PROCESSES OF DISPERSE-PHASE NANOSTRUCTURING IN SUBSURFACE AREAS OF COMPOSITE CERAMIC MATERIALS – THE CURRENT STATE OF RESEARCH (A BRIEF REVIEW)

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Abstract. Ceramic structural materials are considered as a perspective base for constructional units of gas turbines, hydrogen engines, and some other heat-resistant applications since such materials are able to meet hard functional requirements. However, limitations typical for ceramics due to the nature of the material (fragility, high sensitivity to shock load, etc.) are the basic problem restricting wide application of such materials. Nanostructuring of ceramic constructional materials is considered as being the most promising approach to solve this problem. This paper summarizes recent works describing micro and nano-structuring processes in nanoceramics , both for "micro" level (CVD and infiltration) and "nano" level (molecular layering - ALD). The positive effect of micro- and nanostructuring on the critical ceramic materials properties (tensile strength, fracture toughness, etc.) is highlighted; the advantages of ALD method for the direct regulation for "nano-non-homogeneities" (3D nanoparticles, 1D nanowires) are discussed.

Current trends in machine building industry (development of modern gas turbines, hydrogen engines, etc.) require new materials with improved mechanical, thermal, and chemical properties in order to withstand extreme exploitation conditions. Novel ceramic construction materials (CCM) are considered as being very perspective for such applications.

It should be mentioned that one of the basic tendencies in modern material science is the development of new materials with complex chemical structure. The focus [1,2] of these studies is the development of the materials with different organization level - from cluster to high-organized solid compound (material) [3,4] and purposeful regulation of their properties. The present paper reviews the recent investigations in the field of micro- and nanostructuring of oxide ceramics.

It is well known that regular atomic structure of solid materials is determined by endless and periodic repetition of atoms collocation. From the other hand, some randomization could be also found in other materials (regular order in nature is more an exclusion than a rule) and the disorder is higher for complex structures (biological systems, polymers, nanomaterials, glasses, etc.). In turn, the absence of regular structure could be caused by different mechanisms: starting from simple uneven cooling (non-metal glasses, metals, etc.) and finishing with evolution (biological systems).

It is worth to notice that there should be a critical size for nanostructures under which organized disorder is more efficient than a pattern; that is a possible explanation for non-crystal structures existence. Based on the above mentioned, investiga-

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tion of organized but disordered structures is one of the most promising directions for material science development [2].

Moreover, we should mention the importance of other structuring processes in addition to crystallization. Processes leading to the formation of complex substances with non-periodic but regular structure are the point of especial interest here. On this step of investigations, the primary scientific target is to clarify the influence of 1D (nanowires, 1-50 nm) and 3D (nanoparticles, 1-50 nm) structural imperfections on texture and functional (mechanical) properties of bulk ceramic material. This is an important step for elaboration of the scientific base for creation of new composite materials with pre-defined structure and regulated functional properties.

Comparing to metal materials, ceramics possess a complex of unique properties and has got a number of advantages: ability to keep its properties in RedOx environment at 1200 °C and even higher temperatures, good durability, excellent rust resistance, lower densities, and smaller heat expansion. These advantages make ceramics the only option for applications in heat-burden units for aerospace equipment and special mechanic engineering areas. Ceramic composite materials correspond to the highest standards for strength-to-weight ratio and fuel efficiency of power plants, noise, and environment-friendly factors [5-13].

Designing new composite materials based on oxide ceramics, we should keep in mind two features: (1) fragility of the final material and (2) the fact that ceramic materials production requires high temperatures [10,14-19]. One of the weak features of ceramics is its high sensitivity to different stress raisers existing in the material structure: micro cracks on grains borders, pores foreign inclusions, etc.. This is due to the ceramics inability to relax after high strains that occur on strain raisers due to interatomic binding nature in chemical substances that are used as ceramics precursors. That is why ceramics has got wide hardness statistical distribution [20-26].

As mentioned above, one of the main tasks of the new ceramic materials development is to increase ceramic material fracture toughness. Reference data [1,5] indicate that ceramics filling with nanoparticles or nanofibres produced from refractory materials leads to fracture toughness increase. At the same time, nanofibres show better effect comparing to nanoparticles. It should be mentioned that a "side effect" of ceramics arming with nanofibres yields both in fracture toughness increase

and in a lowering of the extremely high rate of material damage.

Since ceramic products are commonly applied at high temperatures, account must be taken of ceramics susceptibility to crack at fast temperature fluctuations. At the same time, investigations [10,11] prove that nanostructured ceramics show less heat-expansion coefficient coupled with increased heat conductivity and crack toughness. So, an increased material resistance to thermal shock could be stated.

Nowadays, aluminum ceramic composite materials reinforced with nanoparticles and nanowires are regularly used for industrial purposes [5,15]. Diesel engine test data [1] for a truck with ceramic piston head, chambers, and collars showed the reduction of fuel consumption rate (27%) while the performance coefficient rised from 35% to 45%.

