

Implementation of Nanoparticles in Materials Applied in Foundry Engineering

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Abstract

The ceaseless progress of nanotechnology, observed in the last years, causes that nanomaterials are more and more often applied in several fields of industry, technique and medicine. E.g. silver nanoparticles are used in biomedicine for disinfection and polymer nanoparticles allow insulin transportation in pharmacology. New generation materials containing nanoparticles are also used in the chemical industry (their participation in the commercial market equals app. 53 %). Nanomaterials are used in electronics, among others for semiconductors production (e.g. for producing nanoink Ag, which conducts electric current).

Nanomaterials, due to their special properties, are also used in the foundry industry in metallurgy (e.g. metal alloys with nanocrystalline precipitates), as well as in investment casting and in moulding and core sand technologies. Nanoparticles and containing them composites are applied in several technologies including foundry practice, automotive industry, medicine, dentistry etc. it is expected that their role and market share will be successively growing.

Keywords: Innovative technologies, Nanoparticles, Materials, Foundry

1. Introduction

Current trends of production technologies are focused on producing new, improved materials of unusual properties together with the development of their production technologies. It is possible due to an intensive development of such fields as material engineering or nanotechnology, which allow to design and produce structures of determined functions and properties by changing e.g. their shape or size.

A close cooperation of scientists forming interdisciplinary teams contributed to the development of the new generation materials

containing nanoparticles such as, among others: hybrid materials or nanocomposites. Hybrid materials are popularly described as materials being homogeneous mixtures of organic and inorganic components of dimensions below 1 μ m [1]. The new generation materials, including hybrid materials, can be produced by *in-situ* (Fig.1) and *ex-situ* (Fig.2) methods.



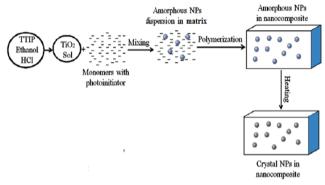


Fig. 1. Schematic of *in-situ* synthesis of hybrid materials [2]

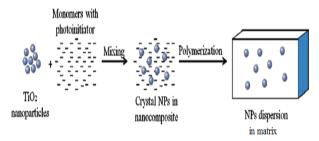


Fig. 2. Schematic of *ex-situ* synthesis of hybrid materials [2]

In accordance with the recommendation of the International Union of Pure and Applied Chemistry – IUPAC. We define the materials as follows [1]:

a) "Composite: multicomponent material comprising multiple, different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase. A foamed substance, which is a multiphase material that consists of a gas dispersed in a liquid or solid, is not normally considered to be a composite."

b)"Nanocomposite: composite in which at least one of the phase domains has at least one dimension of the order of nanometres."

c) "Hybrid material: material composed of an intimate mixture of inorganic components, organic components, or both types of component. The components usually interpenetrate on scales of less than 1 μ m."

- chemically bonded hybrid (material): hybrid material in which the different components are bonded to each other by covalent or partially covalent bonds."

d)"Clay hybrid: polymer-clay hybrid, polymer-clay composite Organic-inorganic composite material in which one of the components is a clay, the particles of which are dispersed in a polymer."

e)"Hybrid polymer: polymer or polymer network comprised of inorganic and organic components." [1].

A continuous development of production techniques of new materials is the reason that these new materials have usually more than one function. Therefore it is difficult to assign them to the explicit classification. The example of the materials classification is shown in Figure 3 [3].

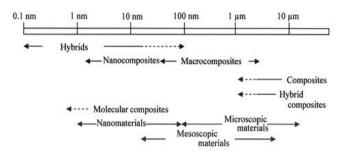


Fig. 3. Classification of the new generation materials, acc. to M. Nanko [3]

According to the author of paper [3] hybrid materials can be divided into **structurally hybridised** (formed by mixing of components up to obtaining a homogenous mixture due to chemical bonding) and **functionally hybridised** (i.e. materials of new functions). The quoted above definitions and descriptions concerning the 'new generation' materials indicate that a wide range of products is illustrated by this name: hybrid materials, nanocomposites and - in some cases - microcomposites [4,5].

