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METAL MATRIX MICRO- AND NANOSTRUCTURAL COMPOSITES (REVIEW)

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Abstract. Liquid phase production technologies of metal matrix micro- and nanostructural composites are considered. A complex using magnetohydrodynamic stirring, ultrasonic treatment of melt during liquid and liquid-solid states and thixocasting advantages are proposed.

Keywords: metal matrix composites, liquidphase technology, magnetohydrodynamic stirring, ultrasonic treatment, thixocasting.

1. Introduction

Research and development of metal matrix composites (MMCs) are given a significant consideration practically in all economically developed countries due to the complex of mechanical and service properties that could be obtained in this class of structural materials, and which are unattainable in the traditional materials produced using the traditional technologies. Metal matrix provides a number of advantages if compared to other (polymer, carbon, ceramic) matrices, in particular higher hardness, strength, electric and heat conductivity, crack resistance, and melting temperature. The use of the liquid phase technologies means that in the process of MMCs production at least one of the components is in the liquid phase (casting technologies, liquid forging, laser and plasma spraying, sintering with liquid phase, *etc*.)

Two types of composites are distinguished: artificial and natural. In artificial composites the strengthening disperse phase is either introduced artificially from the outside or is formed when matrix melt interacts with artificially introduced agents. Natural composites include the alloys, in which the disperse phases are formed under the natural processes of primary, in particular, oriented crystallization. Typical natural composites are graphitized cast irons. The properties of natural composites can also be improved using the technologies typical to artificial composites. However, artificial composites are regarded as the promising materials with unique properties [1].

Composites, reinforced with fibers or whisker crystals, and layered composites are widely used in industry. The technologies of their production are relatively simple and the scientific bases of their development, analysis and prognostication of their behavior while using the articles are thoroughly studied. With the exception of the production of prepregs, that serve as semi-finished articles for the production of the constructions, the composites of this type and the constructions are produced simultaneously, allowing the consideration of the specifics of the use of these constructions and conditions of the exploitation. These composites have a number of positive properties (high specific strength, hardness, wear resistance, fatigue resistance, *etc*.). At the same time these materials possess substantial defects (anisotropy of properties, high cost, low maintenance workability, *etc*.), that given specific technology and engineering properties narrow the range of their application.

Dispersion-reinforced composites include casting and wrought alloys as a basis and disperse particles as reinforcers, artificially incorporated (***ex-situ*** processes) or initiated as a result of the occurring (***in-situ***) processes. Generally, refractory high-strength, high-modulus particles of oxides, carbides, borides, nitrides (more frequently SiC, Al_2O_3, B_4C, TiC) are used as micrometric size reinforcers. Chemical reactions ***in-situ***, occurring in the melt in the process of incorporation of the reactive metals, gases or chemical compounds, form thermodynamically stable, wetted by the melt due to the coherent boundary formation, and thermostable at high temperature of maintenance reinforcing phases [2].

The processes of spontaneous high-temperature synthesis that are used to produce reinforcing particles in the metal melts, pertain, in fact, to ***in-situ*** processes [3].

The main criteria for choosing the matrix melt composition, size, quantity, nature of the reinforcing phase and method of its implantation into the melt, method of shaping and conditions of obtaining properties of the blanks are the requirements to the finished article properties, stability of the structure and the properties of these articles in the process of their use. This requires diversity and complexity of the technological solutions for the MMCs article production.

Three principal processes of MMCs production are used:

– incorporation of particles into the melt with intensive impeller [4] or magnetohydrodynamic (MHD) [5] mixing;

– impregnation of disperse particles or preforms with matrix melt;

– powder technology.

With the exception of the cases when powder technology is implemented by the compaction of the original matrix alloy powders and reinforcing components in the solid state, all three technological schemes involve the use of liquid-phase techniques for producing MMCs.

The problem of the development of the composites with the given level of properties is only a part of the objective concerning the finished article production out of these composites. As a rule, it is necessary to be guided by the optimum value of the property or a group of interconnected properties that determine the operating capacity of the finished product. New engineering solutions may be possibly used for the articles, in which composites substitute the traditional materials.

Despite the abundance of works dedicated to the research and production of MMCs, their implementation is still in the semi-industrial production stage. One of the reasons of such situation is limited possibilities of the MMCs use for the production of the cast shapes of varied weight and dimensions with complex internal cavities. Due to their general-purpose properties, the traditional foundry technologies, implying the filling of the molds with the liquid-state alloys, as well as thixotechnologies, implying the filling of the molds with the two-phase-state alloys, are the most appropriate.

