



# Chemical interaction of liquid aluminum with metal oxides in molten salts



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## ABSTRACT

The metal-matrix composite material Al- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was synthesized at chemical interaction by quasi-autocatalytic mechanism of oxide-containing salt flux with molten aluminum at 700–900 °C under air. Precursors consisted of nanocrystalline oxides, including Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub>, synthesized by means of anodic oxidation of metals in chloride-nitrate molten salts. The formation of uniformly distributed nano- and micro-inclusions of  $\alpha$ -alumina depends on the sizes, time exposure and interaction temperature of the oxide precursors. Poor quality Al-Al<sub>2</sub>O<sub>3</sub> composites result from intensive mixing of nanocrystalline alumina into liquid aluminum: a significant imbalance in the lattice parameters of aluminum and alumina leads to increased nano alumina particle agglomeration formed inside caverns or cavities in the metal. Aluminum- $\alpha$ -alumina composites produced by the interaction of TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> in liquid aluminum are compact and non-porous, with a characteristic metallic shine and good thermal and electrical conductivity and melting point of aluminum. The synthesis of aluminum- $\alpha$ -alumina composites proceeds at a fairly low temperature resulting in the formation of fully wetted nano-oxide up to 10% or micro-oxide up to 40% in metal matrix. The microhardness of Al- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanocomposites is 1.5–1.9 times more than the initial pure aluminum.

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## 1. Introduction

Metallic materials, including aluminum-based alloys, can acquire completely new functional characteristics through the introduction of micro- and nanoscale powders of oxides, nitrides, carbides of metals and nonmetals as well as new carbon materials. Such composite materials exhibit different characteristics from conventional aluminum alloys, offering greater reliability at critical loads and a long service life. The metal matrix composite combines the advantages of structural metallic materials with the benefits of the ceramic fillers. The creation of new aluminum metal composite materials combining low density and high strength with high resource availability characteristics, increasing their suitability for a wide range of products in the aerospace industry, is an urgent research task.

Attempts to create aluminum-based composite materials (CM) by introducing dispersed particles of refractory compounds into a molten metal have been taking place for over half a century. The dispersed particles most commonly introduced into the molten aluminum are SiC, B<sub>4</sub>C, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiB<sub>2</sub>, TiC, Si<sub>3</sub>N<sub>4</sub> [1–8] or carbon materials [9,10] with low densities and high elasticity modulus.

Liquid state processing routes include infiltration techniques [11–13], stirring techniques [14,15], rapid solidification [16–18], as well as some in-situ fabrication methods such as liquid-gas bubbling [19]. Liquid state processing is generally energy-efficient and cost-effective. Moreover, products having complex shapes and chemical composition can be formed directly through the melt. Nevertheless, because of the difficulty of uniform distribution of the particles in the metal melt and the uncontrolled development of the crystallization, an industrial-scale technology for creating CMs using these methods has yet to be realized.

Particular difficulties arise when trying to introduce nanoparticles that form large conglomerates (up to 1–3  $\mu$ m) into the melt due to the high surface energy of the nanoparticles. Therefore, an essential goal of the research is not only the synthesis, but also a uniform distribution of nanosized ceramic particles over the cross section of an aluminum alloy-based composite material. As a consequence of the poor wettability between the metal matrix and ceramic particles, the particulates tend to agglomerate in the matrix. External field forces are needed to break up the clusters and help disperse the particles into the melt. One of the successful attempts is the introduction of ultrasonic cavitation [20–22]. In general, a significant technological hurdle remains to be overcome in terms of the uniformity of distribution of reinforcing particles introduced into molten metals, which significantly affects the subsequent physical and technological properties of the finished composite material.

Among the main difficulties in the preparation of composite materials is the challenge of obtaining an optimum interaction between

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the matrix and hardener without excessive chemical or mechanical degradation of their properties.

Currently, there are some basic methods of producing aluminum metal matrix composites, which essentially amount to impregnation of the molten or semiliquid aluminum reinforcing agents. Unfortunately, the thus-formed composites suffer from a number of disadvantages, including the anisotropy of the properties, the complexity of the production process and the complexity of machining after casting. The only industrial aluminum-based composite material applications consist of reinforced aluminum oxide ( $\text{Al}_2\text{O}_3$ ), which is prepared by pressing aluminum powder followed by sintering (EPS) [23,24]. In recent years, casting techniques have undergone a number of developments. However, the main difficulty with this process remains the need for wetting the fibers and avoiding reactions with the matrix. The resulting composite has a characteristic layered structure, in which alumina precursor particles form alternating layers, connected to each other by sintering on the alumina surface phase. Composites obtained by this method are primarily characterized by their high porosity, which leads to a deterioration of their physical properties such as strength and ductility.

The dispersion reinforcement of metal matrix composite materials is usually carried out by powder metallurgy or casting, whereby the ceramic particles are introduced ex-situ in a solid or liquid matrix, respectively. Recently, a method has been developed for the manufacture of CM based on controlled in-situ chemical reactions; the reinforcing fillers are formed directly in the process of chemical interaction between the components of the matrix and the reactive supplements [25–28]. Such CMs are characterized by their superior physical and mechanical properties due to the formation of coherent (i.e., having a common atomic layer at the interface) or partially coherent boundaries between the matrix and the new phases originated in in-situ reactions.

