Study of nanomechanical properties of thin films using in-situ “Push-to-Pull” method in the column of transmission electron microscope

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Abstract. The purpose of this study was to develop a method for determining the tensile strength of ion-plasma coatings during their nanodeformation in the column of a transmission electron microscope. The advanced oxidation-resistant coating in the Mo-Zr-Si-B system was selected as the object for mechanical testing. Coatings were deposited on alumina substrates by magnetron sputtering with hetero-phase cathode in system MoSi2-MoB-ZrB2 in argon environment. Coating’s characterization and testing were performed using XRD, SEM, EDS, GDOES, TEM, and nanoindentation. Nanomechanical study in TEM column was conducted in binding scheme using Push-to-Pull device and Picoindenter module on lamella prepared by FIB. Problems related to nanomechanical measurements and interpretation of the obtained dependences are discussed. Recommendations for the method of lamella preparing and parameters for testing were developed.

Introduction
Surface engineering is one of the most developing areas of modern materials science. Currently, almost all areas of industry are associated with the creation of new types of coatings and methods of surface modification. Heat-, thermal - wear-, and corrosion-resistant coatings are being actively developed and implemented to protect products of the space, aviation, automotive, nuclear engineering, oil and chemical industries, etc. [1-6]. Predicting the behavior of protective coatings in real operating conditions is an urgent task that requires a comprehensive approach. The key characteristics of coatings are hardness (H) and modulus of elasticity (E), elastic recovery (W), which are usually determined by nanoindentation [7,8]. The H/E index can be used to predict the wear resistance of coatings [9-11]. The value of H²/E is a criterion related to the type of local deformation, which can be either homogeneous or inhomogeneous [12]. An important value that can be useful in determining the prospects of coatings is the crack resistance [13,14]. The behavior of coatings under tribological influence is also related to the values of critical loads estimated during scratch testing [15, 16]. The study of mechanical properties is usually limited to determining the listed characteristics. Determination of values such as the ultimate strength or yield strength typical of bulk materials is usually not possible in the case of coatings due to their small thickness. The study of three-dimensional coated materials using typical schemes is uninformative and difficult to interpret and...
calculate [17-18]. The solution to the problem can be found when switching to testing at the nanoscale using modern high-precision measuring equipment [19]. In this case, you can implement various loading schemes typical for ordinary metals, alloys, and ceramics, but in a small volume.

There are a large number of technologies for deposition of solid protective coatings, such as thermal spraying, pack cementation, cladding and electric spark alloying, slurry method etc. However, the resulting coatings are characterized by high heterogeneity of structure and composition, increased defects and high roughness, which potentially reduces the reproducibility of the experiment and makes it difficult to interpret the results. The most suitable object for nanomechanical testing is nanocomposite coatings obtained by magnetron sputtering. Such coatings have a fine structure with a grain size from units to tens of nanometers [20], high uniformity over the entire thickness [21], extremely low concentration of defects (pores, cracks) [22], smooth relief (the coating inherits the roughness of the substrate) [23], low level of impurities [24], good adhesive and cohesive strength (which is important for sample preparation) [25] and other advantages.

This work is devoted to the development of a method for determining the tensile strength of ion-plasma thin films during their nanodeformation using a Push-to-Pull (PTP) device and a Picoindenter module in a column of transmission electron microscope. The advanced protective coating in the Mo-Zr-Si-B system was chosen as the object for mechanical testing. Earlier, we conducted studies of coatings of this class (MoSiB, ZrSiB), which showed that when optimizing the chemical composition, it is possible to achieve a level of hardness up to 35 GPa and oxidation resistance up to 1500-1700°C, as well as satisfactory wear resistance [26,27].

