SURFACE ENGINEERING OF THE NANOSTRUCTURED FUNCTIONAL-GRADIENT MATERIALS: FEATURES OF SYNTHESIS AND DEVELOPMENT OF NEW FUNCTIONALITIES

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ABSTRACT

The paper describes the modern aspects of research perspectives in the field of surface engineering (high-precision synthesis) of functionally gradient nanostructures. Examples of practical applications of FGM obtained are given.

Keywords: Functional Gradient Materials, Nanostructuring, Titanium Nitrides and Carbides

1. INTRODUCTION

Nowadays situation demands to create new functional materials with new properties. The development of modern equipment is tightly associated with productivity level and durability increment. This requests functional properties improvement that could be reached by creation of new constructional materials or by covering materials with functional coatings.

The most promissing direction thus is to create functional gradient materials (FGM) – combination of different materials to use their strong features.

To create FGM means to create a brand new way of synthesis: chemical and physical processes that lead to the predefined atom order.

We have to solve the problem of structural organization of the substance to get the right order.

It is clear the crystallization (a kind of self-organizing process) is one in the row of getting solid substances, maybe not the main one.

According to our concept [1] we are talking about synthesis of highly organized solid substances from the chemical point of view as a solid chemical compound with higher structural organization than of naturally undergoing organizational processes with the same polyatomic rate with equal chemical structure.

So it is important to start other structure organizational processes investigations particularly that one that allow to synthetize complex substances of aperiodic but regular structure.



Figure 1. The Sceme of Chemical Construction of Oxide Nanostructures by Molecular Layering Method - ALD

We may part two limiting conditions of the structure: heterogeneous distribution of bulding blocks on the one side (monocrystalls, glasses) and multi-element structure where blocks are bonded in a free order (biological objects eg). Changing the bonding order of element-oxygen layers we can create new complex solids that don't occur in the Nature. They can be obtained in the artificial way only. Such structures are presented on Figure 2.



Figure 2. Scheme of two-dimensional nanostructures at silica surface. (A) Uniform distribution of chemical composition and structure. (B) Periodical distribution along the z axis of element-oxygen layers containing a certain number of monolayers (C) Aperiodic distribution of element-oxygen layers along the z axis (D) Aperiodic atomic distribution in the surface monolayer plane (top view): (crosses) Fe-O groups and (circles) Ti-O groups (E) Aperiodic distribution of zero-dimensional structures in the substrate plane.

The only way to create such aperiodic structure in solid phase is to replace ordering processes that lead to thermodynamical balance of the system with ones that finish on a highly orginized meta-stable structures.

Practically synthesis of nanostructured solid substances is carried out by the means of chemical assembly of structural units on corresponding matrices. Step by step we carry out surface reactions in the right order with not less than bifunctional reagents to cover substrate layer by layer (Figure 3). The main difference is shown on pic 4: spatially divided compounds have got inter-atomic bond (Si-O-Ti, the first case). While deposition (e.g. CVD) inter-molecular bonds appear (case 2) that allows to simplify phase formation processes. Thus we process synthesis of 2D nanostructures (nanolayers) consisting of monolayers without any phase formation (at certain temperature range) and create 100% artificial compounds.

It was shown during the investigation of mechanical properties of nanostructured material (Figure 3) based on alternating layers of TiN and TiC that hardness depends on the total thickness of both layers: when their sum thickness is about 30nm hardness greatly increases, further increment leaves it constant. Obviously dislocations are hard to move between layers.



Figure 3. Hardness Dependance on the Bilayer Thickness

Structures examples that are under investigation in our lab nowadays are shown on the Figure 4.



Figure 4. Examples of High-Organized FGM

Lets take a look on a nanostructured FGM Figure 5. It's an urgent problem to develop new sorbents and technologies of separation, so a new nanostructured sorbent for uranium has been worked out. The sorption of uranium ions from artificial seawater has been studied (Table 1). As it can be seen from the table the full dynamic capacity of oxide nanostructures containing is 10 times more for TiO2. Adding Fe-O layer and regulating Fe2+/Fe3+ rate allowed to create a ferromagnetic layer and the optimal ferromagnetic layer thickness is 12A. This allow to exclude ineffective filtration stage and to pass directly to magnetic separation.



Figure 5. Ferromagnetic Sorbent: $1 - SiO_2$ particle (aerosil); $2 - Fe_3O_4$ layer (10-15Å); TiO_2 layer (6-10Å)

№	Sample	S m ² /g	Dynamic Exchange Capacity	
			Mmol/g	Mg/g
1	SiO ₂ (aerosil)	300	Traces	Traces
2	Titaniumgel	100	0.1	
3	[SiO ₂]- 2 Ti-O	230	8.31	1978
4	$[SiO_2] - Fe^{+3}/Fe^{+2} - 2$ Ti-O	215	8.34	1981

2. CONCLUSIONS

The nanotechnology has been created as the result of the work allows to obtain new types of protective coatings for constructive materials – functional-gradient nano-coatings that meet the requirements to be run under the severe conditions (energetics, thermonuclear fusion, petrochemical industry, production of hydrogen engines, cutting tools, gas turbines etc)

ACKNOWLEDGEMENTS

The work was supported with the Federal Target Program of Russian Goverment Educational Department, Contract P-2117, P-1431

3. REFERENCES

 V.M.Smirnov, Nanoscaled Structuring as a Way to Constructing New Solid Substances and Materials, Russian Journal of General Chemistry, Vol. 72, No. 4, 2002, pp. 590-606