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Finely Dispersed Refractory Compounds for High-Temperature Ceramic Matrix Composite Applications

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Abstract—Application of finely dispersed refractory compounds in the creation of high-temperature ceramic matrix composites (HTCMC) is briefly reviewed. Examples of successful combination of nanomaterials and HTCMC technologies are given.

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«…this all gives us grounds today … to consider as more actual ….the four-term formula composition–structure–dispersity–property…»
Academician I.V. Tananaev, 1976

INTRODUCTION

The technologies for production of high-temperature ceramic matrix composites (HTCMC) [1] are based on the most advanced scientific achievements in the field of materials for extreme operational conditions. This is just that field of materials science that creates demand for developing materials with presettable and reliable multiparameter characteristics for operation under extreme exposure. Such technologies may and should form a basis for the development of related technologies for many other fields of science and engineering (chemical sensorics, membrane technologies, production of current sources, sorbents, etc.).

High-temperature ceramic matrix composites are used in aviation, ship building, rocket and space engineering, etc. In view of the rigid operational requirements to such materials, the base range of HTCMC components is not too wide and limited to refractory metal oxides, carbides, nitrides, and silicides.

Ceramic composite materials and their production and properties have been the subject of consideration and discussion at six "High Temperature Ceramic Matrix Composites" conferences organized by the American Ceramic Society. The last of them in New Delhi (India) in 2007 discussed problems concerning nanostructured composites at the first set-up session "Futuristic Composites Including Nanostructured Composites, Ecocomposites and Smart Concept in Composites." The World Ceramic Congresses regularly held in Italy (the organizer is the Italian Ceramic Society) put much emphasis on the nano state of matter and materials. The use of micron- and submicron-size materials, specifically graphite, silicon, aluminum oxide, SiC, ZrC, and B_4C carbides, TiB_2 and ZrB_2 borides, and silicides, primarily molybdenum disilicide is widely discussed [2, 3].

Most research effort on finely dispersed refractory compounds has been focused on the development of dense ceramic matrices (Fig. 1). At the same time, the synthesis of fiber–matrix interfacial layers to form nanostructured coatings preventing active interaction between the fiber and matrix, nanoparticle-modified fibers, as well as surface thermal barrier coatings have been reported.

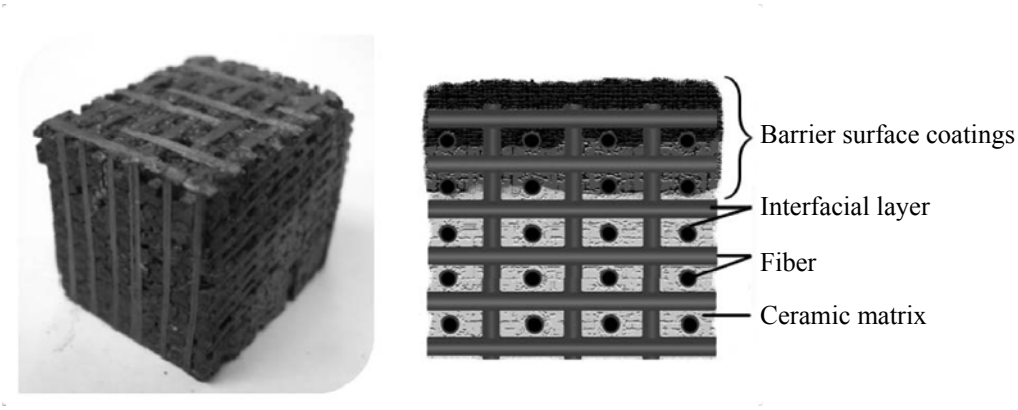

Fig. 1. Example high-temperature ceramic matrix composite with a carbon frame and a silicon carbide matrix.

Analysis of publications on nanomaterials for high-temperature composites, retrieved from the Chemical Abstract Plus database [4–8] shows that the number papers on the use of nanoparticles in high-temperature composites grows exponentially from year to year. Over 15 years (from 1990 to 2005) the number of publications has grown 30 times; among them more than 60 % falls on scientific papers and ~23 % on patents. However, in the body of retrieved information we found no specialized general review of the use of nanomaterials in HTCMC, even though active research in this field is in progress both in Russia and abroad.

