REFRACTORIES IN HEAT UNITS

NANOMATERIALS IN REFRACTORY TECHNOLOGY[1]

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A short review is presented of prospects for using nanomaterials in various refractory technologies, and an estimate is given of existing and future directions of their use for improving the operating properties of refractories. The possibility of controlling material properties at the atomic level makes it possible to create new innovative refractory materials and technology.

Keywords: refractories, nanomaterials, nanopowders, nanoparticles.

The main stimulus in the development of the contemporary refractory industry is improvement of existing and the development of new high-temperature technology with even more severe specifications for refractory operating conditions, i.e. temperature, chemical erosion, mechanism, etc. Here the task of improving the service properties of refractories is inseparably connected with the question of reducing the cost of production, observation of ecological standards, the possibility if utilizing waste products, and recycling refractories.

The requirement for finding comprehensive solutions has led to use in the majority of heating units, in particular ferrous metallurgy, of complex multicomponent composite materials, including oxide ceramics, metals and carbon. During the last thirty years significant success has been achieved in optimizing the physicochemical properties and chemical composition of these refractories for specific operating conditions. Currently the main areas of development include a change-over to controlling the refractory properties for an evermore finer size level, since the microstructure of any material is mainly determined by occurrence within it of different physicochemical processes.

In view of this use in refractories of highly- (0.1 – 1 mm) and nanodispersed (10 – 100 nm) systems with a controlled composition and morphology is very important. In fact, the refractory branch, for tens of years and thousand of tons of consumed technical grade carbon (soot) and silica (microsilica, aerosil) is already one of the largest world users of nanomaterials. Development of new refractory technology has a favorable effect on formation of the market for new industrial nanomaterials, stimulating an increase in the volume of their production and a reduction cost.

Interest in this class of materials is due to the possibility of a marked change in properties of normal substances by converting them to a nanosize condition [1]. An increase in the relative proportion of atoms or molecules, that are at the surface of particles, leads to an increase in the contribution of surface energy in practically all physicochemical processes of nanodispersed system reaction with the surroundings. Such a change, important from the point of view of dispersed refractory systems, may be a reduction in the melting and sintering temperatures, an increase in chemical activity and the rate of occurrence of chemical reactions, the possibility of preparing alloys, compounds and composites, impossible in traditional materials from a thermodynamic point of view. In turn, an increase in the relative interphase surface of bulky compacted refractories leads to a marked improvement in the mechanical properties, since the typical sizes of defects that grow during failure of a component becomes less than the size of structural elements of the material.

These features of nanosize systems create good prerequisites for effective and comprehensive solution of questions connected with forming the required structure and properties in situ in refractories, i.e. directly in the course of heating unit lining operation [2]. As examples of the practical use of nanomaterials it is desirable to refer to experience of the main Japanese companies that are currently leaders with respect to innovative activity in the field of refractories [2]. In the refractory industry of Japan since the middle of the 1990s

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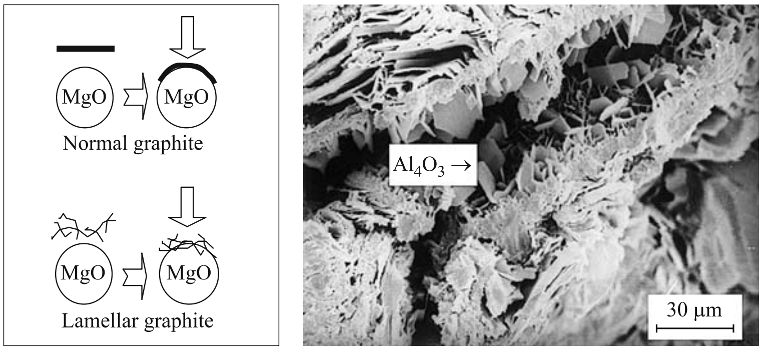

Fig. 1. Formation mechanism and microstructure of carbide layer formed by nanosize antioxidants and lamellar graphite (materials of Krosaki Harima Corp., Japan).

nanosize materials have been used for improving the rheological properties of unmolded refractories, increasing their erosion resistance, strength, and a reduction in monolithic and piecewise lining porosity, including in converters. In particular, in molded periclase-carbon objects for converters as antioxidants there is more extensive use of aluminum metal and silicon. An increase in the fineness of the antioxidants increases their capacity and facilitates formation of carbide phases during operation. A carbide layer not only considerably reduces the rate of carbon matrix particle oxidation in molten slag, but it improves the hot failure modulus. A combination of these nano-oxidants with graphite of the lamellar type, densely encapsulating periclase particles and compensating their thermal expansion (Fig. 2), has made it possible to reduce the carbon content in converter refractories, used by the firm Nippon Steel, to 5 – 7%. Thus, a change in nano-additions has provided a marked increase in the erosion resistance of refractory without worsening its mechanical properties, including thermal shock resistance.