In order to produce a metal matrix composite with high mechanical properties, researchers commonly opt for a system that enables the creation of a finely dispersed strengthening phase. The similarity in the crystalline structure of the matrix and ceramic particles allows for a coordinated interaction between the two phases, which in turn increases the efficiency of the dispersed hardening phase. Furthermore, a small lattice mismatch minimizes the specific surface energy of the phase boundaries, providing stability at high temperatures by reducing the driving force for enlargement of the crystallites, i.e. an excess of free energy associated with the interface between the particles and the matrix.

It should be noted that there is a significant difference in the parameters of crystallographic lattices of aluminum oxide (corundum) and pure aluminum, as well as a substantial difference in the thermal expansion and thermal temperature coefficients. Aluminum has a face-centered cubic lattice ( $a = 0.40403$  nm,  $z = 4$ ) and  $\alpha\text{-Al}_2\text{O}_3$  has rhombohedral lattice with the parameters  $a = 0.512$  nm and  $\alpha = 55.25^\circ$ .

Nevertheless, the introduction of alumina to the molten aluminum matrix is justified due to a number of very valuable properties of corundum, which include a relatively low density, high specific strength, thermal stability, a high melting point and high resistance to oxidation. Furthermore, the alumina hardening phase formed in liquid aluminum has a low diffusion coefficient as well as poor solubility during aluminum cooling.

Thus, we can conclude the desirability of choosing corundum as a potential dispersoid for modification of alumina. In addition, numerous experimental and modeling researchers attribute improved strength characteristics of composite materials using nanodispersoids as structure modifiers, leading to decrease of grain size, as well as possibly the size dependence of the specific solid-liquid interfacial energy [24,29]. It is assumed that with decreasing precursor particle size, i.e. the means of wetting the particles by melt, the contact angle changes. Thus, if the interfacial energy begins to decrease as the particle size decreases, then the nanosized particles (graphene) of those substances, which are not wetted at a macroscale (e.g., carbon

materials), can be wetted by molten aluminum [30,31]. However, these phenomena should occur only when the linear dimensions are less than 10 nm.

The aim of the research was to study the chemical interaction of liquid aluminum with the metal oxide nanopowders ( $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{TiO}_2$ ) under a layer of molten alkali halides, and to investigate the composition, structure and the thermal conductivity of the as-obtained aluminum-alumina composite material.

## 2. Methods

The interaction between the molten aluminum and the nano- and micro-oxide powders of transition metals was performed in molten alkali halide media using an alumina crucible with the mixture of alkali chlorides with weighed portion of oxides on the bottom of the crucible. Salt mixtures of alkali chlorides, such as eutectic molten mixture of sodium and cesium chlorides or equimolar mixture of sodium and potassium chloride flux with melting points of  $<700^\circ\text{C}$ , were used as base electrolyte. The small fluoride additions of  $\text{CaF}_2$  or  $\text{NH}_4\text{F}$  or  $\text{NaF}$  or  $\text{AlF}_3$  ( $<5$  wt%) formed part of the salt flux electrolyte. Metal nanopowders were produced by electrochemical oxidation of subsequent metals (titanium, tantalum) in chloride-nitrate melts. Aldrich  $\text{TiO}_2$  powder with average grain sizes from 20 to 50  $\mu\text{m}$  was also used. The oxide concentration in salt electrolyte varied from 0.2 to 2 wt%.

The aluminum sample with 0.65 wt% impurities (Si – up to 0.62 wt%; Fe, Cu, Mn, Mg – up to 0.05 wt% in total; Zn – up to 0.1 wt%) consisted of a disc 3 cm in diameter and 1 cm in height. The aluminum sample size was equal to the inner crucible diameter. The aluminum was loaded into part of the salt mixture at the bottom of the crucible. The same mixture of alkali-halide metals with the addition of oxide was also placed on top of the aluminum. The alumina crucible was placed into the vertical heating furnace at the required temperature. The temperature interval for the experiments was  $700\text{--}900^\circ\text{C}$ . The interaction temperature was chosen under the melting point of both the aluminum ( $662^\circ\text{C}$ ) and the salt mixture. The exposure time varied from 1 to 5 h. After the high temperature exposure, the liquid aluminum globule was poured into the cold alumina crucible. After the salt mixture had fully solidified, it was dissolved in distilled water and the salts were washed off the surface of the aluminum globule.

The aluminum disc was then cut into two halves. The first half was poured by current-carrying gum and then polished by six different silicon solutions using the “Struers” disc-finishing machine (Austria). The specimen was then examined by means of scanning electron microscopy (SEM) using a JEOL 5900LV and analyzed by grazing-incidence X-ray diffraction (Rigaku DMAX 2200PC).

The aluminum discs were sawn roughly in half, with one half in current-conducting resin, and polished on the polishing machine. The chemical composition of the aluminum-carbon composites was tested for microhardness using the WIN-HCU FISCHERSCOPE HM 2000 XYm system, which is designed to perform a Martens test under a load in accordance with standard ISO 14577. Thermal analysis of aluminum-carbon composites was carried out by means of an STA 449C Jupiter® thermal analyzer by NETZSCH (Germany), allowing measurements to be performed by differential scanning calorimetry (DSC) and thermogravimetry (TG) methods across a wide temperature range.

The quantitative content of aluminum oxide in the produced CM was determined by the volumetric method.

## 3. Results and discussion

### 3.1. High-temperature electrochemical synthesis of precursors – metal oxide nanopowders

Synthesis of metal nano-oxide powders was carried by electrochemical oxidation of the pure metals in chloride-nitrate melt by original method. The nitrate melt is one of the most widely used molten media for

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