

SILICIDE COATINGS STRUCTURE OPTIMIZATION BASED ON MULTISCALE APPROACH

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This paper is an attempt to apply the multi-scale approach to the study of silicide coatings on molybdenum. Macro- and microstructure of silicide coatings largely determines mechanical and corrosion properties of molybdenum-protective coating composites. To prevent unacceptable changes, it is necessary to foresee the evolution of structure during formation of the coating and during operation of the composite. This paper analyzes the factors that determine degradation of properties of the coatings at different hierarchical levels. The requirements for the macro- and microstructure of the silicides with a view to achieving better thermal properties of the protective coating have been formulated.

Keywords: molybdenum, coatings, silicides, micro- and macrostructure

ОПТИМИЗАЦИЯ СТРУКТУРЫ СИЛИЦИДНЫХ ПОКРЫТИЙ НА ОСНОВЕ МУЛЬТИМАСШТАБНОГО ПОДХОДА

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В работе предпринята попытка применения мультимасштабного подхода к изучению силицидных покрытий на молибдене. Макро- и микроструктура силицидного покрытия во многом определяет механические и коррозионные свойства композитов молибден – защитное покрытие. Для предотвращения недопустимых изменений необходимо предвидеть эволюцию структуры при формировании покрытия и в процессе эксплуатации композита. В работе проанализированы факторы, определяющие деградацию защитных свойств покрытия на разных иерархических уровнях. Сформулированы требования к макро- и микроструктуре силицидов с целью достижения более совершенных термических свойств защитного покрытия.

Ключевые слова: молибден, покрытия, силициды, микроструктура, макроструктура.

ОПТИМІЗАЦІЯ СТРУКТУРИ СИЛІЦИДНИХ ПОКРИТТІВ НА ОСНОВІ МУЛЬТИМАСШТАБНОГО ПІДХОДУ

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У роботі зроблена спроба застосування мультимасштабного підходу до вивчення силіцидних покриттів на молибдені. Макро- і мікроструктура силіцидних покриттів багато у чому визначає механічні та корозійні властивості композитів молибден – захисне покриття. Для запобігання неприпустимих змін необхідно передбачити еволюцію структури при формуванні покриття і в процесі експлуатації композиту. У роботі проаналізовано чинники, що визначають деградацію захисних властивостей покриття на різних ієрархічних рівнях. Сформульовані вимоги до макро- і мікроструктури силіцидів з метою досягнення досконаліших термічних властивостей захисного покриття.

Ключові слова: молибден, покриття, силіциди, мікроструктура, макроструктура.

INTRODUCTION

Investigations of fundamental principles and basic mechanisms of structural phase transitions in solids are the most important component in development of new materials for use in modern high technology. Currently, a variety of composite materials, including those containing silicides of refractory metals, are increasingly replacing traditional structural and func-

tional materials for the creation of new technologies, machines, mechanisms and devices in various fields of science and technology [1, 2]. This is largely due to the implementation of previously unattainable complex and/or the level of physical and mechanical, electro-physical, thermal, and other properties in such materials, which allows us to solve relevant technical and consumer problems: from reducing

weight and intake of metals to enhancing their durability, performance and efficiency.

Development of new and improvement of known materials is based on the results of two related areas of work – experimental and theoretical. In theoretical studies, the so-called cybernetic (experimental-statistical) and multilevel or multiscale approaches are distinguished. In the latter case, the material is represented in the form of a complex system – design, where the individual elements of the structure play a role of subordinate components (sub-systems, sub-structures), and conduct a direct simulation of the behavior of the material under the combined influence of external damaging factors including the internal geometry, properties, and interaction of elements. In this simulation, various approaches of continuum mechanics involving numerical or discrete techniques are used [3, 4].

In experimental studies of the mechanisms of formation and evolution of the structure of materials as well as structural phase transitions in them, it is of high importance to take into account the full range of external influences arising during operation (heat treatment, irradiation, corrosion, etc.). Combined external impact initiates the interference processes in materials, which can lead to the formation of quasi-stable states and can influence the formation of defects or other local irregularities in the original structure of the material [5, 6].

In this paper, a multiscale hierarchical approach is applied to the experimental studies of the possibility of raising long-term operational stability of the molybdenum-silicide coating composite material.