Specific feature of the cast MMCs is the need to provide equal distribution of the disperse particles in the melt volume for all stages of cast ingot produced by the traditional casting methods: from the process of particle incorporation into the melt to the process of ingot formation in the mold. Therefore, the problem of sedimentation stability of the cast composites is closely connected not only with MMCs property and structure formation but with the implementation of the casting production methods.

The structure and properties of the composites are determined by the matrix melt properties, by the chemical composition, form, dimensions, quantity of incorporated or formed in the melt disperse particles, and also by the interaction activity and processes on the “disperse particle-melt” boundary. These factors determine the possibility of producing of the metallic suspension, the pouring of the latter into the molding cavity (casting mold, molding tool), provides the production of the articles with the given properties.

2. MMCs Production Technologies

MMCs based on the aluminium and magnesium alloys are the promising materials for the various branches of industry due to low unit weight and higher, in comparison with the matrix alloy, level of the properties (wear resistance, hardness, local strength, bearing capacity, heat resistance, damping, antifriction, transport and other properties).

Magnesium matrix composites have unique specific characteristics [6]. Magnesium alloys with high tendency to vitrification and thermostability are of particular interest as matrices for the MMCs. As the reinforcers the following compounds are used: SiC – due to the satisfactory wetting and chemical stability in the magnesium melt [7], oxides – due to low oxygen solubility in magnesium, refractory metal powders (Cu, Ni, Ti) – due to fine wetting of the metals by magnesium [8]. When using transition metals in ***in-situ*** processes, the produced intermetallides provide high wear resistance and tribological properties of magnesium MMCs.

Nowadays, aluminum alloys are of the high demand and wide-spread among the non-ferrous metals materials, possessing high specific strength and a general-purpose complex of mechanical, service and special properties, creating preconditions for the use of aluminum-based materials to develop engine-building, aeronautical and space engineering.

The possibilities to enhance the service properties of aluminum alloys, produced by the traditional technology of component alloying, their treatment in the liquid state and shaping are exhausted to a large degree. Due to this fact all technically developed countries started the research and development in the field of the alumomatrix composites (AMCs) synthesis.

Microsize particles in the composites, in particular, alumomatrix composites, serve as reinforcers, and the character of interactions on the “particle-melt” boundary is mainly determined by their wettability by the melt. The research [9,10] in the field of alumomatrix composites, reinforced with widely used microsize SiC, Al_2O_3, B_4C, TiC and the experience of use of the articles proved that these alloys provide high level of mechanical and service properties and may be used to produce shaped articles with casting methods.

Liquid phase technologies of AMCs production by incorporating a sufficient amount (up to 20 vol %) of micrometric refractory particles into the melt have been brought to the industrial application.

For example, Talbor company [11] specializes on producing alumomatrix composites, reinforced by SiC, B_4C, and Al_2O_3 microparticles in the process of mechanical mixing. In comparison with B_4C, silicon carbide is better wetted by the melt, provides high level of the composite hardness, and is more commercially appropriate. However, Al_4C_3 creates danger of brittle failure of the articles. The presence of adsorbed gases does not allow to weld and thermally treat the composite. Even if the matrix alloy can be welded, high SiC density with the same incorporated quantity leads to weighting of the articles and tends to the sedimentation. Al_2O_3 is the densest of the three reinforcers, minimally active towards aluminium, provides higher strength of the composites, but its segregation ability in the casting process is high. For the cast composites (sand mold casting and metal mold casting, high-pressure casting, liquid forging) the company uses B_4C as reinforcing and providing the composite with the ability to withhold hard radiation particles. With the density similar to the density of aluminium, B_4C provides higher sedimentation stability of the slurry, allowing of producing thick-section castings by the methods of gravitation casting, using ceramic filters, melt outgassing with argon or nitrogen, B_4C particle passivation, and special construction of the gating system.

In a number of cases, in order to improve the wettability, the disperse particles are plated by the elements enhancing their wettability by the melt (for example, technological coatings of Fe and Cr are used for SiC). For aluminum alloys Mg, Sn, Sb, and Bi serve as interphase-active elements, improving the wettability of the incorporated refractory particles [9].

New generations of military, aerospace and civil equipment require the development of the new structure and functional materials, obtaining properties, unattainable in the traditional structure materials and composites, reinforced with ultradisperse micrometric particles.

At present, special attention is drawn to the works dedicated to the production of the metal matrix nanocomposites (MMNCs) by means of the multipurpose use of ***ex-situ*** and ***in-situ*** processes (polyreinforcement), implying nanosize structural constituents in the form of the nanosize thermostable particles introduced from the outside and intermetallides produced as a result of the occurring processes. It was theoretically proven and experimentally approved that the properties of the composites improve if the particle dispersion is reduced to nanosize level [12-14].

