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Ultraporous Multilevel Nanocomposites with Different Architectures

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Abstract

A new universal approach to obtaining multilevel nanocomposites with different architectures including interpenetrating structures and the nucleus–shell structures was proposed. The approach is based on the deposition of charged aerosol with particle size within the range from 30 nm to 300 μm using electromass classifier. In view of the small excess charge of the particles and large dipole moments, the density of coatings after deposition is very low. After fixing the porous framework by sintering, the achieved relative density of the ceramic coating was 0.04. Filling of the framework provides the possibility to obtain a broad range of interpenetrating composites. The use of mechanocomposites for the generation of aerosol allows obtaining multilevel composite materials with required architecture.

Key words: nanocomposites, mechanocomposites, charged aerosol, self-assembly, porous coatings

INTRODUCTION

One of the most promising directions in materials science is the synthesis of composite materials with required architecture. A special interesting problem is the development of composites with interpenetrating structures (Fig. 1). These composites may combine the best properties of the initial components including a combination of the characteristics that are incompatible in one compound. Natural composites with interpenetrating structure (for example, bone) possess a unique combination of characteristics, such as flexibility and strength of the components. It should be noted that even 10 years ago there were no approaches to the preparation of interpenetrating ceramic composites [1]. The method of obtaining these composites is unique in each case and is determined by the properties of individual components. For example, interpenetrating composites from superhard borides with copper, possessing high wear resistance and electric conductivity were obtained by agglomeration in electric fields with the formation of plasma at the contacts of conducting particles [2]. In rare cases interpenetrating structures are formed in the spinodal disintegration of solid solutions within a narrow range of compositions, for example during cooling of the alloy of almost immiscible Be and Al. The development of interpenetrating composites from various polymers, metals is possible in the liquid medium or in the melt in the case of a definite arrangement of the processes of polymerization (cooling). Interpenetrating composites can optimally combine the properties of components in the region of compositions remote from the percolation threshold (~1/5) in

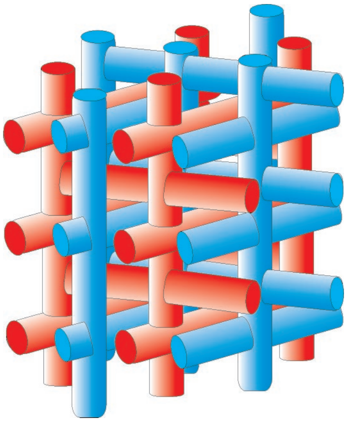

Fig. 1. Scheme of a composite with interpenetrating structure.

irregular composites. A 2-dimensional analogue of interpenetrating composites is a modern textile cloth.

The goal of the present work was to develop a universal approach to obtaining composites of different materials with different architectures on the basis of the technology of precipitation of charged aerosol with the help of the instrumentation of Electromass classifier class (EMC) [3, 4]. The use of mechanocomposites as structural elements with render a pulse to further development of mechanochemical ecological technologies.

EXPERIMENTAL

Reagents of ch. d. a. grade (pure for analysis) were used in the work, as well as carbon soot, powder of non-purified carbon nanotubes, polymer binder IP-5, elemental sulphur of the rhombic modification obtained in the purification of natural gas, Portland cement of M400 grade, flue ash (from the Troitsk Power Station) composed of glass microspheres. Powders of mechanocomposites were obtained by treating the mixtures of powders in planetary mill AGO-2 using a known procedure to decrease their contamination by making protective coatings [5]. Treatment time was 30–300 s, the mass of the material charged for treatment was 15–30 g, the mass of steel balls 8 mm in diameter was 200 g. Under these treatment conditions, the size of individual powders usually reaches 5–100 nm [6]. To separate aggregated powders into narrow fractions and to deposit coatings on substrates, we used modified microseparator EMK of the Nanoporoshkovye Tekhnologii Co. (Novosibirsk, Russia). Fixation of the framework of ultraporous coatings by agglomeration was performed through thermal treatment in the air or in a closed crucible with limited access for air. The reduction of copper oxide in the composite CuO–Ni was carried out in the flow of the mixture of hydrogen with argon at $T = 523$ K.