GENERAL CHARACTERISTICS OF SILICIDE COATINGS AND MULTI-SCALE ELEMENTS IN THEM

Silicide coatings are the most effective means of protection of refractory metals, particularly molybdenum from high-temperature oxidation [7, 8]. Silicides are used due to their heat resistance, ability to retain sufficient mechanical properties within a wide temperature range, higher conductivity and compatibility of silicide obtaining operation with a total production technology of the final products. Furthermore, silicides have a number of advantages, e.g. a high melting point, a wide range of resistivity, ability to form epitaxial layers forming the Schottky barrier of the predetermined value, possibility to grow the oxide film on the silicide. [9] At temperatures above 1500 °C in oxygenated atmospheres

on the surface of the silicides the oxide film consisting of practically pure silicon dioxide SiO_2 is formed. This film provides a high heat resistance of silicide coatings, preventing penetration of oxygen to the metal surface.

Increased use of silicide coatings is constrained by a number of negative factors, significant of which is the lack of stability at high temperatures. This instability is caused by the initial thermodynamic instability of the substrate-coating system and its tendency for chemical reactions [10].

To achieve the best performance characteristics of molybdenum products with coatings, it is important to fully define the connection between the composition, structure and properties of the coatings, to simulate the optimal coating and develop a technology of its formation. At the same time, the simulation should take a large scale of object into account – from the macro-scale of the whole coating and its individual layers (with the size of hundreds of micrometers, fig. 1) to sub-micron elements (crys-

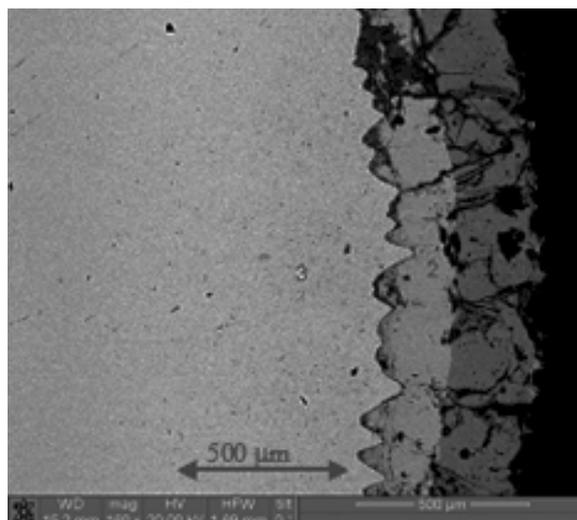
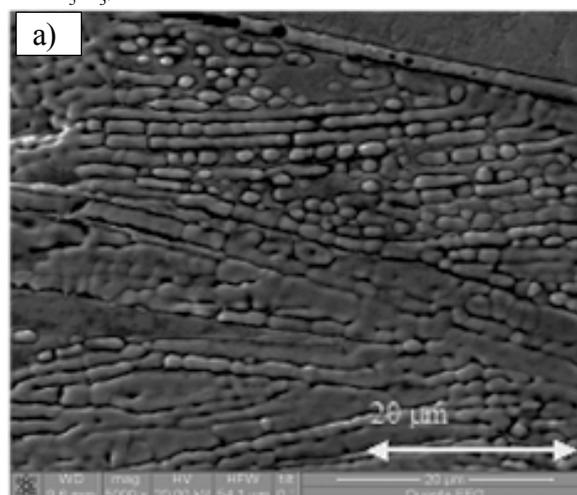


Fig. 1. Macroscale elements of the molybdenum substrate – two-phase silicide coating composition: 1 – MoSi_2 ; 2 – Mo_5Si_3 , 3 – Mo.



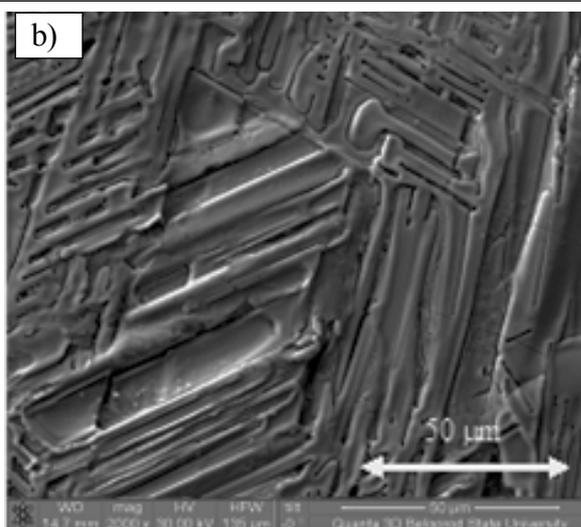


Fig. 2. Submicron elements of the MoSi_2 - Mo_5Si_3 eutectic mixture.

tallites of eutectic mixtures, fig. 2) and the smallest nanoscale objects (pores, microcracks nucleus, interstitial atoms and molecules, vacancy clusters, fig. 3).

