STRUCTURE and PROPERTIES OF SUPERHARD and HARD NANO-COMPOSITE PROTECTIVE COATINGS on BASE Zr-Ti-Si-N and Mo-Si

N.A.Azarenkov[1] ,*I.B.Denisenko* [1*], V.M.Beresnev[4,1], S.V.Lytovchenko[1], A.D.Pogrebnjak[2,3,]
[1] V.N. Karazin Kharkiv National University, Kharkiv, Ukraine
[2] Sumy Institute for Surface Modification, P.O.Box 163, 40030 Sumy, Ukraine.
[3] Sumy State University, 40007 Sumy, Ukraine, alexp@i.ua
[4] Science Center for Physics and Technology, Kharkov, Ukraine

Zr-Ti -Si-N coating had high thermal stability of phase composition and remained structure state under thermal annealing temperatures reached 1180 ^{o}C in vacuum and 830 ^{o}C in air. Effect of isochronous annealing on phase composition, structure, and stress state of Zr-Ti-Si-N-ion-plasma deposited coatings (nanocomposite coatings) was reported. Below 1000 ^{o}C annealing temperature in vacuum, changing of phase composition is determined by appearing of siliconitride crystallites (B-Si_3N_4) with hexagonal crystalline lattice and by formation of ZrO_2 oxide crystallites. Formation of the latter did not result in decay of solid solution (ZrTi)N but increased in it a specific content of Ti-component. Vacuum annealing increased sizes of solid solution nanocrystallites from (12 to 15) in as-deposited coatings to 25 nm after annealing temperature reached 1180 ^{o}C. One could also find macro- and microrelaxations, which were accompanied by formation of deformation defects, which values reached 15.5 vol.%. Under 530 °C annealing in vacuum or in air, nanocomposite coating hardness increased, demonstrating, however, high spread in values from 29 to 54 GPa (first series of samples). When Ti and Si concentration increased (second series) and three phases nc-ZrN, (Zr, Ti)N-nc, and α-Si_3N_4 were formed, average hardness increased to 40,8 ± 4 GPa.(second series of samples). Annealing to 500 ^{o}C increased hardness and demonstrated lower spread in values H = 48 ± 6 GPa and E = (456 ± 78) GPa.

Silicides of refractory metals are more and more widely used in various fields of science and technology as construction materials to make specific products; composition elements of composite materials; protection high temperature coatings; materials to make semi-conducting devices and integrated circuits.

Their use instead of traditional materials is caused by the fact that they have certain advantages: high heat and thermal resistance, ability to preserve sufficient mechanical properties within a wide range of temperatures, rather high conductivity, combination of operation on obtaining silicides with the overall technology of producing the final product. Besides, one should also note high melting point, wide range of electric resistance values, forming of epitaxial layers that make up Schottky barrier of desired value, and possibility to grow oxide film on silicides. Among refractory metals silicides, molybdenum silicides occupy an important place. Most works on high temperature materials based on molybdenum silicides describe either technological aspects of their formation and use, or deal with fundamental questions (thermodynamics and kinetics).

Comparatively few works describe relation of products' operating properties and structure-phase characteristics of silicides. In most part these works are more or less successful attempts to calculate and predict products' behavior. There are very few works on molybdenum silicides Mo_5Si_3 and Mo_3Si. These silicides have not been studied sufficiently yet.
Today, in spite of obvious advantages of refractory metals silicides, there are a number of aspects in technology of their obtaining and their application that are not clear yet. In particular, leading experts do not share a common point of view as to the optimal choice of a silicide which is the most appropriate to perform definite functions. Analysis of published data witnesses that there is no common approach in description of technological processes, and therefore in a number of cases researchers compare objects that are totally different both in phase composition and structure.

For high-temperature silicide materials it is essential to preserve stability of their properties in a wide range of temperatures. Irreversible structure-phase changes, which take place in temperature increase (1000 – 2000 ^{o}C), change properties of materials and their operating abilities. There is a standard way to slow down structure-phase changes – setting up barrier layers in silicides, which is normally done by doping (boron or rare earth elements). However, such doping may lead to negative consequences as well, e.g. decrease of operating temperature, release of different volatile chemical compounds into operating environment, changes in mechanical properties. We developed the method to modify silicide structure without doping and obtained to increase high temperature stability of silicides only by conducting control and optimization of reaction diffusion parameters. Our studies in the field of multi-layer composite materials development showed that one of the ways to solve this problem is to form eutectic interlayers Mo_5Si_3-$MoSi_2$ and Mo_5Si_3-Mo_3Si with regular structure in the coating.