Relative density (RD) of ultraporous coatings from charged fine and nanosized powders resembling cotton wool was estimated after fixing the framework on the basis of the data on the density of the materials comprising the composite, mass and geometric size of the coating. Characterization of the composites, including an independent evaluation of RD, was performed with the help of JSM-6700F and Hitachi TM-1000 electron microscopes (Japan) with gold spraying and in the low-vacuum mode, in order to decrease interference from sample charging and to prevent their destruction. Nanocomposite based on the polymeric binder was studied with the help of atomic force microscope. A probe with the tip curve radius of ~10 nm and convergence angle of 20° was used.

RESULTS AND DISCUSSION

About the mechanism of the formation of ultraporous coatings

During the EMC treatment of powder samples differing from each other in chemical nature, the generation of aerosol from charged particles occurs. The behaviour of aerosol is adequately described by the term gas-dust plasma [3]. Aerosol composed of solid particles having mainly the likely charges, but the excess charge on the particles is very small. Estimation gives about 10 elementary excess charges per a particle 1 μm in size. At the same time, the particles have strong dipole moments that lead to the so-called dipole self-assembly of the ultraprous coating (Fig. 2) [3]. Strong dipole moments are characteristic of the particles of different kinds including metal powders, which may be connected with the features of the composition and the structure of the surface. After the coating is formed, the excess charge gradually flows off, in particular due to the reactions with air ions present in the air. The ultraporous framework is very unstable because the strength of the contacts between particles

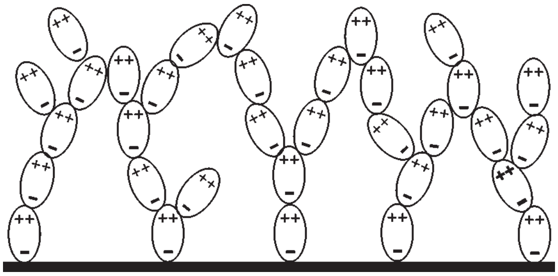

Fig. 2. Scheme of dipole self-assembly from charged particles with large dipole moments during the deposition of gas-dust plasma.

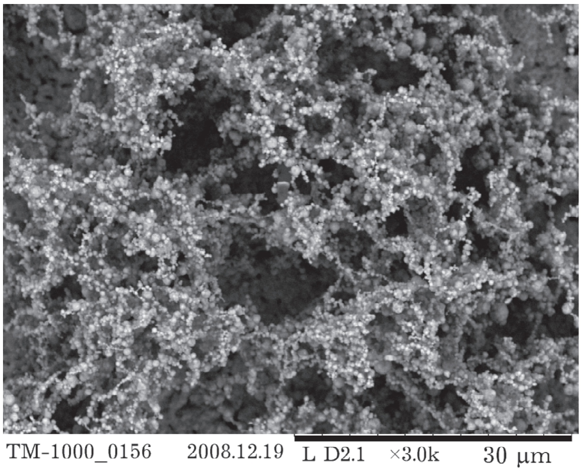

Fig. 3. Ultraporous coating composed of the spherical nickel particles.

is provided only by electrostatic charges and adhesion. In order to perform subsequent manipulations and technological operations, ultraporous coatings need fixation of the framework. The simplest and the most efficient method to strengthen the framework is agglomeration as a result of thermal treatment [3]. However, for developing a new universal method of obtaining composites, other methods of fixing the framework are also necessary to provide its filling with other components, for example through the gaseous or liquid medium.

Ultraporous composites of metals

An ultraporous coating formed from spherical nickel particles about 1 μm in size is shown in Fig. 3. Fixation of the framework was achieved by agglomeration during heating to 1000 K in the atmosphere of CO + CO_2. The formation of Ni framework with RD ~ 0.05 proves the presence of dipole moments on the surface of particles, even metallic ones.