In other classes of refractories, such as mixes for hot semidry torcreting of converters, the increased chemical activity of metal additions may be a negative factor due to the possibility of their oxidation by water before contact with the working layer of the lining. One way of resolving this problem is creation at the surface of antioxidants of a thin (50 – 100 nm) oxide or polymer layer, that prevents contact of aluminum and silicon particles with water. Apart from protection from oxidation, oxide nanocoatings based on silicon oxide (Fig. 2) or aluminomagnesia spinel [3], are able of confer hydrophobic from hydrophilic properties to metal and carbon particles, and to accomplish control of rheological characteristics of a torcrete mix. In particular, a complex combination of these measures has made it possible to Japanese producers to reduce the relative water content required for applying torcrete mixes to the working layer of a converter lining from 9 – 11 to 5 – 6% and correspondingly to increase considerably the stability of the torcrete layer.

Nanosize oxide powders are very promising from the point of use in other types of unmolded refractories such as, for example, low-cement corundum thixotropic mixes that are used extensively in ferrous metallurgy [4 – 6]. In particular, studies performed in MISiS show that addition of 0.05 – 0.20 wt.% of nanopowders makes it possible to increase the ultimate strength in compression for corundum monolithic components by 25 – 30%. (Fig. 3).

Undoubtedly the high cost of nanomaterials has so far been the main factor in delaying their extensive use, includ-

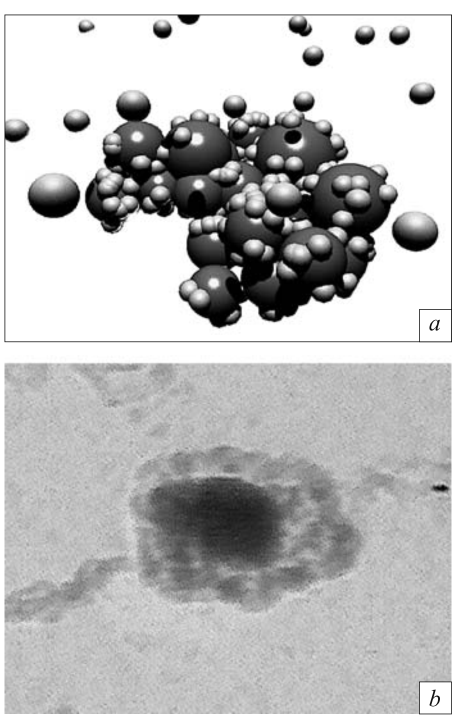

Fig. 2. Formation scheme (*a*) and microstructure (*b*) of hydrophobic nanoparticles of nickel in a shell of hydrophilic particles of silicon dioxide (material prepared in NITU MISiS).

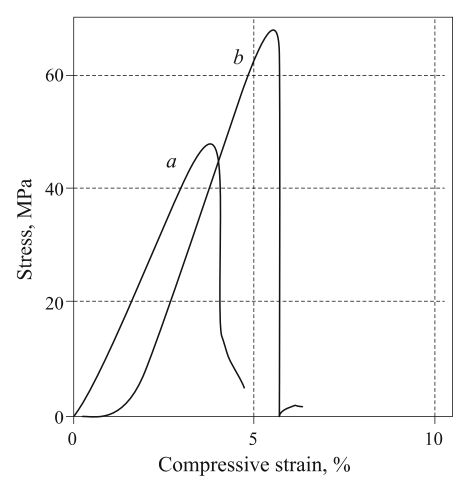

Fig. 3. Results of testing fro ultimate strength in compression of concrete specimens prepared from mix grade SMN-72: *a*) specimens without addition; *b*) specimens modified with 0.2% silicon dioxide nanopowder.