2. Selected aspects of the nanomaterials application in foundry engineering

The ceaseless progress of nanotechnology, observed in the last years, causes that nanomaterials are more and more often applied in several fields of industry, technique and medicine. E.g. silver nanoparticles are used in biomedicine for disinfection and polymer nanoparticles allow insulin transportation in pharmacology. New generation materials containing nanoparticles are also used in the chemical industry (their participation in the commercial market equals app. 53 %). Nanomaterials are used in electronics, among others for semiconductors production (e.g. for producing nanoink Ag, which conducts electric current) [6].

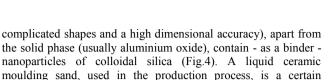
Nanomaterials, due to their special properties, are also used in the foundry industry in metallurgy (e.g. metal alloys with nanocrystalline precipitates), as well as in the moulding and core sand technologies [7].

2.1. Investment casting

Castings obtained by means of the investment casting technology are applied in several industry fields, e.g. power, automotive, aircraft industry: in aircraft engines, aircraft supporting structures, gas turbines (blades) as well as in arts (decorative castings). In medicine such castings are applied as endoprosthesis: e.g. artificial limbs, replacement hips, as elements joining broken bones (implants), as surgery tools etc. Castings are also used in dentistry as elements of bridges, crowns, implants etc.

a) Liquid ceramic moulding sand with colloidal silica

The ceramic moulding sands used in the investment casting technology for the ceramic moulds production (for castings of www.czasopisma.pan.pl



50 nm 50 nm

composite with nanoparticles of colloidal silica.

Fig. 4. Examples of TEM pictures of colloidal silica: A) dispergated, B and C) aggregated [8]

b) Modification of wax pattern surfaces by colloidal solutions of nanoparticles

Investigations presented in [9] indicate the possibility of using nanoparticles for modifying wax pattern surfaces, due to which a good wettability by liquid ceramic sand is obtained and - in consequence - a better surface quality of the produced casting. Within the patent application [10]: 'The way of producing moulds and cores by the investment casting technology', a group of modifiers and the way of modification of wax patterns by nanoparticles of metal oxides, ensuring the proper wettability of wax surfaces by liquid ceramic sand, was developed (Fig.5). The invention essence constitutes the formation - on the wax pattern surface - of a homogeneous monolayer built of alkaline metal oxides nanoparticles for example: ZnO, MgO or Al_2O_3 of a size from 1 to 50 nm. Covering the wax pattern by such monolayer decreases the wetting angle twice (to app. 40 deg.)

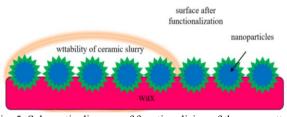


Fig. 5. Schematic diagram of functionalising of the wax pattern surface, used in the investment technology

2.2. Moulding sands technology

Nanocomposites: sodium silicate modified by nanoparticles

Sodium silicate is a cheap, easily available and not toxic, material binding mineral matrices. Due to that, moulding sands with sodium silicate fit well into the EU recommendations concerning the environment protection in the foundry industry (limiting, among others, harmful substances emission). A negative side of these sands is their knocking out property worse than of sands with organic binders, a weak reclamation ability and also a high price of ester hardener used in the Floster S technology, small resistance to atmospheric conditions. Therefore investigations concerning sodium silicate modification by nanoparticles of metal oxides were performed in study [11].

Nanoparticles of metal oxides such as: MgO, ZnO and Al_2O_3 in organic solvents: methanol, ethanol and propanol, were applied in tests. As the result of the modification performed by means of nanoparticles of the mentioned metal oxides solutions the nanocomposites: sodium silicate /metal oxides nanoparticles, were obtained. These nanocomposites (Fig.6) had physical and chemical properties as well as structural ones different than sodium silicate before its modification.