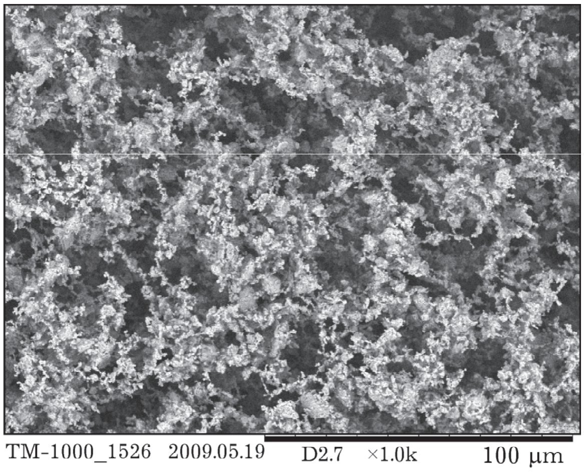

Fig. 4. SEM image of nanocomposite Ni + Cu with RD ~ 0.1.

An example of the synthesis of ultraporous metal composite with nanopores is shown in Fig. 4. The process of obtaining the composite includes grinding of the powdered mixture CuO + Ni in the planetary mill leading to the formation of mechanocomposites with a broad size distribution 1–100 μm. The characteristic size of Ni and CuO crystallites is 50–100 nm [6]. During the treatment in EMC, the mixture undergoes partial destruction of agglomerates, separation of the fine fraction <2 μm and its deposition on the substrate in the form of ultraporous coating. The coating was kept in the reducing atmosphere at 523 K, which resulted in the reduction of CuO to Cu with volume shrinkage by ~40 %, and the framework of the composite was fixed by means of agglomeration. Taking into account the size of CuO crystallites, pores having the size of ~10 nm are formed in the particles of Cu–Ni composite about 1 mm in size. It is possible to govern the parameters of metal nanocomposites within a broad range by varying the conditions of operations and choosing the initial reagents, for example Cu_2O. By varying the time of treatment of the powdered mixture $CuO(Cu_2O)$–Ni in the planetary mill, it is possible to obtain the crystallites of copper oxides within the size range of $10–10^3$ nm. By increasing the time of annealing during reduction or by increasing temperature, one achieves agglomeration of copper nanocrystallites with shrinkage and the corresponding decrease in the size of nanopores. So, variation of the size of nanopores in Cu–Ni composite is possible within the range from several nanometres to ~200 nm.

Ultraporous composites of ceramics and oxide metal materials

Three ultraporous frameworks of different nanocomposites based on layered perovskite $La_{1.4}Sr_{0.6}Fe_{0.6}Ni_{0.4}O_4$ (LP) and NiO, fixed by agglomeration at 1573 K, are shown in Fig. 5. A scheme of obtaining the composites includes

