Comparative investigation of Zr-Mo-Si-B thin films using picoindener module and nanohardness tester

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Abstract. Zr–Mo–Si–B coatings were successfully deposited using non-reactive magnetron sputtering of ceramic ZrMoSiB target. Structural investigations have been carried out using X-ray diffraction analysis, high-resolution transmission and scanning electron microscopy, glow-discharge optical-emission, and energy-dispersive spectroscopy. The coatings were subjected to the indentation using nanohardness-tester and picoindenter module placed in the column of transmission electron microscope. The obtained results show that the coatings consist of hcp-ZrB2 phase with needle crystallites 5–10 nm in diameter elongated in the direction of growth. The coatings demonstrated relatively high mechanical properties and recordable elastic recovery up to 84%. Results of indentation tests exhibited the close results.

1. Introduction
Promising from the point of view of practical use are protective coatings based on ZrB2, which have a hardness of up to 40 GPa, high adhesion and corrosion resistance, and good heat resistance [1-3]. It is known that the oxidation resistance of coatings can be successfully improved by doping with silicon [4, 5]. Also, to increase the mechanical properties and work temperatures above 1100°C, ZrB2 is doped with silicon-containing compounds, such as SiC, TaSi2, MoSi2, etc. SiC additive enhances oxidation resistance due to the formation of borosilicate glass when heated in air, which acts as a barrier to oxygen diffusion [6, 7]. Studies of the oxidation resistance of ZrB2-TaSi2 and ZrB2-MoSi2 coatings at a temperature of 1500°C were carried out in [8, 9]. The appearance of defects (cracks and pores) in the oxide layer of the ZrB2-TaSi2 coating with increasing exposure time was observed. At the same time, a defect-free dense layer of SiO2 was formed on the surface of the ZrB2-MoSi2 sample. The authors attribute the discovered effect to the positive influence of the MoB phase, which maintains the integrity of the silicon oxide layer. A similar comparative study of the ZrB2-based coatings showed that MoSi2 doping increases the oxidation resistance of coatings by 3 times compared to SiC [10]. Note that Zr-Si-B and Mo-Si-B coatings with high Si content can achieve record values of oxidation resistance up to 1400-1700°C [3, 11].

ZrB2-based coatings can be obtained by various methods, including plasma spraying [12-14], diffusion saturation [15], salt electrolysis [16], electric spark alloying [17], chemical vapor deposition [18], and cathode-arc evaporation [19]. Magnetron sputtering has a number of advantages including: low roughness and preservation of the substrate surface geometry, low defects and porosity of coatings, high adhesive strength when using pre-ion cleaning, flexible control of structural characteristics by controlling the deposition parameters, versatility in relation to the substrates used,
the possibility of obtaining multi-component coatings with a uniform distribution of elements through the thickness of coatings [20-29]. Hard wear resistant coatings for various applications can be successfully deposited by magnetron sputtering of composite targets fabricated using self-propagating high-temperature synthesis (SHS) [30].

It is important to determine the coating’s characteristics in the in-situ mode [31] and mechanical properties at the nanoscale level using transmission electron microscope [32]. To do this, we need to make sure that the data obtained on the measuring instruments adapted to the microscope is correct. The aim of the present work is to study the structure of Zr-Mo-Si-B coatings, as well as to compare the results obtained by indentation of samples in the column of transmission electron microscope using a Picoindenter module and a standard procedure using Nanohardness Tester.

2. Experimental part
The ZrMoSiB target (at.\%: 28.14 Zr, 57.06 B, 9.35 Si, 5.45 Mo) was synthesized from exothermal powder mixture using the combined force SHS-pressing technology, as described elsewhere [30]. The charge from elemental powders was calculated based on the formation of a phase composition of 80% ZrB\textsubscript{2}-20% (90%MoSi\textsubscript{2}-10%MoB). The typical scheme of vacuum chamber of PVD apparatus is presented in [33]. The targets were subjected to DC magnetron sputtering (current 2 A, voltage 500 V) in pure Ar (99.9995%). The total pressure was maintained at 0.1-0.2 Pa. The diameter of targets was 12 cm and the target to substrate distance was 8 cm. Deposition time was kept constant at 40 min. Polished plates of polycrystalline alumina, 2x4 cm\textsuperscript{2} in size, were used as a substrate material. The substrates were cleaned ultrasonically in isopropyl alcohol for 5 min, after which they were etched for 20 min in a vacuum chamber by Ar\textsuperscript{+} ion with average energy of 2 keV.