1. Experimental part
Protective oxidation-resistant Mo-Zr-Si-B coatings were deposited in vacuum by direct current magnetron sputtering. The hetero-phase 72%MoSi2-8%MoB-20%ZrB2, Ø120x10 mm in size, disk cathode for sputtering was produced by self-propagating high-temperature synthesis (SHS) [28]. The internal configuration of working space of UVN-2M (Russia) deposition machine is shown in [29]. Pinnacle + (Advanced Energy, USA) power supply unit maintained the power level of 1 kW (current 2 A, voltage 500 V) during the deposition process. The total pressure of 99.9995% Ar was ~0.2 Pa (residual pressure below 0.005 Pa). Deposition on cathode-substrate distance of 80 mm were performed for 40 min. Alumina (VOK-100 trade mark) substrates polished to Ra=10 nm were subjected to a) ultrasonic treatment with frequency of 22 kHz in the C3H8O environment for 3 min, b) sputtering by 2 keV argon ions for 20 min in a vacuum chamber before deposition.

Complex study of Mo-Zr-Si-B samples were performed by glow discharge optical emission spectroscopy (GDOES) using a Profiler-2 device from Horiba JY [30], transmission and scanning electron microscopy (TEM and SEM, respectively) using a JEM-2100-JEOL and S-3400N-Hitachi microscopes, energy-dispersive spectroscopy (EDS) using Noran-7-Thermo module, X-ray diffraction (XRD) using a D2-Phazer-Bruker device equipped by Cu-electrode, nanoindentation (NI) using a Nanohardness-tester from CSM Instruments with triangle diamond pyramid. PI 95 Picoindenter-Hysitron module [31] and “Push-to-Pull” (PTP) device (Bruker, USA) [32] were used for tensile test of film in direction of normal to the sample surface. Experiment was conducted in the column of JEM-2100 JEOL microscope.

The foils were prepared at a sample preparation facility with PIPS II System (Gatan, USA) and FIB focused ion-beam (FEI Quanta 200 3D FIB instrument, USA). The ion etching process was stopped when the etched layer depth was 8-10 microns. After that, the lamella was removed with a micromanipulator and installed on a copper lift-out grid, where it was additionally thinned. Thickness should be optimal, since, on the one hand, the mechanical strength of the lamella is provided during transportation from the lift-out grid to the PTP device, and on the other hand, at least half of the lamella must be electron transparent for a transmission electron microscopy. The lamella was thinned after turning perpendicular to the ion source, which allowed obtaining plane-parallel surfaces. The thinned lamella was transferred to the surface of the PTP device using a micromanipulator. Then, a layer of Pt was deposited on the edges of the lamella above the PTP device body to secure it.
The material behavior under plastic deformation was studied using micro-electro-mechanical systems (MEMS) in situ in a transmission electron microscope column. The PTP device was placed in the PI 95 Picoindenter module (figure 1a).

![Figure 1. Photo of “Picoindenter” mechanism (a) and scheme of “Push-to-Pull” device (b). 1 – area of sample’s deformation, 2 – springs, 3 – indenter](image)

The PicoIndenter module is a 1D (normal force only) transducer that consists of the force/displacement sensor, drive circuit board and hardware used to mount the transducer to the TEM system. The load generated in the module is transmitted further to the PTP device due to a specific geometry. In turn, the PTP device is a silicon spring with a slot for installing the sample and a platform (figure 1a), which is pressed by a diamond indenter (figure 1b). The design of PTP devices allows you to transform the test scheme from compression to tension. During the application of the load, the movable support on which one of the sides of the sample is fixed moves, thereby transmitting the tensile stress to the sample. Tests are performed before the sample breaks.