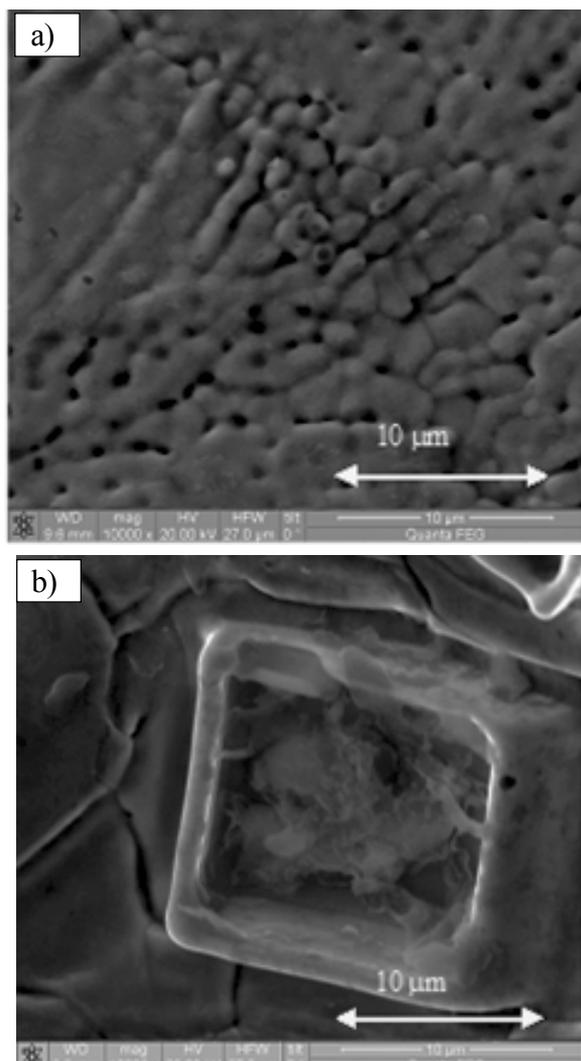


Fig. 3. Elements of the smallest scale in the silicide coating: a) – cluster of pores, b) – impurity.

It is known that the best coating from the perspective of uniform stress distribution, bonding strength and the greatest thermodynamic stability is a diffusion layer which is a continuous series of solid solutions [11]. Such a layer, for example, is formed in a place of contact of molybdenum and tungsten under high annealing (about 2000 °C) in vacuum. The same is observed while chromium-plating of molybdenum, tungsten and other metals. However, there is a relatively small amount of systems where due to the counter diffusion the monophasic layer with continuously varying concentration of the doping component is implemented. This concentration continuously varies from the boundary value (at one boundary) to zero (at the other boundary).

OPTIMIZATION OF MACRO-AND MICROSTRUCTURE OF SILICIDE COATINGS

In many cases, including molybdenum siliconizing, multiphase compositions consisting of the layers of chemical compounds and sequentially arranged bounded solid solutions are formed.

When modeling a coating at macro level in systems with intermediate compounds (namely Mo-Si relates to such systems, where there are stable compounds of MoSi_2 , Mo_5Si_3 , Mo_3Si [12, 13]) it is necessary to strive for creating a composition the structure of which is very close to continuous series of solutions. This can be achieved through meeting several requirements simultaneously.

Firstly, the greatest concentration of silicon must be on the surface of the coating. Implementation of this condition ensures rapid formation of an oxide film of SiO_2 and achievement of the desired protective effect.

Secondly, the concentration of silicon from the side of the molybdenum substrate should be the lowest, this will slow down the diffusive dissolution of the silicides inside it.

Thirdly, to achieve and maintain a reliable adhesive interaction between the coating and the substrate, it is necessary to relieve the mechanical stress in the system during formation of the coating as well as during the operation of the substrate-coating composite as much as possible.

Meeting the above requirements for the molybdenum-silicon system means that the silicide coating must be multiphase, and it is preferable to carry out its formation sequentially, starting from the lowest

silicide phases (phases with the less silicon atoms in the molecules of silicides).

The implementation of the proposed scheme to form a coating provides minimal changes in specific volumes on the phase boundaries and the lowest difference between the thermal expansion coefficients of the individual layers with a common boundary.

It should be noted that during the establishment of diffusion coatings the phase composition is often determined by the rate of their formation. In most cases, due to economic considerations, they traditionally tend to maximize the saturation velocity [14]. During siliconizing at high saturation speeds, the coating consists mostly from the higher silicide phase, i.e. the phase richest in silicon. In the studied system it is molybdenum disilicide MoSi_2 . Since the specific volume ratio of this phase and the base metal (molybdenum) are significantly different, in the process of saturation, the coating is exposed to significant stresses relaxation of which leads to the formation of micro- and macro-cracks, pores and other defects. During operation of the coating, the amount of defects increases, they combine into larger formations, which leads to a rapid loss of protective effect of the coating. It is therefore extremely important to organize the technological process of coating deposition in a way to provide a gradual decrease of stress by the thickness of the coating. The stated comments also lead us to conclusion about the reasonability of forming a coating through the lower silicide phases [15].