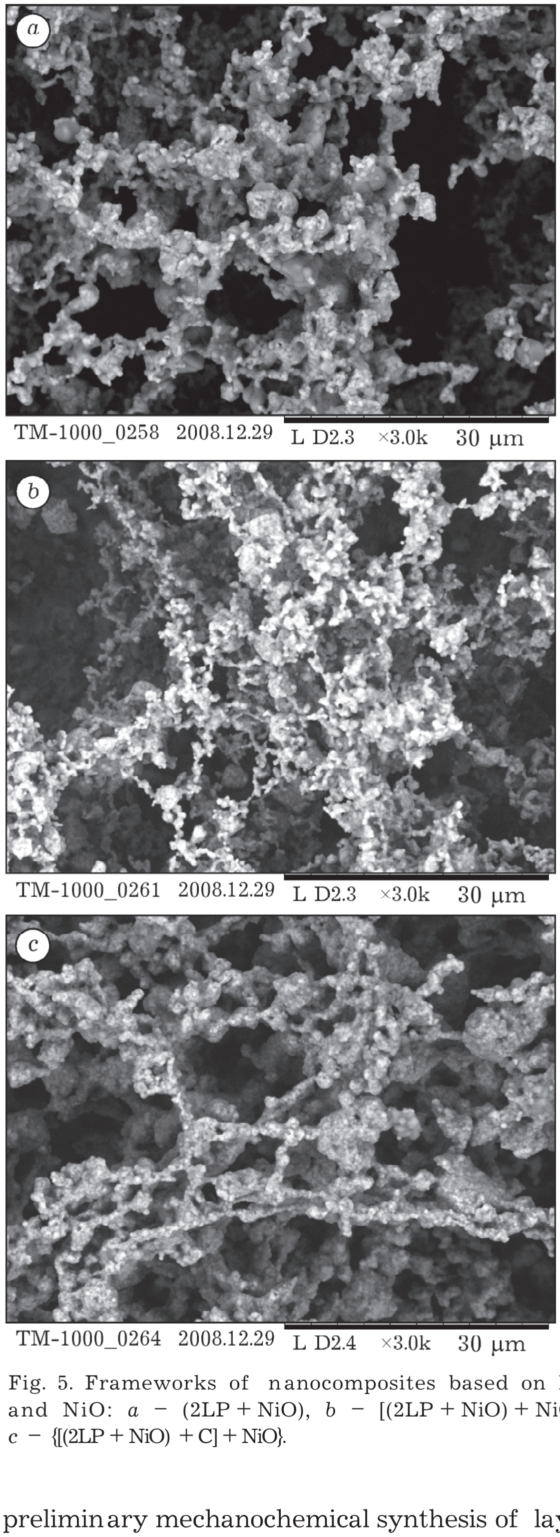

Fig. 5. Frameworks of nanocomposites based on LP and NiO: *a* – (2LP + NiO), *b* – [(2LP + NiO) + NiO], *c* – {[(2LP + NiO) + C] + NiO}.

preliminary mechanochemical synthesis of layered perovskite from a mixture of La_2O_3, NiO and $SrFeO_3$. To remove residual carbonates and adsorbed moisture, the powder of layered perovskite obtained by mechanochemical synthesis was calcined at $T = 1100$ K.

The conditions of the preparation of nanocomposites – the elements of the framework – were different. For the first composite we used the powders having the composition NiO + 2LP treated in the planetary mill for 240 s (the dimensions of the individual phases are of the order of 30 nm because the mechanochemical interaction between LP and NiO is weak). To prepare the second composite, we used the fraction 2–4 μm of powdered nanocomposite having the composition NiO + 2LP and the fine NiO powder with submicrometer-sized particles. Mixing was carried out in EMC with the deposition of the charged aerosol of the composite, its type being "nucleus + shell" (nucleus: NiO + LP composite, shell: NiO) with the approximate overall composition NiO + LP (in the discrete mode, due to the differences in particle size, enrichment of the coating with NiO occurs in EMC). The third composite was creating using the nanocomposite having the composition NiO + 2LP treated in the planetary mill with carbon black for 180 s (mass composition: NiO + 2LP + 0.1C) and mixed with NiO in EMC (final composition: ~2NiO + 2LP + 0.1C).

After fixation of the framework at relatively low temperature (T ~ 1300 K) the above-described model ultraporous composites possess the potential for shrinkage by ~10 % during agglomeration at 1633 K. The addition of carbon black burnable during the fixation of the framework increases the total porosity, in particular makes nanometer-sized pores inside the nanocomposites. The composites with high shrinkage potential (~15 %) of ceramics with mixed ion-electron conductivity are necessary for obtaining porous layers in catalytic membrane reactors (CMR) and porous electrodes in solid oxide fuel elements (SOFE) to avoid mismatching of shrinkage with the dense layer providing selective permeability of the membranes [7]. During the final assembling procedure for the SOFE with multi-layer membrane, NiO is reduced to metal nickel thus providing high electric conductivity of the anode. The ceramics with the structure of layered perovskite is chemically compatible with the material of the dense membrane layer with perovskite structure having the mixed conductivity; this material also has a close thermal expansion coefficient.