Especial attention is drawn today to composite materials where silicon carbide (SiC) is both matrix and disperse phase [9,10]; investigations usually focuses on the improvement of the work capacity of flame tubes made of CCM SiC/SiC that are placed into annual combustion chambers of land gas turbines [8]. As for oxide ceramics functional properties improvements, we notice a lack of up-to-date investigations. For example, authors of [27] reported that CCM based on aluminum with surface TiN nanotubes possess better plasticity after compaction.

Another work [28] deals with disperse titanium nitride formation and describes the use of titanium dioxide (rutile and anatase) and ammonia as precursor reagents, where anatase was chosen as preferable option due to higher surface and smaller medium particle size of final TiN in that case.

Composites based on AlN and TiN (TiN content of 0, 5, and 10 vol.%) were obtained [29] with and without yttrium oxide (for better sintering process) at 1850 °C. The sintering time was widely varied here - from 1 to 20 hours, as a result, sintering of almost non-porous materials was reported. Moreover, TiN particles observed on most of grains interfaces hold their round shape and small size. That kind of material formation allowed to increase kinematic heat conductivity.

Thin layes $(Ti_{1-x}Al_x)N$ on Si mounts oxidation investigations at different temperatures has been carried out using Auger spectroscopy [30]; atmospheric oxygen was chosen here as an oxidant. Most films oxidized at 800 °C led to band Al_2O_3/TiO_2 structures. However, Al_2O_3 top-coat prevented TiN from further oxidation.

Paper [31] reports the investigation of TiSiN nanocomposite coatings obtained at 850 °C by CVD method on stainless steel mounts using fluidized bed reactor with $TiCl_4$, $SiCl_4$, and NH_3 as reagents. It is stated that TiSiN coatings with Si content about 9% showed hardness of about 28 GPa and low oxidation rate by dry air at 600 °C. Authors recommended the described method for obtaining nanocomposite ceramic coating.

Investigation of $Ti_{1-x}Al_xN$ layers (0.55< x <0.57) formed by reactive magnetron sputtering on polished steel (100Cr6) has been carried out in [32], the positive effect of the nitride layers on material hardness was highlighted. It was shown that some structure features found in the specimens are due to surface structure formation (super grating); this surface structure consists of alternating AlN and TiN layers as thick as 3 nm. Authors concluded that the specimen hardness is mostly affected by the existence of a particular super grating that prevents formation and motion of dislocations. Layers are characterized by high resistance to oxidation at temperatures up to 800 °C. This fact could be explained as being the result of thin (50-200 nm) aluminum nanolayers formation that passivate oxidation. Authors declare further possibilities to improve TiAlN hard coating properties by fine adjustments of their chemical composition and microstructure.

During investigations carried out with two-component films based on titanium oxide and nitride that cover titanium alloy of artificial heart valve [33], titanium oxide was shown to play the main role in bio-compatibility, while titanium nitride was used as mechanical properties improvement additive.

Another investigation [34] has been carried out to understand the mechanism of formation and further growth of nanolayers of titanium nitride obtained by ALD method. Authors [34] used tetrakis(dimethylamido) titanium and ammonia as starting materials; they mentioned that the control of the film growth is extremely difficult. The grown nanolayers possess high porosity (about 40%), this porosity level is considered as a limiting factor for the application of the materials as diffusion barriers.

Deposition temperature should be kept within the range of 450-600 °C to unveil interactions that limit the growth kinetics, affect composition and properties of TiN nanofilms obtained by LPCVD with $TiCl_4$ and NH_3 as starting materials. In doing so, one can exclude surface pollution with inappropriate carbon containing substances, but, at the same time, higher temperatures are usually required for reasonable growth rate values. Classical method describes the above mentioned procedure to undergo at 800 °C, but some researchers report it as proceeding at 450-500 °C [35]. Nanolayer growth rate of LPCVD was controlled here by titanium chloride and ammonia pressures. As expected, lower Cl content resulted both from ammonia pressure and temperature increase. At that, films maximum density of 5.02 g/cm³ has been achieved. Films hardness depends on their thickness - uncontrolled growth rate results in degradation of Young modulus and hardness. Films nanoindentation allowed to estimate hardness values that were inside 15-250 GPs range.

Account must be taken of arming fibres thickness - usually arming fibres are close to 0.1 mm and more. That leads to numerous interlayer phase boundaries and prevents us from a breakthrough improvement of composite functional properties [1,10]. Note that ceramics arming by nanowires (1-100 nm) should dramatically increase composite oxide material strength and fracture toughness [1].

Most papers dealing with matrix nanostructuring (including ceramic matices) contain information of nanoparticles application. Only a few of them describe nanowires structuring processes, it is due to the fact that nanowires-provided structuring process is much more difficult to accomplish. However, paper [2] describes a potential ability to obtain material structured by nanowires. As it can be seen from the paper, the main problem of the process is to carry out surface reactions that force nanostructuring process [36-39]. That is why main mechanical properties of obtained material (hardness and fracture toughness) should be provided by the means of nanostructuring of aluminium-oxide matrix.

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