The investigation [15] studies the prospects of using nanoparticles as reinforcement agents to gain improved performance of A356 Al cast alloy by adding up to 5 % Al_2O_3 and TiO_2 particles. The particles size was intentionally reduced from 10 mm to 500 nm and to 40 nm. The results showed that introducing nanoparticles into semisolid slurries has a beneficial effect on optimizing strength–ductility relationship in Al–Si cast alloys. The new material showed higher strength values with improved ductility compared to the monolithic alloy under the same casting conditions. Those particles were incorporated and entrapped within the interdendritic and/or grain boundary interface, as well as within the grains, developed during solidification.

It is noted [16] that SiC microparticles are mainly located at the boundaries of the eutectic grains, and SiC nanoparticles – in the dendrites of the primary solid solution. The tendency of the microparticles to locate at the boundaries of the grains leads to the lower fracture toughness, strength and hardness at high temperatures, and also to the machining deterioration. Nanosize SiC and Al_2O_3 particles affect the size and morphology of the intermetallic compounds formed in the melt; as a result of the interaction of the nanosize SiC and Ti particles, the reinforcing phase TiC is formed.

However, high energy potential, high specific surface and interphase particle energy, and high surface tension of the melt impede the incorporation of the nanoparticles into the melt, and the tendency of the nanoparticles to develop aggregates. The possibility of their fusion in the melt requires special technology solutions different from the technologies of the microsize compound production. Thermal activation of the incorporated particles in the process of their preparing to the incorporation into the melt and the processes occurring in the liquid composite during the dwell time, pouring into the mold and finished article solidification, contribute to the intensification of the diffusion and recrystallization processes, to the disappearance of the non-equilibrium phases, residual stress relief and, correspondingly, to the modification of their unique properties. The higher the technological temperature is, the more intensively those processes occur and the lower the viscosity of the melt is.

Concerning the specific processes of interaction between the nanoparticles and the melt, it is evident that the decrease of temperature of the inoculation of the particles into the melt to the two-phase state and successive heating of the blanks during the shaping process to the temperature of the two-phase state (not to total dissolution) create preconditions for the effective problem solving in the field of cast MMNCs production (in particular, sedimentation and aggregative stability, gas porosity). Therefore, the processes of solid-liquid shaping (thixoforming) are most promising for MMNCs and MMCs products [17-20].

It is evident that irrespective of the influence of the nanoparticles on the crystallizing alloy, they remain as isolated inclusions in the solid composite and affect the processes of composite destruction, depending on the place of their location regarding the boundaries of the structure elements [21].

In the process of cast nanocomposite production it is necessary to provide the inoculation of the nanoparticles into the melt and their equal distribution in the volume of the slurry and sedimentation stability of the melt, prevent nanoparticles from aggregation in the process of feeding the composition into the molding cavity and in the recycling process of the composites and reheating before the shaping of the previously produced nanocomposite charges. Concurrently, the problem of providing the peak level of the necessary complex of composite properties by affecting the processes of crystallization and structure formation of the matrix melt is of great value.

The inoculation of the nanoparticles into the melt and their uniform distribution in the slurry is mainly implemented by means of the mechanical [4] and MHD [5, 22] stirring of the particles. The reinforcing particle powders may be introduced not only in the initial state using plasma torch, injection in the gas current, but also in the form of the pellets, briquettes, flux cored wire, and extended pressed compositions. In the process of the mechanical mixing the optimum performance of the mixer provides the onset of the shear deformation in the melt, especially when mixing the melt in the liquid-solid state. It prevents the agglomeration of the particles and provides better wetting and uniform distribution of the particles in the melt volume. The ensuing dwell time of the melt in the mixer with low mixing speed enables its transporting to the casting molds using various casting methods.

Plasma synthesis method along with the biplanar MHD-mixing and incorporation of the nanoparticles into the melt in the form of nanosize powder composites, produced by mechanical alloying in high-energy mills, possesses a number of advantages [23]. Biplanar MHD mixing of the hypoeutectic silumins in the liquid and two-phase states allows solving the problem of equal distribution of the particles in the melt volume, ensuring the degeneration of the dendrite structure and the possibility to use all the advantages of thixocasting for producing nanocomposites.