The "Nanotechnology White Book" [9] contains information on the research on nanoparticles, nanostructures, and nanocomposites, performed in Russia, and lists industry institutions, for instance, VIAM State Research Center, PROMETEY Central Research Institute of Structural Materials Federal State Unitary Enterprise (FSUE), and TEKHNOLOGIYA Obninsk Research and Production Enterprise FSUE, which declared the development and implementation of synthesis technologies for refractory nanosized compounds (metal oxides and carbides, intermetallides, and their composites).

The problem in focus can be discussed and treated from two viewpoints. On the one hand, one of the rapidly progressing fields of the up-to-date HTCMC technology involves production of nanosized powders, slurries, and sols, as well as starting materials for matrix densification (including those for filling the smallest pores). Denser matrices provide more uniform mechanical load distribution in the resulting materials. Moreover, a possibity arises to produce materials at moderate technological parameters: The large specific surface area and chemical particle activity favor lower composite synthesis temperatures, thus preventing undesirable chemical reactions between matrix components and reinforcing fibers. It should be noted that the fine dispersity of nanomaterials is generally partly lost during the technological production of the target composite.

On the other hand, a research is performed into the synthesis of finely dispersed refractory compounds which preserve their dispersity when incorporated in an HTCMC material and, owing to the large specific surface area of nanoparticles, impart the composite with desired properties. An example is provided by the preparation of nanofiber or nanocrystal dispersion–reinforced ceramic materials.

Here we review the use of finely dispersed refractory compounds in the production of high-temperature ceramic matrix composites and give the most typical examples of successful combination of nanomaterias and HTCMC technologies.

Refractory Chemical Compounds as Components of High-Temperature Ceramic Matrix Composites

At present we can already speak about the availability of nanomaterials but still to a lesser extent about the availability of HTCMC production nanotechnologies. Requirements to such materials, their production and purification conditions, and, first of all, structure and contents of the principal component and limited microimpurities are still under development.

High-temperature ceramic matrix composites can be produced from refractory carbides, borides, nitrides, silicides, and oxides, as well as from high-melting glass ceramic compositions [10–13]. The melting point is not the only criterion for selecting composite components.

Account is taken of such characteristics of chemical activity, temperature dependence of vapor pressure, vapor composition, presence or absence of phase transitions in the operating temperature range, thermomechanical properties, emission coefficient at elevated temperatures, possible catalytic activity, etc.

The most common starting materials for HTCMC are the disperse forms of silicon and carbon carbides. The feasibility of SiC for creating materials for extreme operating conditions has been evidenced by its long application history. Finely dispersed silicon carbide products of various morphology (single crystals, powders, needle-like whisker crystals, polycrystalline core and coreless fibers) possess such unique properties as resistance to oxidation, thermostability, chemical inertness, and hardness and other high mechanical characteristics. At present nanosized SiC is a commercial product: high-dispersity powders (mean particle size up to 10–20 nm, specific surface up to 200 $m^2 g^{-1}$), nanotubes (diameter ~50–80 nm, length 4–10 μm), and whickers (diameter 10 nm, length 100 nm, specific surface area 120–140 $m^2 g^{-1}$) [14–18]. This makes possible goal-directed research into the synthesis of HTCMC materials on the basis of finely dispersed silicon carbide.

Dispersed carbon forms, primarily carbon nanotubes, are also attractive as components of high-temperature composite materials. Presently a variety of carbon nanotubes are commercially produced: single-, double-, and multiwall nanotubes differing in diameter and physical properties (for example, themo- and electroconductivity) and bearing functional substituents on the surface. Many commercial catalogs [14–18] contain a special section devoted to nanotubes, and their nomenclature includes tens of names. The other dispersed carbon forms, specifically nanofibers, fullerenes, and onion structures, too, attract some, but much less, interest as components of high-temperature composite materials.