Currently, lower molybdenum silicides are used mainly as individual additives in composite materials [16, 17], which is a consequence of rather widespread belief of their insufficient heat resistance. The standard approach to the formation of silicide coatings is the formation of sufficiently thick (500 microns or more) layers, the significant (most frequently – the major) part of which is represented by disilicide (fig. 4).

During the further use of the product with such coating, only its minor part is used as intended (i. e., to form an oxide layer of SiO_2 on the surface), and the rest turns into lower silicides as a result of diffusion reaction, which is activated by the high performance temperatures [18]. The process of redistribution of silicide phases in the coating is accompanied with the mechanical stress of alternating sign (tensile stress

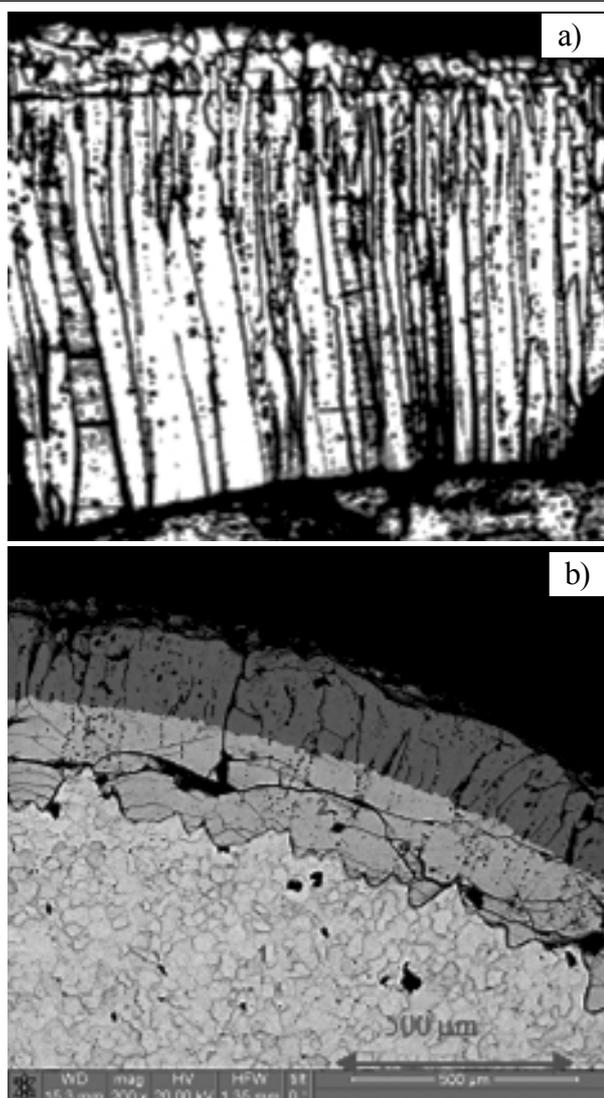


Fig. 4. Disilicide layers in the coatings on molybdenum: a) – almost entirely disilicide coating with the thickness of 450 microns, MIM-8 microscope; b) – complex coating on molybdenum (1) with an inner layer of silicide Mo_5Si_3 (2) and an outer layer of about 200 microns of molybdenum disilicide (3), Quanta 200 SEM.

and compressive stress), which is due to the natural thermodynamic and structural properties of individual silicide phases [19]. These stresses can lead to a failure of uniformity of the coating.

The specific list of macroscale factors may be adjusted depending on the actual operating conditions (e.g., the case of coatings with different configuration and structure on different parts of the same product can be implemented in the presence of a temperature gradient on the surface of a product or different curvature of the surface on different areas).

Optimal modeling of the structure of the silicide coating on the microscale primarily requires creation of such a crystallite composition which can reduce

the grain boundary flow of silicon, slow down the diffusion phase dissolution and increase efficiency of the coating without significant phase transformations in it. In this sense, a coating with a fine-grained structure of the silicide formed by equiaxed (spherical or polyhedral) grains has the best potential. In our view, the better stability would be provided by a microstructure with grains elongated along the phase boundaries, and not oriented perpendicular to them (fig. 5).

