Investigation of the influence of substrate materials on oxidation resistance of TaSi$_2$ and Ta-Si-N coatings using SEM, EDS and GDOES methods

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Abstract. Coatings were obtained by magnetron sputtering of a Ta-Si target onto Al$_2$O$_3$, Mo, Si and Ni-based substrates. Samples were studied in terms of their structure, mechanical properties and oxidation resistance by SEM, EDS, nanoindentation and GDOES methods. It was found that an increase in the concentration of nitrogen leads to an increase in the hardness of coatings by 60%. The behavior of coatings and various types of substrates during annealing at a temperature of 1000-1200 °C.

1. Introduction

Silicides of transition metal have attractive combined properties such as high melting points, relatively low density, high mechanical properties, and oxidation resistance in the air. For example, tantalum disilicide TaSi$_2$, in comparison with titanium disilicide TiSi$_2$ and tungsten disilicide WSi$_2$, has a higher melting point (TiSi$_2$: 1500°C; WSi$_2$: 2160°C; TaSi$_2$: 2200°C) and high hardness (TiSi$_2$: 8.6 GPa; WSi$_2$: 13.1 GPa; TaSi$_2$: 15.6 GPa) [1]. TaSi$_2$ coatings are stable at temperatures up to 800 °C [2, 3]. At higher temperatures (up to 1300 °C), a rapid increase in mass ~ 17 mg/cm$^3$ is observed in 60 min of exposure [4]. TaSi$_2$ coatings are usually produced by vacuum plasma spray [2], pack cementation [5, 6], and magnetron sputtering [7-10]. Alloying TaSi$_2$ with various elements has a positive effect on the properties of the coatings. Thus, the deposition of TaSi$_2$ coatings in a nitrogen-containing reaction atmosphere leads to an increase in the mechanical properties [7, 8]. In [8] was shown that with an increase in the nitrogen concentration, the hardness (H) and the modulus of elasticity (E) of the coatings grow: the maximum values of H = 36 GPa and E = 265 GPa are achieved at a nitrogen concentration of 35 at. %. Nitrogen has an ambiguous effect on the resistance of coatings to oxidation: the introduction of nitrogen promotes an increase in the oxidation rate; however, upon reaching the optimum concentration of N, the growth rate of the oxide film decreases [9]. Previously, complex coating compositions such as Ta-Si-Cr-N [10], Ta-Ti-Zr-Si [11], Ta-Si-Zr-BCN [12, 13] were studied, which showed high hardness at 30 GPa and resistance to oxidation at a temperature of 1200 °C. However, to determine the effect of alloying components, it is of interest to study the basic composition of TaSi$_2$ coatings.

The aim of this work is to research the structure, elements and phase composition, and mechanical characteristics of the TaSi$_2$ and Ta-Si-N coatings, as well as to assess their heat resistance depending on the substrate material.

2. Experimental Part

Magnetron sputtering refers to methods of sputtering materials by ion bombardment. Application of coatings in a vacuum through sputtering systems is to spray the sprayed solid target material with ions
of inert gas, resulting in plasma of anomalous glow discharge at imposing a magnetic field whose lines of force orthogonally cross the magnetic field lines. Magnetron sputtering of a TaSi$_2$ ceramic target Ø120×6 mm was performed in Ar, Ar+N$_2$ and N$_2$ atmospheres. The schematic diagram of the installation and technological parameters of deposition are indicated in [14, 15]. Disks made of aluminum oxide VOK-130, molybdenum MCH-1, and nickel alloy KHN65VMTYU were used as substrates. Before deposition, the substrates were mechanically polished, then cleaned by ultrasound in C$_3$H$_8$O. Adhesion between the film and the substrate was achieved by bombarding with low-energy ions at the initial stage of deposition using an additional Ar ion source operating at a fixed energy of 2 keV. The elemental and phase compositions and structure of the coatings were studied using scanning electron microscopy SEM (Hitachi S-3400), energy dispersion analysis (EDS) (Noran-7 Thermo) and X-ray diffraction analysis (XRD) (Phaser D2 Bruker). The element distribution profiles were obtained using the Profiler-2 HORIBA-JY glow discharge optical emission spectrometer (GDOES) according to the method [16]. The mechanical properties of the coatings were studied by the nano-hardness tester at a load of 2 nm. In order to determine the heat resistance of coatings, air annealing was performed in a muffle furnace SNOL-7.2/1200 at a temperature of 1000 for MCH-1 and KHN65VMTYU substrates and 1200 °C for VOK-130 substrates. The isothermal exposure time was 60 minutes. After high-temperature treatment, the coatings were examined using SEM-EDS and GDOES using the equipment described above.

3. Result and discussion

The sample numbers and composition of coatings can be written as follows: coating 1 – Ta$_{41}$Si$_{59}$, coating 2 – Ta$_{24}$Si$_{38}$N$_{38}$, coating 3 – Ta$_{16}$Si$_{35}$N$_{49}$. SEM images of a cross-section of coatings 1-3 are shown in Figure 1. For the sample, obtained in Ar, a columnar structure was observed characteristics of PVD coatings [17]. Coatings 2 and 3 had a dense low-defect structure without pronounced columnar elements. According to the typical GDOES profile (Figure 1b), all elements were distributed evenly over the thickness of coatings 1-3. The growth rates for samples 1 and 2, calculated from SEM data, were close and were 0.22 and 0.21 µm/min. When the coatings were deposited in 100% N$_2$, the growth rate decreased to 0.07 mm/min, which is ~3 times less than the data obtained for samples 1 and 2, which can be clearly seen in Figure 1a. The decrease in the growth rate of coatings when the working gas is changed from argon to nitrogen may be due to the poisoning of the target (TaN formation) on the one hand and to a lower yield of N$_2$ ions during sputtering compared to Ar [18].

