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CREATION OF NEW BORIDE, SULPHIDE, PHOSPHIDES AND OXIDE NANOCOATINGS ON HARD ALLOY

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The possibility of creating high-entropic boride and oxide coatings on a solid T12A alloy was researched, and the possibility of applying borides and oxides of hafnium, zirconium, molybdenum, tungsten, yttrium and nickel was considered. For that, on the basis of the joint problem of thermal conductivity and thermoelasticity, the volume of grain and the depth of occurrence for the elements considered, as well as boron and oxygen were determined.

For the case of the action of boron ions, the grain size increases: it lies in the range of $4.4 \cdot 10^{-9} \dots 1.364 \cdot 10^{-7}$ m. So, in the last case we deal with submicrograin, the depth of its occurrence: the minimum lies in the range of $1.2 \cdot 10^{-9} \dots 9.29 \cdot 10^{-8}$ m, and the maximum – $2.9 \cdot 10^{-9} \dots 1.07 \cdot 10^{-7}$ m. In this case, the depths of occurrence exceed all the previous ones, so well as the grain size.

The transition to oxygen ions (for the formation of oxides) leads to a significant reduction in grain size to $3.94 \cdot 10^{-9} \dots 1.04 \cdot 10^{-7}$ m, the latter value already corresponds to submicrograin. The range of depths of occurrence of the grain: $7.49 \cdot 10^{-9} \dots 6.4 \cdot 10^{-8}$ m – the minimum and $2.65 \cdot 10^{-9} \dots 7.7 \cdot 10^{-8}$ m – the maximum values.

In the future, depending on which sequence of layers we want to obtain based on the adhesive and strength properties of the coating, we select the surface layer of the coating and their alternation. To fulfill the high-entropy condition, we determine the fraction of hafnium involved in the process, taking into account the requirement which zirconium should not exceed 30 %. Then we estimate the duty cycle of the voltage pulses on the evaporator with the ZrHf20 cathode and the fraction of the remaining components for which it is necessary to have one two-component cathode with a component ratio 50 %/50 % and two evaporators with one-component cathodes (moreover combining in the two-component cathode elements with close partial pressures at the same temperatures). Next, we consider (depending on the chosen sequence of layers), the first layer is external, for it we choose the range of depths: minimal and maximal, and also the grain size. The second in depth will be a layer of compounds, elements (or intermetallic compounds) depending on the nature of the operation of the CT: if the CT works with a shock load, the second layer should be made of pure metal (intermetallic) or a compound that dampens the information of the first layer. The second in depth will be a layer of compounds, elements (or intermetallic compounds) depending on the nature of the CT works: if the CT works with an impact load, then the second layer should be made of pure metal (intermetallic) or from a compound that dampens the information of the first layer. Subsequent layers can be from chemical compounds.

It was found that the volume corresponding to the NS is realized up to an ion energy of the order of 700...800 eV and a depth: for a minimum of $0 \dots 2.2 \cdot 10^{-8}$ – m; for the maximum – $1.8 \cdot 10^{-9} \dots 3.2 \cdot 10^{-8}$ m. It is seen that with increasing of ion mass, the volumes of NS and the depth of their occurrence are significantly reduced. This trend is tracked for practically all the ions considered. In order for nitrides to form, it is necessary that the charge and energy of the nitrogen ions be suchlike, and the depth of its occurrence were close to that obtained for hafnium.

Turning to the zirconium (Zr^+) dependencies, we find that NS is realized for practically all the energies studied. Moreover at 200 eV the

depths of occurrence are: the minimum – $0...6.3 \cdot 10^{-10}$ m; the maximum $3.34 \cdot 10^{-9}...5.43 \cdot 10^{-9}$ m. At 2000 eV the minimum – $6.37 \cdot 10^{-10}...5.37 \cdot 10^{-9}$ m; Maximum – $5.4 \cdot 10^{-9}...1.25 \cdot 10^{-8}$ m. For 20 keV, the minimum depth of occurrence is $4.6 \cdot 10^{-9}...2.48 \cdot 10^{-8}$ m; the maximum is $1.54 \cdot 10^{-8}...3.52 \cdot 10^{-8}$ m.