Below we consider the examples of application of finely dispersed refractory compounds for producing the key HTCMC components: reinforcing fibers, interface coating, and ceramic matrix.

Nanosized Materials in the Production of Reinforcing Fibers

As known, reinforcing fibers (short or continuous) are capable of improving the mechanical properties of composite materials. In view of unique properties of carbon fibers (C_f), most research effort was focused on the development of methods for production of HTCMC on the basis of C_f and a carbon or a silicon carbide matrix, specifically C_f/C and C_f/SiC composites. With the advent in the market of the SiC fibers Nicalon and Hi-Nicalon (Nippon Carbon) and their analogs, researcher's attention was turned to the synthesis and production technologies of SiC_f/SiC and SiC_f/Si_3N_4 composites, as well as composites with other refractory matrices, including glass ceramic ones.

To create a domestic SiC fiber is an important task associated with a great number of problems to be solved. A technique for stabilization of polycrystalline SiC fibers manufactured by long-time pyrolysis of preceramic polymers (polycarbosilanes) at 1300–1400°C [19]. It was found that the temperature range when SiC crystallites grow at a high rate can be shifted to 1600–1700°C by introducing refractory metal nanoparticles into the system. To this end, the polymeric precursor was modified with organic zirconium compounds, specifically cyclopentadienyls or alkylamides, which formed nanosized particles (20–30 nm) of zirconium carbides or carbonitrides in the course of pyrolysis. It was noted that the use of zirconium tetrakis(diethylamide) as a precursor modifier allows one to preserve the fiber-forming properties of polycarbosilane, shorten the synthesis time, and raise the ceramics yield. According to [19], the development of production of nanopowders of SiC, BN, Si_3N_4, and other refractory substances can stimulate research into modification and perfection of fibers from polycarbosilanes and organic polymers (polyacrylonitrile, viscose).

One-dimensional (whickers, wires, nanofibers, and nanotubes) and three-dimensional (spheric) crystalline particles of refractory compounds represent a growing fraction of starting materials in the modern technologies using HTCMC materials as reinforcing and dispersion-strengthening elements.

Introduction into a ceramic or a glass ceramic matrix of carbon nanotubes and silicon carbide whickers changes the properties inherent in the bulk materials and impart the latter with new properties. Thus, carbon nanotubes not only improves mechanical properties, but also enhances electro- and thermoconductivity [20]. From the practical viewpoint of particular interest are the anisotropic properties of materials with preferentially oriented nanotubes. The strength parameters and elasticity modulus of carbon

fibers produced on the basis of polyacrylonitrile doped with single-wall nanotubes increase no less than two times due to the fact that one-dimensional particles undergo spontaneous axial arrangement as the polymeric thread is stretched [20]. Ye et al. [21] reported that β-SiC whickers 0.5–1.0 μm in diameter and 30–100 μm in length changed the mechanical characteristics of a dispersion-strengthened barium silicate glass ceramics. The strength of the composite containing 40% of β-SiC increases 2.6 times (from 156 to 408 MPa) and its fracture strength increases 3 times (from 1.40 to 4.30 MPa $m^{1/2}$) compared with an unstrengthened glass ceramics. Filament SiC crystals introuced into alumina ceramics produced similar effects [22]. Moreover, as the fraction of SiC whickers increased, the thermo-conductivity of the material increased and its electroresistance and thermal expansion coefficient decreased.

Nanosized Materials for Interface Coatings

Dense coatings on reinforcing fibers, functioning to minimize fiber–matrix interactions and effect of aggressive gas meadia, are most commonly manufactured by means of chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP), and sol–gel technique. The latter method is primarily used for coating oxide fibers, such as Nextel 720 (on the basis of α-Al_2O_3 and mullite [23]). Chemical vapor infiltration processes make use of gaseous reagents or reagent mixtures which form a target compound, including silicon carbide, its compositions, or pyrolytic carbon, upon thermolysis on hot fiber frames [24, 25]. This technique provides fairly dense layers enhancing matrix adhesion to fiber surface and hindering frame–filler interactions.