![Figure 1. SEM images of as-deposited coatings 1 and 3 (a), GDOES profile of coating 2 (b), XRD pattern (c) and nanoindentation data (d) of coatings 1-3.](image-url)
nitrogen was introduced, the peaks expanded in the range of 25-40 2Ѳ*, which indicates amorphization of coatings 2 and 3. For coatings 3, pronounced peaks of the Al2O3 substrate are observed, which is associated with a small coating thickness of ~3 µm.

According to the data, obtained as a result of nanoindentation (fig.1d), the non-reactive coating had the lowest hardness at 6 GPa. The coating deposited in Ar+N2 was characterized by a maximum hardness of up to 20 GPa. A further increase in the nitrogen concentration resulted in a 20% decrease in hardness relative to the sample deposited in Ar+N2. Note that the hardness of the coating with the maximum nitrogen content is 60% higher than the values obtained for the non-reactive sample. Thus, the coating deposited in the Ar+N2 gas mixture had the best mechanical properties. The introduction of the optimal nitrogen concentration has a positive effect on the hardness and other mechanical properties of coatings, which is consistent with the data obtained in [8, 19].

The oxidation stability of Ta-Si-(N) coatings obtained on KHN65VMTYU substrates was evaluated at 1000 ºC since the Nickel alloy is oxidized above this temperature [20]. Figure 2 shows the depth distribution profiles of elements for coatings 1-3.

![Figure 2](image2.png)

**Figure 2.** GDOES profiles of coatings 1(a), 2(b) and 3 (c) after annealing at 1000 ºC for 60 min.

It can be seen that annealing at 1000 ºC resulted in the diffusion of Ni and Cr into the composition of both reaction and non-reaction coatings. As a result, the assessment of the heat resistance is difficult due to changes in the composition of coatings.

As a result of single-stage isothermal annealing, it was found that the coatings deposited on Mo substrates had a different oxidation mechanism. Along the boundaries of the sample obtained in Ar, regions of complete oxidation of the molybdenum substrate were observed, which occupied ~10 % of the total sample area. This can be explained by the penetration of oxygen along the boundaries of the columns, as a result of which the formation of molybdenum oxide is observed at the coating-substrate interface (Figure 3a).

![Figure 3](image3.png)

**Figure 3.** SEM images and element distribution maps of coatings 1, obtained on Mo after annealing at 1000 ºC for 60 min (a) and Si (b) substrate after annealing at 1200 ºC for 10 min.
In turn, the oxidized regions of nitrogen-containing coatings 2 and 3 accounted for ~70 and 75% of the total sample area. Probably, during annealing, oxygen reacts with nitrogen and evaporates, resulting in the formation of pores in the oxide layer. Since the samples withstood annealing at 1000°C, additional tests were performed at 1200 °C using silicon and aluminum oxide substrates. The SEM image of the coating obtained on a single-crystal silicon substrate in an Ar medium after annealing at 1200 °C is shown in Figure 3b. Oxygen diffuses along the boundaries of columnar grains deep into the coating, which leads to oxidation of the substrate and delamination of the coating. A similar effect was observed in [12, 13].

SEM images of coatings deposited on Al₂O₃ substrates after annealing at a temperature of 1200 °C are shown in Figure 4.

Annealing resulted in the formation of a layer of SiO₂ oxide on the surface of the non-reactive coating with a denser structure on the surface and a loose one at the interface with the coating. The thickness of the oxide layer was ~12 µm. The oxide layer on the surface of the coating obtained in Ar+N₂ medium had a porous structure. The thickness of the SiO₂ layer was within ~10 µm. The coating with the maximum nitrogen concentration was completely oxidized, and light Ta₂O₅ grains were formed in the amorphous SiO₂ matrix.

It can be assumed that oxygen diffuses through columns with non-reactive coating in the same way as in the samples described above. The coating obtained by the Ar+N₂ method effectively protects the Al₂O₃ substrate from oxidation at 1200 °C due to the suppression of the columnar structure. However, an increase in the nitrogen concentration led to complete oxidation of the coating due to the interaction of nitrogen and oxygen during the oxidation process.

4. Conclusion
Magnetron sputtering was used to obtain coatings in the system Ta-Si-(N) in the atmosphere Ar, Ar+N₂ and N₂ on nickel alloy, molybdenum, silicon and aluminum oxide. The non-reactive coating had a columnar structure, while the introduction of nitrogen contributed to the grinding and suppression of columnar grain growth. The non-reactive coating consisted of h-TaSi₂ grains, and the introduction of nitrogen led to the amorphization of the coatings. The best mechanical characteristics were observed at the optimal nitrogen concentration in the coating. During annealing at a temperature of 1000 °C, a diffusive interaction of the coating with the nickel substrate occurs, which leads to a violation of the composition of the coatings. In the case of non-reactive coatings, diffusion along the grain boundaries leads to rapid oxygen penetration to the substrate, after which the substrate is oxidized and the coating is detached. The best resistance at a temperature of 1200 °C was provided by a coating with an optimal nitrogen concentration. Coatings, sputtering in 100% N₂, are completely oxidized at a temperature of 1200 °C.

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6. References
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