Ceramic composites based on layered perovskites after fixing by agglomeration at

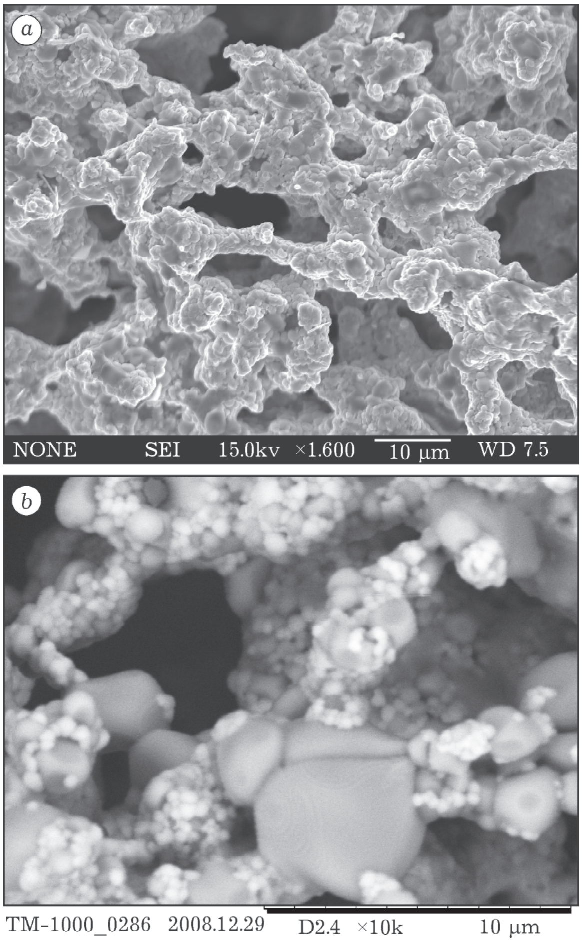

Fig. 6. Frameworks based on complex perovskites: *a* – P1 + P2, *b* – P + NiO.

$T = 1633$ K are shown in Fig. 6. These composites may be used, for instance, in the same areas as ceramic foams, and also for making the porous layer in CMR to provide efficient incorporation of oxygen into the lattice and its supply to the dense membrane with high oxygen mobility [7]. Ceramic foam usually has RD ~ 0.06–0.4, while the composites presented in Fig. 6 have substantially lower density (RD ~ 0.04 even after high-temperature treatment). The initial complex perovskites were obtained by means of mechanochemical synthesis, which decreases the temperature of framework fixation due to the high agglomeration activity of mechanochemical powders [8]. For making the first framework (see Fig. 6, *a*), a nanocomposite of two complex perovskites P1 + P2 (P1 = $La_{0.6}Sr_{0.2}Ca_{0.2}Ga_{0.6}Fe_{0.2}Mg_{0.2}O_4$, P2 = $La_{0.8}Sr_{0.2}Fe_{0.6}Co_{0.2}Ni_{0.1}Al_{0.1}O_4$) was used. Complex compositions are necessary to achieve adjustment of all the layers of the membrane with respect to agglomeration temperature and and improvement of chemical compatibility. The submicrometer fractions of perovskites P1 and P2 isolated with the help of EMC were mixed and treated for 30 s in a planetary mill. Perovskites are mainly conserved as individual phases during such a short time of treatment (the characteristic time of mechanochemical transformations under these conditions is about 200 s) and form strong mechanocomposites (RD ~ 0.8) [8]. The powder of mechanocomposite P1 + P2 was treated in EMC; thus isolated submicrometer fraction was deposited onto the substrate and annealed. For another framework (see Fig. 6, *b*), a mixture of NiO powder and the submicrometer fraction of complex perovskite $La_{0.6}Sr_{0.3}Ca_{0.1}Fe_{0.7}Co_{0.2}Ni_{0.1}O_4$ were used. The components were mixed in EMC and simultaneously co-precipitated onto the substrate as a coating. One can see that in this case due to the differences in agglomeration activities perovskite grains are much larger than the grains of nickel oxide, which allows us to observe the fine details of morphology that are indistinguishable in the usual recording mode. By governing the annealing temperature during the fixation of the framework, it is possible to achieve the required shrinkage potential for making large-size multiplayer membranes [7].

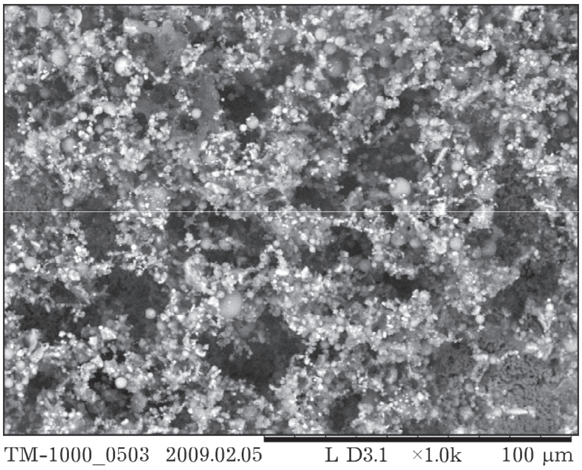

Fig. 7. Ultraporous multilevel nanocomposite based on cement.