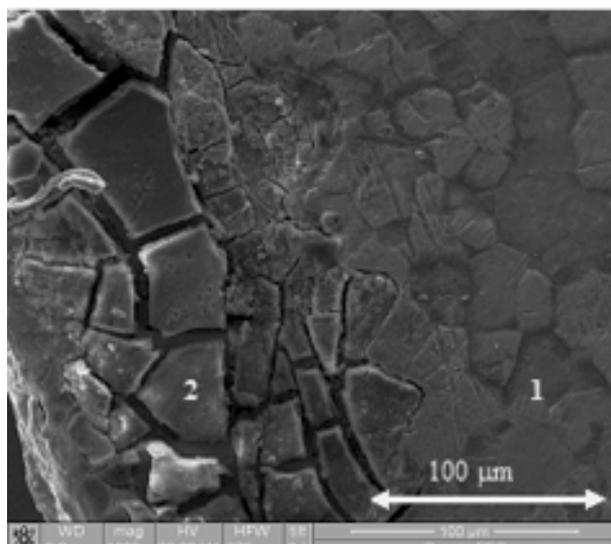


Fig. 5. Large-block silicide coating (2) on molybdenum (1), Quanta 200.

Much attention is paid to the fight against diffuse dissolving of disilicide phase and increase of the protective effect of the coating [20]. Attempts of insertion of additional elements to the composition of the coating, which form the barrier layers from the foreign substances to slow the diffusive dissolution of the higher phase, gave some positive result at moderate temperatures (up to 1650 – 1700 °C). At higher temperatures, the material of the barrier layer rapidly pollutes the protective film of silicon dioxide, and the heat resistance of the coating is sharply reduced [21].

Point insertion of additional chemical elements in the form of individual embedded or substituted atoms with formation of sub-micron inclusions of third phases of nanoscale inclusions of individual atoms will eliminate the negative factors that are inherent in conventional barrier layers, but the experimental data of such modification of the coating are practically absent. There is another model approach, viz. creation of chemically-related barrier layers in the coat submicron scale ing, which are obtained without the

insertion of additional chemical elements. Examples of such layers are eutectic mixtures of nano- and submicron particles of various molybdenum silicides, as well as their solid solutions [22]. One of the options to obtain such compositions (fig. 6) can be contact melting of different silicide layers [23], co-sputtering of elements, followed by condensation and reactionary diffusion or there can be some other methods.

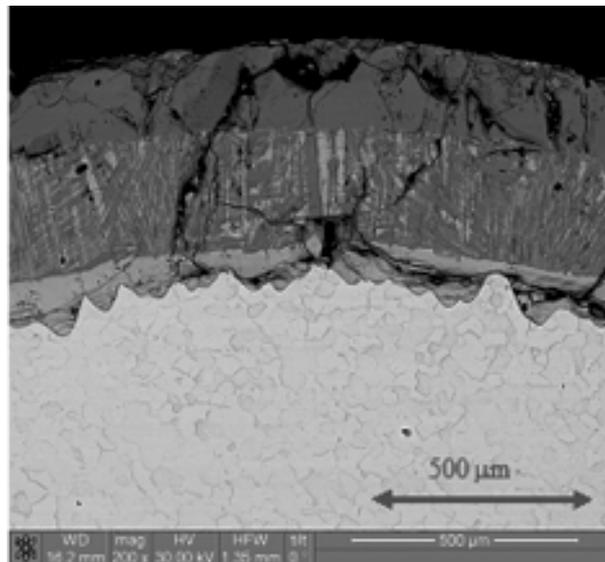


Fig. 6. The result of contact melting of silicides: MoSi_2 - Mo_5Si_3 eutectic layer in silicide coatings on molybdenum, Quanta 200.

CONCLUSION

Multi-level hierarchical approach (multiscale approach) is an important tool for optimizing the structure of composite materials. To achieve the best performance of materials in different operational conditions it is necessary to know the full range of both structural characteristics of the composite material, and environmental factors, which initiate evolution of the structure at each hierarchical level. Such knowledge allows to choose the acceptable level of degradation for each structural level and thereby simulate a coating with optimal structure-phase state.

The factors determining the implementation and changes in the structure of molybdenum silicides, are the initial structure of the substrate, material defect, stress-strain state of the material, method of processing, temperature, composition and the source of diffusion impurities. The requirements to the chemical composition of individual areas of the coating, to the sequence of phase layers and to the microstructure of the layers have been formulated.

The options of the construction of the coating with improved stability have been proposed.

For a system of molybdenum-silicide coating, practically in all cases, the best combination is a multi-layer multi-phase silicide coating with a gradual decrease in the concentration of silicon from the surface to the substrate.

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