High-power ultrasound treatment (UST) of the alloys in the liquid and two-phase state is one of the most efficient methods of affecting the processes of alloy structure formation [24-28]. Structural changes in the ultrasound-treated metal are determined by the processes occurring in the melt in two-phase zone – nucleation of crystals, their growth and dispersion, by mixing processes, which, in turn, are connected with cavitation and acoustic streaming development in the melt, and by the parameters of supersonic field in the melt, its properties, volume, impurities, and dissolved gases [29].

The impact of ultrasound diminishes with increasing the distance between the alloy and the ultrasonic horn; therefore it is advisable to use ultrasound treatment along with the MHD-mixing. This allows solving the problem of non-dendrite structure formation in the process of composite thixocasting at the stage of the primary treatment of the melt, considerably decreasing the duration or excluding the reheating of the blank aimed at final "degeneration" of dendrites.

The development in the field of production of MMNCs using nanocarbon materials as reinforcing complexes, in particular, fullerenes C_{60}, nanotubes, nanodiamonds, nanosize products of the modification of the natural carbonaceous rock (shungites), is highly promising [30].

The problem of the nanoparticles inoculation into the melt may be simplified due to the preliminary production of rich nanocomposite alloys in the liquid-solid state with their further incorporation into the melts.

Special attention is given to the innovative development of cast and wrought MMNCs industry – the superdeep penetration (SDP) phenomenon. It may be regarded as the new physical instrument to affect the existing materials. The new concept of the physical phenomenon of the SDP is based on the consequent implementation of the complex of the physical effects, such as higher energy density (accumulation) in the local zones of the barrier material due to shutdown of the system, creation of dynamically stable local zones of high pressure, and the level of the latter sufficient to implement the dynamic phase transition. The use of SDP allows to incorporate into the volume of the solid body the alloying elements tens millimeters deep at an interval of 10^{-3}–10^{-7} s. In the volume of the solid body the fibrous elements, obtaining specific nano- and microstructures, allowing producing the materials with unique properties, are created [31-33]. Nowadays SDP is used for the solid-state processes; however, there is a reason to believe that complex technologies would make it possible to use SDP for the liquid phase methods of metallomatrix nanocomposite production.

As a rule, the foundry specialists are concerned with the production of the shaped castings out of the casting alloys by various casting methods. However, the development of the thixoforming (thixocasting, thixoforging) processes proves the effectiveness of the cooperation of the foundry specialists and the specialists in the field of the forging processes. The field of mutual cooperation may include the production of sheets and shapes out of nanocomposites using the methods of the ingotless rolling.

At present the granular technologies develop rapidly, especially the new material science branch of nanostructure granular composites, combining the advantages of the metallurgy of granules and the principles of producing the volumetric composite out of granules [34]. As a rule, uniform (isostatic), hydrostatic or gas-static pressing is used for the compaction. Considering the experience of the foundry specialists in the field of suspension casting, the possibility of the use of the nanostructure granules for the inoculation of the nanoparticles into the melt, the cooperation of the foundry specialists with the specialists of the metallurgy of granules in the field of the development of the hybrid processes, capable of providing the production of the shapes out the new class of nanocomposites, is highly promising.

3. Conclusions

1. Metal matrix micro- and, especially, nano-structural composites provide a number of advantages as compared to traditional matrix alloys. MMCs and MMNCs based on the aluminium and magnesium alloys are the promising materials for the various branches of industry due to low unit weight and higher, in comparison with the matrix alloy, level of the properties (wear resistance, hardness, local strength, bearing capacity, heat resistance, damping, antifriction, transport, and other properties).

2. The problems of nanocomposite article production using liquid phase technologies require the system approach to the solving of the whole complex of the occurring problems, involving specialists in various fields (thermodynamics, physics and chemistry of the melt and solid state, fracture mechanics, technologies of the production and treatment of the alloys in the liquid and two-phase state, *etc*.)

3. The promising technologies are the complex technologies of MMNCs production, implementing the external influence (UST, MHD) on the liquid and crystallizing matrix alloy with incorporation of the reinforcing particles along with the thixoforming of the finished article production.

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МЕТАЛО-МАТРИЧНІ МІКРО- ТА НАНОСТРУКТУРНІ КОМПОЗИТИ (ОГЛЯД)

Анотація. *Розглянуто рідкофазні технології виробництва метало-матричних мікро- і наноструктурних композитів. Запропоновано комплексне використання магнітогідродинамічного перемішування, ультразвукового оброблення розплаву в рідкому та рідинно-твердому стані та тиксолиття.*

Ключові слова: *метало-матричні композити, рідкофазна технологія, магнітогідродинамічне перемішування, ультразвукове оброблення, тиксолиття.*