The coating elemental compositions were determined from the elemental depth profiles obtained by glow discharge optical emission spectroscopy (GDOES) using a PROFILER 2 instrument (Horiba Jobin Yvon) [34]. The microstructure of coatings was examined by a JEM-2100 JEOL transmission electron microscope and a S-3400N Hitachi scanning electron microscope equipped with a Noran 7 Thermo energy dispersive X-ray spectrometer. X-ray diffraction (XRD) patterns were recorded using a D2 Phazer Bruker X-ray diffractometer using Cu-radiation. Picoindenter PI 95 module (Hysitron) equipped by Berkovich diamond indenter were used for indentation of coatings in direction of normal to the sample surface. Experiment was conducted in the column of JEM-2100 JEOL microscope. The coatings also were characterized in terms of their hardness and Young’s modulus using a Nano-Hardness Tester CSM Instruments with same type of indenter [35]. Applied load of 0.440 mN were used for both cases of indentation tests.

3. Results and Discussion
The EDS, SEM, and XRD data are presented on Fig. 1. The chemical compositions of Zr-Mo-Si-B coatings according to the EDS data (Fig. 1a) has been found like, at.\%: 28.2 Zr, 8.5 Mo, 11.4 Si, 30.0 B, 1.3 Al, 9.2 O, 11.3 C. This method probably gives incorrect data for light elements such as boron, oxygen and carbon. Aluminum detection may be due to the fact that the signal excitation region affects not only the coating, but also the Al\textsubscript{2}O\textsubscript{3} substrate. The GDOES analysis showed that all element were homogeneously distributed through the coating thickness and real composition is close to the, at.: 36.5 Zr, 54.5 B, 4.6 Mo, 4.4 Si. Coatings contained some oxygen and carbon (total amount not exceeding 0.3 at. %) whose presence is explained by their traces either in the targets or in the residual gas in the vacuum chamber. The B/Zr and Si/Mo ratios in the coatings were 1.5 and 0.9 correspondingly. The results showed that the coatings had elemental composition as in the SHS target except Si which concentration decreased 2 times. The cross-sectional SEM image of the coating is shown in Fig. 1b.

The thickness of Zr-Mo-Si-B coatings was found to be 5 \(\mu\)m. According to the SEM the coatings demonstrated dense and homogeneous structure. But high-resolution TEM results (Fig. 2), showed that coatings possess fine columnar structure with individual column width in the range of 5-10 nm. Each columnar grain is elongated in the direction of growth of the coating, and its length is close to the thickness of the coating. Figure 1c shows typical XRD pattern of the coating recorded in the range of 2\(\theta\) = 20-70 degrees. Two reflexes from planes of (001) and (002) in positions of 25.8 and 52.9
degrees corresponded to the hexagonal ZrB$_2$ phase (JCPDS card 89-3930) were observed. The coating was highly textured in the [001] directions. The crystallite sizes calculated from the (001) and (002) XRD peaks using the Scherrer formula were of 45 and 24 nm, respectively. Other narrow peaks on the XRD pattern are corresponded to the alumina substrate.

![Figure 1](image1)

**Figure 1** - EDS (a), SEM (b), and XRD (c) data for Zr-Mo-Si-B coating

![Figure 2](image2)

**Figure 2** - TEM (a) and HR TEM (b) data for Zr-Mo-Si-B coating. For clarity, the microphotograph of a separate column structure element is shown with a 90-degree rotation (b).

The indentation curves of 9 measurements obtained by Nanohardness Tester are shown in Fig. 3a. The average curve of penetration depth vs. load dependence is also presented in Fig. 3b. It can be seen that at load of 0.44 mN, the indenter penetrates to a depth of about 20 nm. The calculation using Oliver and Pharr algorithm [36] showed that coating demonstrated relatively high hardness of 10 GPa, elastic modulus of 173 GPa and elastic recovery of 86%.

The second indentation experiment was performed in the TEM column using the Picoindenter module. Photo on fig. 4a demonstrated the coating-indenter contact zone. Loading was performed on normal to the surface. Indentation curve obtained during the test of the Zr-Mo-Si-B sample is shown in fig. 4b. Maximum penetration depth of the indenter was 20 nm, which corresponded to a maximum load of 0.44 mN. Thus, the results are similar to the data obtained by nanoindentation. It is important to note that the nature of the indentation curves was different: the loading-unloading curves in the case of a standard nanohardness tester were very close to each other. In the case of picoindenter reverse stronger differed from the stage of loading. Elastic recovery in this case was about 62%, which was different from 86% for the case of nanoindentation.
4. Conclusion
Hard Zr-Mo-Si-B coatings with a fine-columnar structure and uniform distribution of elements through the coating thickness were deposited onto alumina substrates by magnetron sputtering of composite ZrMoSiB target produced by the self-propagating high-temperature synthesis method. The as-deposited coatings consisted of $h\text{-ZrB}_2$ needle grains, 5-10 nm in diameter, elongated in the direction of coating growth. The coatings had hardness of 10 GPa and elastic modulus of 173 GPa. Comparative experiments on coating’s indentation using standard nanohardness tester and picoindenter device mounted in the column of TEM were carried out. The same penetration depth of ~20 nm was reached in both cases at load of 0.44 mN. The shape of indentation curves was slightly different. Elastic recovery values obtained in case of pico- and nanoindenter was 60 and 84 % correspondingly.

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