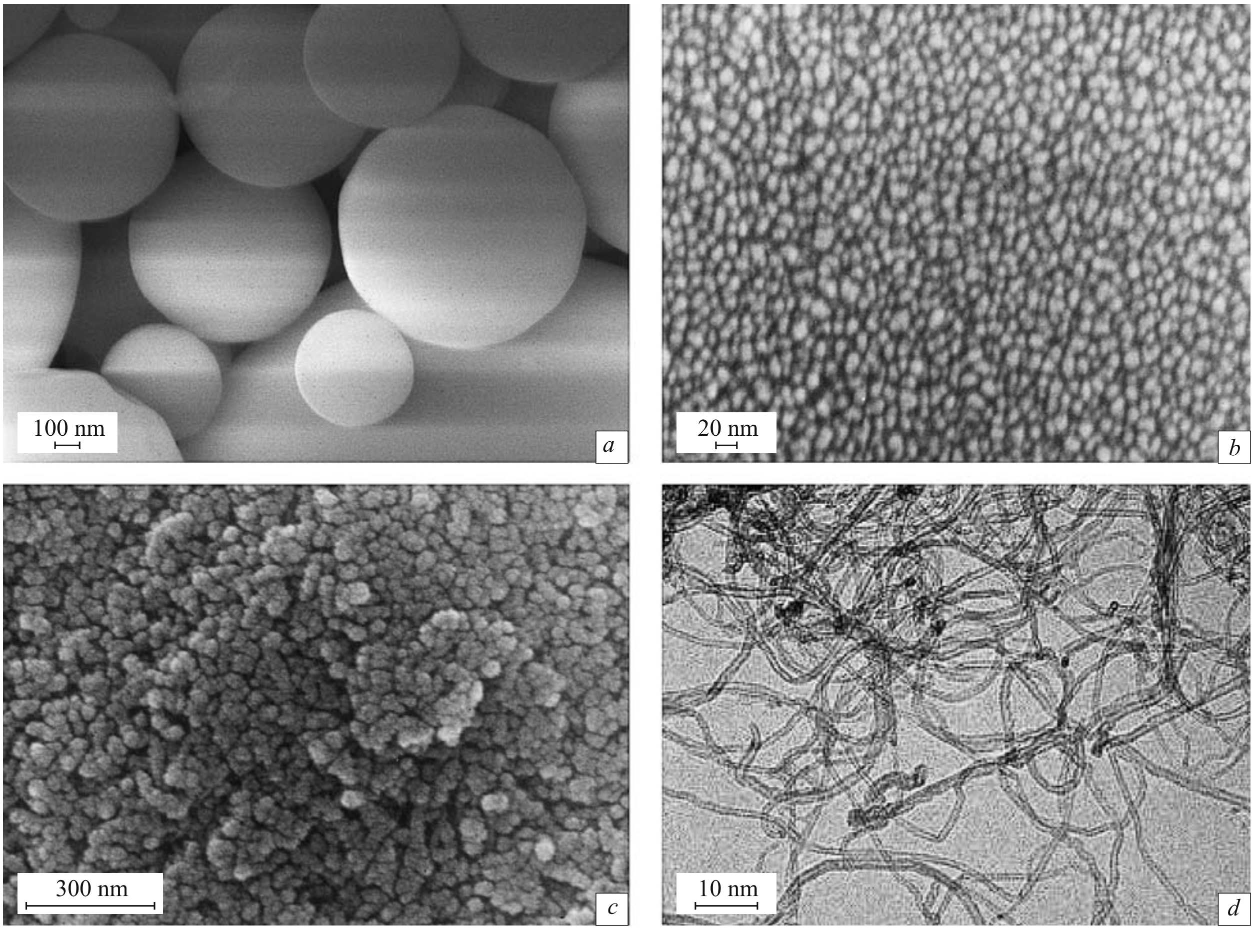

Fig. 4. Examples of nanomaterials developed by Russian scientists: *a*) hollow nanostructured corundum microspheres (NITU MISiS), *b*) silicon nanopowder (NITU MISiS); *c*) silicon carbide nanopowder (NITU MISiS); *d*) carbon nanotubes (NP IVTs, SO RAN, Novosibirsk).

ing in the refractory branch. It should be noted that now use of nanomaterials is capable of adding a marked economic effect. In particular, experience of the Japanese companies TYK and Krosaki Harima has shown that microadditions of carbon nanotubes to material for submersed lances increase their cost by 5%; here the indices for resistance to erosion and thermal shock resistance increase by 15 – 20%. Experience of overseas colleagues merits attention, especially that Russian producers pf refractories have an undoubted competitive advantage, i.e. the cost of domestic nanomaterials is considerably lower than in developed countries, and the range produced is very varied (Fig. 4).

Experience of MISiS in the field of practical use of different nanomaterials indicates that nanotechnology undoubtedly is not a panacea for resolving all existing questions of either the refractory branch or neglected problems of the Russian economy. However, the possibility of manipulating the properties of materials at a level close to atomic opens up broad perspectives for resolving specific applied problems in refractory material technology, creating new innovative highly competitive products.

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