2. Results

The comparative studies of chemical composition of Mo-Zr-Si-B films using GDOES and EDS were performed. According to EDS sample contained about 32 at.% of Mo, 8 at.% of Zr, and 60 at.% of Si. The absence of boron signal can be explained by relatively low concentration of B in film and low sensitivity of EDS to measurement of light elements. In contrast, GDOES revealed a presence of high amount of boron. The real composition was close to the, at.%: 20 Mo, 8 Zr, 30 B, and 42 Si. The Mo, Zr, B, and Si were distributed with high uniformity inside sample. GDOES demonstrated also that films contained O and C impurities (<3 at.% and <1 at.% respectively). This fact that can be connected to the existing of the contaminations in the cathode or gas impurities in the working gas environment. The Si/Mo and B/Zr ratios in the films were close to the 2 and 4, correspondingly. The results showed that film’s compositions should be close to MoSi₂+ZrB₂+B.

Figure 2a shows the XRD pattern for Mo-Zr-Si-B coating deposited onto alumina substrate. Sharp reflexes with high intensity from the Al₂O₃-plate (substrate) were observed. Set of lines from planes of (100), (110), (111), (200), (211), (220), (400) of hexagonal h-MoSi₂ phase were also detected [33]. Note that coating demonstrate a pronounced texture in the [110] direction. From the broadening of the lines, the grain size of molybdenum disilicide was estimated to be about 10 nm. The lattice periods of the hexagonal phase were \( a = 0.4700 \) and \( c = 0.6557 \) nm, respectively. Information about coating’s microstructure obtained using SEM and TEM are presented on Fig. 2b and 2c respectively. Average thickness after measurement in different areas of sample was about 14 µm. Coating posses low
concentration of defects and exhibited features-less fracture typical for multicomponent films obtained by sputtering of multiphase SHS-targets [34].

![Figure 2. Structure of Mo-Zr-Si-B film: XRD (a), SEM (b), and TEM+SAED (c) data](image)

However TEM observation at normal and high resolutions revealed the formation of a needle-like nanostructure in which thin columnar crystallites elongated in the direction of growth over the entire thickness of the coating. Comparing the size of crystallites determined from XRD and the length of columnar grains, we can conclude that each grain contains several subgrains by analogy with [35]. The selected area electron diffraction (SAED) pattern proved the presence of a phase with an interplane distance close to h-MoSi2. The halo observed on SAED can be attributed to an amorphous boron-containing phase. According to the nanoindentation data the film demonstrated relatively high hardness of 23 GPa, elastic modulus of 280 GPa and elastic recovery of 62%.

The tensile test was performed in the TEM column using the Picoindenter module and “Push-to-Pull” device. Photo on figure 3 (a-c) demonstrated the deformation zone of lamella.

![Figure 3. Microphotographs of deformation zone during tensile test of Mo-Zr-Si-B film using PTP device in column of TEM. (a-c), SEM-image of lamella after tensile test (d) ](image)

Loading was performed on normal to the surface of clamps. The width of thin place of lamella was about 400 nm. The figure shows three key points: the initial state before loading, the stage of destruction of the lamella, and the return of the holder to its original position. Load vs. displacement curves obtained with and without sample prepared from the Mo-Zr-Si-B film are shown in fig. 4. To correctly determine the maximum load value, the stiffness of the PTP device was previously measured without a fixed sample. It was found that the load dependence on the indenter movement is linear in
the range 0 – 500 nm (Figure 4a). Figure 4b shows the curve of the load dependence on the indenter movement during the lamella tensile tests. On this curve, you can distinguish two sections: with a small (G1) and a large angle of inclination of the curve (G2) relative to the X-axis. The second section of the curve is linear and indicates the elastic nature of the lamella deformation before failure.

![Figure 4](image_url)

**Figure 4.** Load vs. displacement curve recorded without sample (a), and with Mo-Zr-Si-B film (b) during tensile test in column of TEM using “Push-to-Pull” device

The maximum elongation before destruction was 160 nm. The load in this position in the case of testing the PTP device without a sample was 20 µN. The maximum load before failure when testing the lamella was 185 µN (when moving 160 nm). Thus, the load causing the actual destruction of the coating was: 185-20=165 µN.