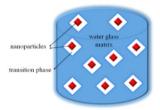


Fig. 6. Nanocomposite of the type: sodium silicate /metal oxides nanoparticles

It was shown by investigations [11], that the modification increases the quartz matrix wettability by a binder and - in consequence - improves strength properties of the hardened moulding sand. Good wettability causes formation of 'not coating' connections within a sand (Fig.7), where a thin film of nanocomposite binder (sodium silicate - MgO nanoparticles in propanol) flows down to contact points of mineral matrix grains.

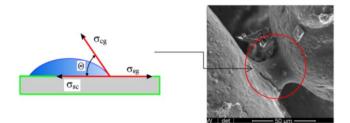
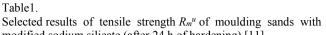


Fig. 7. Bridge joining the mineral matrix. 'Not coating' connection: binder/nanocomposite of the type: sodium silicate -MgO nanoparticles in propanol [11]

The cohesion strength σ_K of the modified sodium silicate was exponentially changing in dependence of the binder layer thickness [11]. Moulding sands with nanocomposite binders were characterised by increased strength properties at lower binder amounts (strength increase of sands with the modified sodium silicate depends on the kind of solvent applied (Table 1)) and by better knocking out property than sands with not modified sodium silicate. The best results were achieved when the binder was modified by 5 mass% of colloidal solution of MgO nanoparticles in propanol. The obtained knocking out property improvement equalled approximately 50 % as compared with the sand knocking out property when not modified sodium silicate was used [11].





modified sodium sificate (after	24 n of nardel	ning) [11]	
MgO nanoparticles,	Organic solvent/		
fraction of the modifier	Tensile strength R_m^u [MPa]		
solution in a binder: 5 mass	Methanol	Ethano	Propano
%.		1	1
	1.60	1.27	1.72

Very essential is also the fact, that apart from the technological aspects, nanocomposite: sodium silicate /nanoparticles (group of inorganic binders) satisfies also the EU requirements concerning the environment protection. There is a high probability that the presented innovatory solution will be broadly applied in the foundry industry in the future.

2.3. Selected aspects in metallurgy

Nanocrystalline structures in alloys and metals improves - to a high degree - their functional properties. Therefore nanocrystalline materials belong to the group of materials, which are finding application as structural elements of the required high resistance to abrasion, impact toughness, strength, etc. They are usually used as machine elements in the mining, metal-forming, military, building industry, etc.

Studies presented in [12], concerning ultrahigh strong steels of a nanocrystalline structure indicate that, out of the Fe-based structural steels and alloys, maraging steels are characterised by the highest yield point value (Fig.8).

Modern nanocrystalline materials, such as e.g.: Ni-Al alloys, AlSi25 alloys containing nanophases of the type: S-Al₂CuMg and S'-Al₂CuMg of dimensions app. 50 nm, or composites: Ti/SiC_f reinforced by TiB₂ nanoparticles of a diameter 3 nm, are produced in liquid-phase metallurgy [13]. Structural investigations of silumines modified by sodium (Na) and strontium (Sr) confirmed the presence of silica nanoparticles in a fibrous or flake form. In bearing alloys e.g. Cu-Pb, as the result of fast under-cooling, the structure refinement occurs and the uniformly situated lead nanoparticles (Pb) of dimensions 5-20 nm in aluminium matrix appear. Nanocrystalline materials are also applied in modifications of aluminium alloys. The properly selected new generation modifiers are extremely efficient in the microstructure refinement of aluminium alloys [11,13].