From a comparison of the depths of NS for hafnium and zirconium ions, we see that many nitrogen energies cannot be used, because the depth of their penetration is greater, and in many of the regimes borides and oxides will not be formed, but there will be a rather large amount of intermetallides that have small physical and mechanical characteristics, so consequently there will be zones in the material with reduced properties, that will not provide the appearance of highly entropic nitride coatings with good characteristics. For molybdenum (Mo^+) the depth of occurrence of NS at an energy of 200 eV is: the minimum – $0...1.18 \cdot 10^{-9}$ m, the maximum – $1.89 \cdot 10^{-9}...4.49 \cdot 10^{-9}$ m. At an energy of 2000 eV: the minimum – $6.12 \cdot 10^{-10}...5.65 \cdot 10^{-9}$ m; the maximum – $5.59 \cdot 10^{-9}...1.23 \cdot 10^{-8}$ m. At 20 keV: the minimum – $4.47 \cdot 10^{-9}...2.44 \cdot 10^{-8}$ m; the maximum – $1.52 \cdot 10^{-8}...3.48 \cdot 10^{-8}$ m.

For tungsten (W^+) ions, similar graphs are presented. The depths of occurrence of the NS at an energy of 200 eV are: the minimum – $0...9.89 \cdot 10^{-10}$ m, the maximum – $1.77 \cdot 10^{-9}...4.33 \cdot 10^{-9}$ m. At an energy of 2000 eV: the – $4.38 \cdot 10^{-10}...5.1 \cdot 10^{-9}$ m; the maximum – $5.17 \cdot 10^{-9}...1.17 \cdot 10^{-8}$ m. At 20 keV: the minimum – $3.79 \cdot 10^{-9}...2.19 \cdot 10^{-8}$ m; the maximum – $1.42 \cdot 10^{-8}...3.20 \cdot 10^{-8}$ m.

For nickel the minimum and maximum depths of grain occurrence decrease with ion mass increasing, and grain volumes are decreased significantly. The energy zone where is possible to obtain nanostructures increases, which has a positive effect on the physic and mechanical characteristics of the coating, which for a nanostructured grain has a large microhardness, yield stress, ultimate strength. Corrosion resistance is also increased, while the ability to absorb impact loads due to a decrease in the modulus of elasticity is increased. it is allows us to withstand high loads in the elastic zone, that is, for large deformations we have low stresses.

Dependences of nanocluster volume, minimum and maximum depth of NC on phosphorus ion energy are obtained. It can be seen that the volume of NC ranges from $3.58 \cdot 10^{-28}$ to $8.56 \cdot 10^{-24}$ m³ (200 eV, $z=1$ and 20 Kev, $z = 3$), respectively, the minimum depth from $0-2.01 \cdot 10^{-8}$, the maximum is from $1.43 \cdot 10^{-9}$ to $3.25 \cdot 10^{-8}$ m (respectively 200 eV, $z = 1$ and 20 Kev, $z = 3$).

The transition to sulfur ions (S^+) leads to a decrease in the volume of NC to $3.58 \cdot 10^{-28} - 7.82 \cdot 10^{-24}$ m³, the minimum depth will be $0-1.92 \cdot 10^{-8}$ and the maximum $1.4 \cdot 10^{-9} - 3.14 \cdot 10^{-8}$ m, respectively, at $E_i = 200$ eV, $z = 1$ and $E_i = 20$ Kev, $z = 3$.

It is seen that the values for these ions are close, but for phosphorus they are greater, since its atomic weight is less (30.97 AE) than that of sulfur (32.068) close values are reduced with a slight difference in the masses of ions. All this allows almost in the same layers to obtain phosphides and sulfides and this layer will increase both wear resistance and performance at sufficiently high temperatures (up to 2000 °C).

The actual size of the nanosilver for sulfides varies from 5.6 to 26 nm, for phosphorus ions and from 5 to 24 nm. That is, nanostructured layers can be realized for phosphides and sulfides.

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