To calculate the tensile strength using the formula (1), it was necessary to determine the cross-sectional area of the lamella in the working area. The width was measured before the test using TEM images at the narrowest point (414 nm) (Figure 3a). After the test, the PTP device was removed from the holder and placed in a scanning electron microscope with a 90° tilt. The sample thickness was 595 nm (Figure 3d).

The calculation of the tensile strength of the lamella was carried out according to the standard formula (as for bulk samples):

\[
\sigma = \frac{F}{S}
\]

where \( \sigma \) is the ultimate tensile strength, \( \text{Pa} \);
\( F \) – maximum load to failure, \( \text{N} \);
\( S \) – cross-sectional area of the sample, \( \text{m}^2 \).

Value of the tensile strength of the lamella was 670 MPa.

The Young's modulus for the lamella material was determined after testing using the formula (2):

\[
E = \frac{F*L}{S*\Delta L}
\]

where \( L \) is the length of the working part of the sample, \( \text{nm} \)
\( \Delta L \) – maximum elongation to break, \( \text{nm} \).

The maximum elongation to break was defined as the difference between the distance between the sample heads before the start of the test and at the time before the sample broke. It was found that this value was 35 nm with the length of the working part of the sample of 722 nm. The calculated value of the Young's modulus is 12 GPa. It is more than an order of magnitude lower than the values obtained when testing bulk samples of ceramics based on MoSi2 (310–450 GPa) [36, 37]. At the same time, the test sample showed high tensile strength (2.2-3.5 times higher than the table values of 190-310 MPa).
and ductility. It is also important to note that nanoindentation of Mo-Zr-Si-B coatings showed the elastic modulus value ~ 280 GPa, which is generally close to the table data for bulk MoSi2.

3. Discussion
An unusual combination of mechanical characteristics can be caused by a number of factors. One possible explanation is the specific nanocomposite structure of the coatings (nanocrystallites of the phase based on molybdenum silicide separated by amorphous regions based on boron compounds). Accurate identification of the causes requires additional experiments and optimization of in situ tensile tests, as well as sample preparation for testing. Probably, the mechanical properties of the coating were affected by internal compressive stresses. Indirectly, their influence on the material is confirmed by the nature of the load-displacement curve in figure 4b. The first section of this curve may indicate that the lamella straightens when a load is applied to the PTP device. Another possible reason for this behavior of the material during deformation may be the texture of the sample associated with the coating formation mechanism. The discrepancy between the mechanical characteristics calculated from the results of the in situ tensile test and the tabular data is a consequence of the anisotropy of the structure and properties of the coating in different directions. A more accurate interpretation of the results is possible when conducting similar experiments on thinner, electron transparent samples (100-150 nm). In this case, it will be possible to observe changes in the structure when a load is applied to the sample and, consequently, determine the preferred mechanisms of deformation.

Thus, it can be concluded that in situ tensile tests in the TEM column allow obtaining data on the mechanical properties of materials that cannot be tested by traditional methods due to geometric features. The optimal research strategy is to combine testing of samples of large (400-600 nm) and small (100-150 nm) thickness. In the first case, the samples will have high stiffness and uniformity in thickness, which will allow you to get more correct values of mechanical characteristics. In the second case, it is possible to observe changes in the structure under load. However, obtaining such lamellas is problematic due to compressive stresses (twisting may occur when transferred to a PTP). In addition, surface defects and other undesirable features created by ion etching of samples will make a greater contribution to mechanical properties.

Conclusion
The purpose of this study was to develop a method for determining the tensile strength of PVD coatings during their nanodeformation in a column of transmission electron microscope. The Mo-Zr-Si-B protective coating was selected as the object for mechanical testing. The results showed that the coating has a composite structure and consists of nanoscale crystallites of the hexagonal h-MoSi2 phase with Zr atoms dissolved in it, as well as an amorphous phase close in composition to MoB. When stretched, the brittle nature of the material destruction was observed. Taking into account the movement of the clips at idle, the strength was determined, which turned out to be significantly higher than the value typical for bulk ceramics based on MoSi2. Possible reasons for such high values are discussed. The data obtained using the PTP device in TEM under high vacuum and the results of nanoindentation under normal conditions are compared.