Other nanocomposites

An attempt to prepare an ultraporous composite without the high-temperature fixation of the framework was made (Fig. 7). The nanocomposite of Portland cement and anatase was prepared in the planetary mill through treatment for 120 s, then elemental sulphur was added as hot-melt glue, and the mixture was treated once more for 30 s. The powder of nanocomposite [(10PC + TiO_2) + S] together with the fraction of glass microspheres ~10 μm separated from the fly ash at the ratio of 1 : 1 was mixed in EMC with the formation of charged aerosol and precipitation on the substrate. The glass microspheres absorb the excess $Ca(OH)_2$ which is formed during hydration of Portland cement and thus enhance the strength. The ultraporous coating composed of the particles with the size less than 10 μm was heated up to sulphur melting point at $T = 393$ K for preliminary fixation of the framework. Then the coating was kept in humid atmosphere for 24 h to achieve cement hydration and to increase the strength. However, using the above-described procedure we only succeeded in achieving the strength of the porous framework sufficient only for characterization by means of SEM but insufficient for the conservation of the shape during tempering with water.

EMC possesses a unique ability to mix the components suspended in the gas medium in the form of charged aerosol. Such a possibility was realized to prepare the precursor for the composite for construction purposes made of the polymer binder and carbon nanotubes. At a temperature of about 650 K, the polymer binder forms an amorphous carbon material with low thermal conductivity, and carbon nanotubes as filler are able to improve thermal conductivity sharply in the case of the development of self-penetrating structure. To make the composite, carbon nanotubes were added in the amount of 15 mass %, which is slightly below the percolation threshold for irregular composites. The formation of interpenetrating structure was monitored by measuring the electric resistance. After four cycles of grinding + agglomeration at $T = 393$ K in EMC with the isolation of the fine fraction <5 μm, the agglomerated composite demonstrated insulating properties (resistivity $>10^6$ Ohm · m). However, after the fifth cycle of mixing a sharp decrease of the resistivity by five orders of magnitude was observed, that is, a bound structure of nanotubes in the polymeric matrix was formed. The fracture surface of this composite is shown in Fig. 8. The size of heterogeneities in height is about 50 nm, which can be connected with the aggregates of nanotubes. A disadvantage of the described method of obtaining interpenetrating composites is the high content of expensive filler – nanotubes. When making interpenetrating composites by filling ultraporous frameworks with RD ~ 0.02–0.06, the filler content can be decreased by a factor of approximately five with respect to the composites with irregular structure.

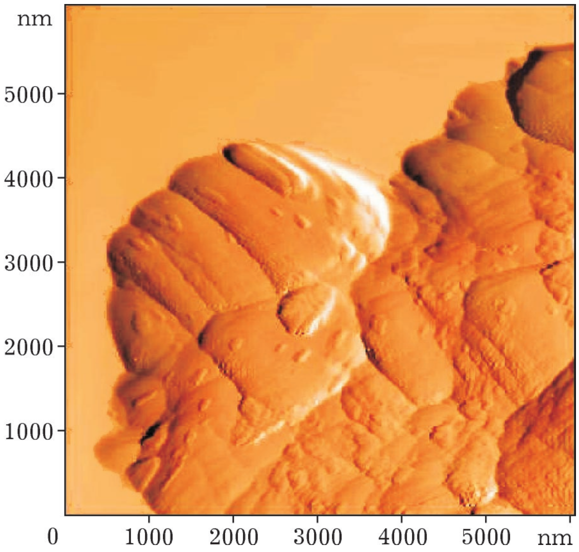

Fig. 8. AFM image of the composite based on polymer binder with nanotubes.

CONCLUSION

Manufacture of ultraporous coatings by the deposition of charged aerosol through the EMK procedure was implemented for different materials including metals and dielectrics, as well as mechanocomposites obtained using the mechanochemical technologies. The framework with uniquely low relative density (RD ~ 0.04) is fixed by means of high-temperature agglomeration in order to carry out subsequent manipulations and technological operations. Search for other techniques of fixing ultraporous frameworks is also necessary in order to develop a universal method of obtaining complex composites with different architectures by filling the framework through the liquid or gaseous medium.

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