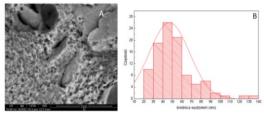


Fig. 8. Photo of the fracture of maraging steel with nanoprecipitates (a) and the distribution of precipitates diameters (b) [12]

2.4. Protective coatings (self-cleaning, anticorrosive)

Protective coatings with hybrid materials, apart from their basic protective tasks, are gaining new functions, e.g. ability for self-cleaning. Such coatings with nanomaterials are effectively applied in the automotive industry [14] e.g. on metal surfaces, aluminium wheel rims, etc. A thin coating film forming hydrophobic surface warrants practically total non-wettability by water, lubricants or various oils. Due to that, the effect of material self-cleaning is obtained since all contaminations are freely flowing down.

3. Summary

Specific properties of the new generation materials, including hybrid, cause that there is a possibility of designing their properties accurately (in the nano scale and sometimes even at the molecular level). Connection of conventional materials with nanoparticles is the reason that a wide range of new materials, which properties strongly depend on applied components and synthesis methods, is available [4].

Nanoparticles and containing them composites are applied in several technologies including foundry practice, automotive industry, medicine, dentistry etc. it is expected that their role and market share will be successively growing.

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References

- [1] Alemán, V., Chadwick, A.V., He, J., Hess, M., Horie, K., Jones, R.G., et all. (2007). Pure and Applied Chemistry The Scientific Journal of IUPAC, Definitions of terms relating to the structure and processing of sols, gels, networks, and inorganic-organic hybrid materials (IUPAC Recommendations 2007). *Pure Appl. Chem.* 79, 1801-1829.
- [2] Guo, Q., Ghadir, R. & Weige, T. (2014). Comparison of in situ and ex situ methods for synthesis of two-photon polymerization polymer nanocomposites. *Polymers.* 6, 2037-2050.
- [3] Nanko, M. (2009). Definitions and categories of hybrid materials. *AZojomo*. 6, 1-8.
- [4] Kickelbick, G. (2007). Introduction to hybrid materials, Synthesis, characterization and applications. Publisher: Wiley-VCH pp. 1-48. (Hybrid Materials).
- [5] Przadka, D.M (2014). Hybrid polymers and polymer composites containing functionalised polyether oligomeric silsesquioxanes. Unpublished doctoral dissertation, Poznań. (in Polish).

www.czasopisma.pan.pl



- [6] Corr, S.A. (2013). *Nanoscience:* volume 1: Nanostructures through Chemistry, 1 pp. 180-207.
- [7] Kmita, A., Dańko, R., Holtzer, M., Hutera, B. & Stypuła, B. (2014). Utilisation of nanoparticles in technologies of producing castings for the needs of power engineering. *Nanomaterials and Energy.* 3, 53-60.
- [8] Zhang, H., Dunphy, D.R., Jiang, X. et all. (2012). Pathway dependence of amorphous silica nanoparticle toxicity: colloidal vs pyrolytic. *Journal of the American Chemical Society*. 134(38), 15790-804.
- [9] Nowicki, P. & Kmita, A. (2012) Meaning of wax surface modification in investment moulding technology. *Zeszyty Studenckich Prac Naukowych "SFEROID"*. 12, 137-140. (in Polish).
- [10] Hutera, B., Stypuła, B., Rzadkosz, S., Holtzer, M., Zych, J., Nowicki, P., Kmita, A., Starowicz, M., Hajos, M. (2014).

Polish patent: Method for producing forms of the melted models technology. AGH Krakow, 2014-03-11 ; Publish: 2014-11-28. (in Polish).

- [11] Kmita, A. (2014). Modification of water glass as binder for molding sands by metal oxide nanoparticles in organic solvents. Unpublished doctoral dissertation, AGH Kraków. (in Polish).
- [12] Garbarz, B., Marcisz, J., Burian, W. (2010). Ultra highstrength steels with nanocrystalline structure Nanotechnologia -*PL*, Warsaw University of Technology, 14 september 2010, Warsaw, Conference Materials. (in Polish).
- [13] Sobczak, J. (2003). Selected aspects of nanotechnology and nanomaterials. *Composites*. 3(8), 387-391. (in Polish).
- [14] http://www.felgi.pl/felga/aez/lascar.