Acknowledgments
This work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation (Project No. 0718-2020-0034 of State assignment).

References
[1] Bogdan M, Blachnio J, Spychała J and Zasada D 2019 Engineering Failure Analysis 105 337
[2] Jin D, Yang F, Zou Z, Gu L, Zhao X, Guo F and Xiao P 2016 Surf. Coat. Technol. 287 55
[3] Bueno A H S, Solis J, Zhao H, Wang C, Simões T A, Bryant M and Neville A 2018 Wear 394–395 60
[4] Lobanov L M, Ustinov A I, Volkov V S, Mokhniuk A A, Telichko V A and Demchenkov S A 2018 Thin Solid Films 666 30
[5] Haye E, Deschamps F, Caldarella G, Piedboeuf M-L, Lafort A, Cormil H, Colomer J-F, Pireaux J-I and Job N 2020 Int.J. of Hydrogen Energy 45 15358
[6] Bobzin K, Bagciivan N, Theiss S and Yilmaz K 2010 Surf. Coat. Technol. 205 1502
[7] Rezaei S, Arghavani M, Wulfinghoff S, Kruppe N C, Brögelmann T, Reese S and Bobzin K 2018 Mech. Mater. 117 192
[8] Shtansky D V, Kiryukhantsev-Korneev F V, Sheveiko A N, Malochkin O V, Levashov E A, Dyakonova N B, Bardin I P And Lysatosky I V 2005 Phys. Solid State 47 252
[9] Leyland A and Matthews A 2000 Wear 246 1
[10] Murray J W, Ahmed N, Yuzawa T, Nakagawa T, Sarugaku S, Saito D and Clare A T 2020 Tribol. Int. 150 106392
[11] Shtansky D V, Petrzhik M I, Bashkova I A, Sheveiko A N and Levashov E A 2019 Appl. Sci. 9 4977
[12] Musil J, Novak P, Cerstvý R and Soukup Z 2010 J. Vac. Sci. Technol., A 28(2) 244
[13] Bobzin K, Bagciivan N, Theiss S and Yilmaz K 2010 Surf. Coat. Technol. 205 1502
[14] Leyland A and Matthews A 2000 Wear 246 1
[15] Zhang S and Zhang X 2012 Thin Solid Films 520 2375
[16] Shvindina N V, Levashov E A and Potanin A Yu 2018 Prot. Met. Phys. Chem. 54(6) 1147
[17] Levashov E A, Mukasyan A S, Rogachev A S and Shtansky D V 2017 Int. Mater. Rev. 62 203
[18] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[19] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[20] Majumdar S, Sengupta P, Kale G B and Sharman I G 2006 Surf. Coat. Technol. 200 3713
[21] Babaei K., Fattah-alhosseini A., Elmkhah H and Ghomi H 2020 Surf. and Interfaces 21 100685
[22] Fu K, Sheppard L R, Chang L, An X, Yangial C and Ye L 2018 Mater. Charact. 139 165
[23] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[24] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[25] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[26] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[27] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[28] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[29] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[30] Schmidt S, Höglund C, Jensen J, Hultman L, Birch J and Hall-Wilton R 2016 J. Mater. Sci. 51 10418
[35] Dziedzic A, Bochnowski W, Adamiak S, Szyller Ł, Cebulski J, Virt I, Kus-Liśkiewicz M, Marzec M, Potera P, Zaczek A and Zdeb B 2020 Surf. Coat. Technol. 393 125844

[36] https://www.azom.com/properties.aspx?ArticleID=512

[37] Hague J R. Refractory Ceramics for airospace. A materials selection handbook. American Ceramic Society. 1964 Columbus, Ohio, 440 p.