sufficient for various high temperature applications (exceeding 1000°C).

Nowadays, much attention is dedicated to the study of thin films based on transition metal diborides - TMB_2. TMB_2 represent a group of ceramic materials with excellent mechanical properties. Due to very high hardness (> 40 GPa) and the assumed chemical stability in their bulk form at elevated temperatures, these materials have high potential as protective coatings on cutting tools inhigh temperature applications, where standard nitride coatings fail.

From an experimental point of view, the mechanical properties of the diboride films depend significantly on the B/Metal ratio and the internal structure. The B/Metal ratio and structure are affected during growth by several mechanisms such as a) the angular distribution of the sputtered B and metal atoms and b) the resputtering of boron from the growing film by high energetic neutrals of inert gas.

In the first part of this work, we concern on the preparation of the system ZrB_{2+x} by unique technology of HiTUS (High Target Utilization Sputtering), which allows to control mentioned mechanisms. By modifying the deposition

parameters, we managed to prepare thin films in a wide concentration range of B/Zr ϵ (2.02 - 2.91) with indentation hardness values from 46 GPa - 26 GPa and values of Young's modulus from 470 GPa - 390 GPa. The influence of deposition parameters on the resulting chemical composition and mechanical properties was explained and supported by theoretical calculation software SRIM.

A major weakness of diboride films is their brittle nature (expressed by high values of Youngs modulus ≈ 450 GPa) and low oxidation resistance (600°C) in humid air. In the second part of our work we propose solutions to deal with these shortcomings of diboride films and we demonstrate them on the system ZrB_{2+x}. The methodology was the preparation of the ternary system $Zr_{1-x}Al_xB_{2+\Delta}$ by alloying the system ZrB_{2+x} with aluminum, mainly due to the expected improvement in toughness and oxidation resistance, but the motivation was also to verify age-hardening, i.e. whether heat-induced processes can lead to separation of the crystalline phases, which may be accompanied by a further increase in hardness.

Firstly, we performed theoretical *ab − initio* calculations on the hexagonal solid solution $Zr_{1-x}Al_xB_2$ for x ϵ (0 - 1 with step 0.125). We analyzed the effect of alloying on chemical and mechanical stability, evolution in elastic constants and the nature of chemical bonds. The calculations clearly showed a strong tendency for phase separation of solid solution already at 0 K and therefore a stronginsolubility of Al in the ZrB_2.

Experimentally, $Zr_{1-x}Al_xB_{2+\Delta}$ films were prepared by non-reactive magnetron sputtering - co-deposition from $Zr_{0.66}Al_{0.33}B_2$ and Al targets. We have shown that the addition of Al causes a rapid decrease in hardness (already 8 at. % of Al leads to a decrease in the value of indentation hardness from $H(ZrB_{2.2})$ = 39 GPa to $H(Zr_{0.72}\ Al_{0.28}B_{2.64})$ = 23 GPa). On diffraction patterns we identified hex-$Zr(Al)B_2$ at lower Al concentrations, however we also identified fcc-Al reflections at the concentration of Al > 13 at. %. Supported by transmission electron microscopy (TEM), we pointed out strong Al insolubility in the ZrB_{2+x}, which is again consistent with the theoretical predictions. Sample with 8 at. % of Al was annealed up to 1100°C. However there was only a slight increase in hardness at 1000°C, not due to structural changes, but due to locally increased concentration of point defects, which is clearly explained by diffraction patterns and images from TEM.

On $Zr_{1-x}Al_xB_{2+\Delta}$ samples, we investigated in-situ oxidation resistance by XRD measurement, where on a sample containing - 8 at. % Al we noticed an increase in oxidation resistance of approximately 100°C compared to the sample with 3at. % Al. For the sample with 13 at. % the reflections did not disappear even at a temperature of 1100°C and the sample remained protected from total oxidation. In the following part of our work we have theoretically investigated the potential for improving mechanical properties by alloying the ZrB_2 system with other elements from transition metal group Ta, Nb, W, Mo, Y and Si. The output of this part is an analysis of chemical, thermal stability and mechanical propertiesof $Zr_{1-x}TM_xB_2$. Based on the results, we propose the most promising candidates for further experimental work.

The second method (in addition to alloying), which can lead to improved mechanical properties of diboride films, is the creation of superlattice structures. In our work, we used $ab-initio$ calculations to design a set of the promising superlattice candidates, in which there was an improvement in toughness, or a slight decrease in toughness at the cost of improving its hardness.

In final part of our work, results of durability tests of coatings based on $Zr_{1-x}Al_xB_{2+\Delta}$ in real conditions are also enclosed. Using cutting tools with our coatings, we machined the carbon CFC (Carbon Fiber Composite) plate and compared the wear rate against competitors ta-C (tetrahedral amorphous Carbon) and PCD (Poly Crystal Diamond) coatings. The cutting tests showed that due to significant micro abrasiveness of the plate, and high values of the coefficient of friction and lower hardness values compared to competing coatings, our coatings proved to be less efficient for machining CFC material.

Key words: hard films, HiTUS, magnetron sputtering, transition metal diborides, superlattices, $ab-initio$