Nanosized Materials in the Production of Ceramic Matrices for High-Temperature Ceramic Matrix Composites

The methods for filling HTCMC frames with finely dispersed refractory particles can be arbitrarily divided into two types:

(1) methods involving nanoparticle formation in bulk materials due to destruction (hydrolysis or thermolysis) of precursors: sol–gel technique, CVI and CVD, melting-through of or impregnation with a polymeric reagent, followed by thermolysis;

(2) methods involving prefabricated finely dispersed materials (powders, suspensions, or sols): slip processes, NITE process (vide infra), subsurface densification, and production of oxidation-resistant coatings.

The sol–gel technique is most commonly used for forming nanoparticles of refractory substances directly in composite bulk [26]. The in situ synthesis of a refractory matrix by the sol–gel procedure involves impregnation of a composite with a certain reagent mixture and hydrolysis with gel formation followed by thermal treatment to form oxide nanoparticles (refractory matrix components) or chemically active starting metal oxide–carbon mixtures for subsequent carbothermy. A characteristic feature of this technique is that it also makes it possible, if right precursors and hydrolysis and thermal treatment conditions are chosen, to synthesize individual nanomaterials, including aerogels.

The synthesis of ceramic matrices by chemical infiltration has much in common with the manufacture of ceramic fibers, except that polycarbosilanes or other precursor polymers imregnate into bulk composite between reinforcing fibers, where they undergo stepwise cross-linking and thermodestruction to form a nanocrystalline ceramic matrix [27].

As to prefabricated finely dispersed ceramic materials, they are in a high demand for the production of dense ceramic matrices. These products are synthesized by usual methods for forming dispersion phases: chemical precipitation, hydrothermal [28–33] and sol–gel techniques, vapor deposition, self-developing synthesis, etc. In particular, the hydrothermal technique was used to synthesize in aqueous medium nanodispersions of the refractory oxides ZrO_2 and HfO_2, as well as pyrochlore phases ($La_2Zr_2O_7$, $La_2Hf_2O_7$, $Nd_2Zr_2O_7$, etc.) with the mean particle diameter 4–20 nm

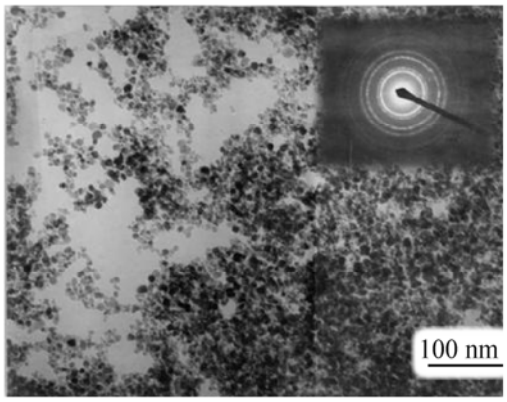

Fig. 2. Electron microphotograph of the $La_2Zr_2O_7$ powder obtained by hydrothermal synthesis [43]. (Insert) Nanoparticle diffraction.

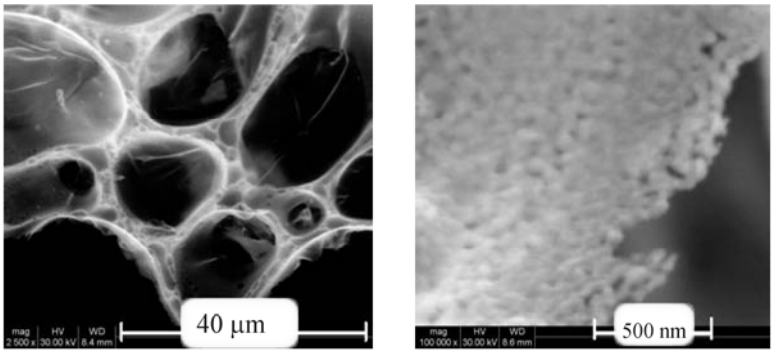

Fig. 3. Morphology of the neodymium hafnate nanoparticles synthesized by pyrolysis of organic acid salts [43].

[33, 43] (Fig. 2). The technique allows preparation of well-formed crystals with a narrow particle size distribution: The size can be varied by varying synthesis conditions (pH, temperature, time of thermal treatment). Zirconates and hafnates of rare-earth metals, including lanthanum and neodymium, have high melting points and are chemically stable. They are suggested as candidate components of refractory coatings and matrices [34–37].

A series of ultrafine refractory oxides, carbides, borides, and nitrides were synthesized in plasma in an atmosphere of methane, nitrogen, and other gases [38–41].

Sychev and Merzhanov [42] have reviewed the use of self-propagating high-temperature synthesis of nanomaterials, both oxide, including those of complex composition (for example, an Al_2O_3-ZrO_2 solid solution), and non-oxide (carbides, silicides, and nitrides). One of the modifications of this technique was used to synthesize the refractory compounds $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Nd_2Zr_2O_7$, and $Nd_2Hf_2O_7$ from polymeric salts of zirconium and lanthanum organic acids in the presence of ammonium nitrate [43]. In the course of the synthesis, a self-organizing structure is formed; nanoparticles 20–40 nm in diameter (according to X-ray phase analysis, the mean crystallite size is 4–8 nm) form ordered thin folded films (Fig. 3).

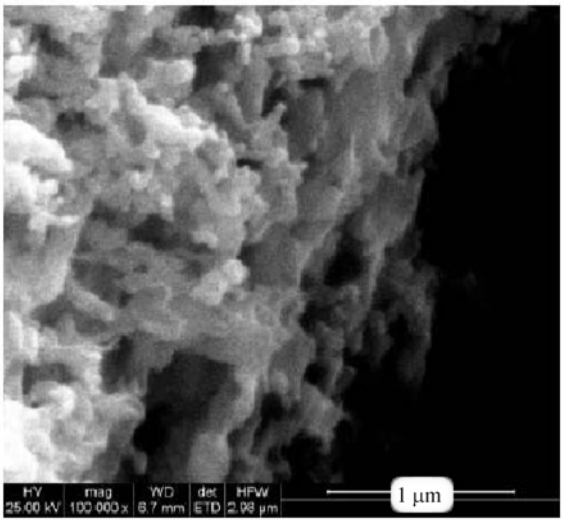

Fig. 4. Morphology of the silicon carbide material synthesized using multiwall nanotubes [49].

The sol–gel technique is a classical approach to preparing finely dispersed particles, it allows synthesis of refractory oxides, both individual and of complex composition, including glass-forming. This technique was used to synthesize nutride, carbide, and boride nanocrystals [44–46]. For controlled morphology of refractory particles obtained by the sol–gel technique, template synthesis on various carriers, such as carbon nanotube surface [47, 48] or mesoporous material pores, and also synthesis involving preservation of the morphology of the starting reagent [49, 50] are performed (Fig. 4). The synthesis of nanosized composites on the surface of finely dispersed refractory carbides or carbon nanotubes is accompanied by a modification of the chemical properties of the matrices. Thus, for example, the oxidative stability of carbon nanotubes is much enhanced by SiC layers applied by the sol–gel technique [47].

A homological series of promising starting reagents of the stoichiometric composition $a(SiCl_4)$:bSi:cC:d(SiC) for producing silicon, silicon carbide, or carbon nanoparticles from the gas phase was suggested [51, 52]. The thermolysis of a precursor, specifically gaseous tetrakis(trichlorosilyl)methane $C(SiCl_3)_4$, at 600°C under argon gave fine particles of amorphous

SiC, while the reaction at 700–900°C gave β-SiC with a mean crystallite size of 2–6 nm.

Ultrafine refractory particles have found application in up-to-date HTCMC technologies, primarily in dynamic slip densification of ceramic matrices. The higher efficacy of nanoparticles com-pared with traditional powders is explained by the capacity of the former to fuse under milder conditions and to fill smaller size voids in bulk material, and, as a consequence, to provide a minimum open porosity [53–56].

Finely dispersed refractory compounds, especially glass-forming, are used for densifying HTCMC subsurface layer and for producing oxidation- and erosion-resistant coatings [57]. Additional densification of HTCMC subsurface with fullerenes by means of gas-phase silicification of the latter (silicon vapor, CVI-CVD silicon precursors), forming a dense silicon carbide protective layer which sharply enhanced the oxidative stability of the material, was suggested in [58].

The progress in manufacturing technologies of SiC nanopowders resulted in the development of a nanopowder infiltrated transient eutectic phase (NITE) process for the synthesis of a dense SiC/SiC composite on the basis of silicon carbide fibers [59–62]. The essence of the technique is as follows. Silicon carbide nanopowders (mean particle diameter <30 nm) are ground together with about 10–20 wt % of a mixture of yttrium and aluminum oxides {n(Al):n(Y) = 5:3, which corresponds to the stoichiometry of yttrium–aluminum garnet $Al_5Y_3O_{12}$) and then subject to hot pressing (temperature 1800–1950°C, pressure 15–20 MPa). Under these conditions, an Al_2O_3–Y_2O_3–SiO_2 liquid phase is formed at SiC grain interfaces (SiO_2 is formed due to partial surface oxidation of SiC particles). The melt film favors mobility of matrix nanoparticles and controls their orientation in bulk material due to capillary forces. By varying HTCMC manufacturing conditions, primarily the temperature of the process and the SiO_2 content on the SiC surface, almost nonporous composites can be obtained: On cooling, either $Al_5Y_3O_{12}$ crystallizes in the intergrain and interfilament space or a thin amorphous film forms on the SiC grain interface. The density of the resulting oxide-doped silicon carbide matrices is close to calculated values.

At present KJTD (Japan) produces SiC/SiC plates, blocks, tubes, and cylinders (Fig. 5) by the NITE process from Tyranno-SATM fibers. The density of these materials (trade mark Cera-NITE) is 3 g cm^{-3}, they exhibit good mechanical characteristics (stress limit 400 MPa, elasticity modulus 310 GPa) and resistance to oxidation [63].

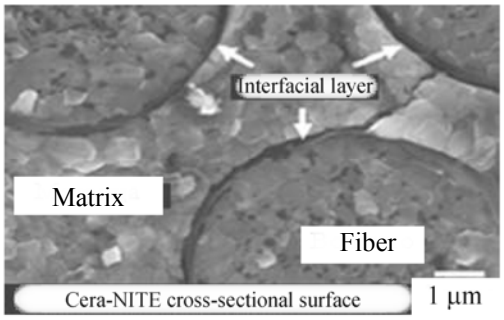

Fig. 5. Cross-section of a Cera-NITE SiC/SiC high-temperature composite material [63].

CONCLUSIONS

The works on synthesis, properties, and application of finely dispersed refractory compounds for manufacturing high-temperature ceramic matrix composites are mostly focused on the development of heat- and oxidation-resistant materials for operation in extreme conditions.

For progress in the use of nanomaterials in HTCMC manufacturing technologies, a number of problems have to be solved. To this end, research in the following directions should be continued.

– Development of synthetic approaches to nanosized refractory compounds, study of the chemical and physical properties of the latter and possible transformations during composite synthesis and exploitation, and determination of functionally significant performance characteristics of nanomaterials (dispersity, structure, contents of principal component and limited microimpurities, sorption parameters, stability, catalytic properties, emission coefficient at elevated temperatures, etc.).

– Development of composite synthesis methods involving ultrafine materials (powders, suspensions, and sols).

– Search for novel precursors for nanoparticle generation in bulk composite by means of the sol–gel technique and polymer melting-through or impregnation followed by thermolysis.

– Creation of a domestic base of nanomaterial components for HTCMC applications, including silicon carbide, nanosized carbon forms, and refractory metal oxides, carbides, borides, nitrides, and silicides in various forms (micropowders and sols), as well as nanomaterial precursors and auxiliary reagents (starting reagents, solvent, etc.).

Effects of ultrafine components on the properties of composite materials and correlations between particle properties and size, as well as surface chemical and physical phenomena undeniably necessitate further detailed investigations, and their results will be implemented in high-performance construction materials for aviation, rocket and space, ship and reactor building, and chemical industries.

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