Metal-Ceramic composites via “in situ” methods

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Abstract. Several “in situ” methods for obtaining composite materials with ceramic particles were developed in order to overcome some of the inherent problems associated with conventional processes. This paper reviews the obtaining processes of composite materials with a greater emphasis on nitriding and oxidation by directed melting. These obtaining methods provide microstructures with different combinations of metal–ceramic. Metal matrix composites with controlled amounts of dispersed ceramic particles are obtained by “in situ” processes. The composite materials obtained are having different properties by controlling various processing variables such as temperature, time, the reactant phases and the reinforcing material. The properties of the “in situ” obtained materials depend mainly on the matrix and volume fraction of constituent phase. Briefly are reviewed the mechanical properties, hardness mechanisms and possible applications of these composite materials. Nitridation is much more attractive because with the variation of process parameters is obtained a wider range of microstructures and properties. The activation energy for the formation of AlN (AlN ~ 100 kJ/mole) is smaller than that of oxidation (Al2O3 ~ 400 kJ/mole) and growth rates (3 × 10^-2 gm/cm²/s) are at least three times higher for oxidation.

1. Introduction

Composite materials are found in nature; only the notion of composite materials was stabilized by human beings. Wood is considered a composite material with natural glue (lignin) matrix cellulose fiber reinforced. Another example of composites is the shells on freshwater invertebrates (snails and oysters). These shells are stronger and tougher than advanced composites obtained nowadays. Recent investigations prove that the fibers taken from cobwebs are more powerful than synthetic fibers. For several hundred years, in countries such India and Greece, to build houses have been used straws or husks mixed with clay. An ancient example of making a composite reinforced with particle is the mixing of sawdust with clay and the straw mixing with clay lead to a short fiber reinforced composite. Both particles and fibers, called reinforcement, are used to improve performance of the material. The main concept of a composite is that is formed by the matrix and reinforcement elements [1]. Metal matrix composite captivated the attention for their applications in aerospace and automobile industry due to low density, specific strength, thermal expansion low coefficient, wear resistance and high elasticity modulus [2].

The most used reinforcement elements are SiC, TiC, Al2O3. Instead, elements such as aluminum, magnesium and their alloys are used as matrix.
In order to obtain metal matrix composites are generally used three methods: - powder metallurgy [3, 4], in which metal matrix and ceramic particles are degassed, mixed, pressed, and sintered; - high temperatures "in situ" methods [5-7], in which the composite material is obtained by the reaction of a mixture of powders and gas; - infiltration technique [8-10] where the liquid metal penetrates a porous preform to fill it, sometimes it is required to apply an external mechanical force like in the case of squeeze casting [11, 12].

2. Materials and methods

The paper presents a synthesis of development of AlMg/AlN "in situ" composite by bubbling nitrogen with high purity through AlMg melt. Gas flow and bubbling time are variable parameters. Also there are discussed the possible reaction mechanisms.

When the aluminum alloy is introduced unto a nitrogenous atmosphere above its melting point, a nitride layer is formed on the surface, a stable layer which prevents further reactions. In the presence of alloying elements e.g. magnesium, the nitride layer becomes unstable and exposes the matrix material which leads to the continuous formation of nitride. For the same reasons the process is also observed in oxidation [14], where the phenomenon is explained to a large extent. An Al/Al2O3 composite is formed by oxygen diffusion through a magnesium layer in the aluminum alloy. Also, Al/AlN composites present similar microstructures which evolve through adsorption and precipitation of nitrogen in molten aluminum [15].

Schematic drawing of the experimental plant is shown in figure 1. A Carbolite furnace was used for the composite materials obtaining. For melting the aluminum alloy has been used a graphite crucible which was placed in a larger crucible made of steel. This site was sealed at the bottom and the outer end was provided with a lid with tubes for gas circulation. The tube used for gas infiltration was made from graphite with holes of 3 mm diameter. The tube was submerged in the melted alloy and held at the bottom until the gas infiltration was finished.

The initial material used for matrix was Al (99.75% purity). Were also conducted experiments in which the matrix material was AlMg alloy with 5wt% Mg.

For obtaining of investigated composite was used high-purity nitrogen (99.997%). The bubbling temperature was maintained at 1000 °C. Reaction temperature was controlled at 1000 °C and the bubbling time varied within 4 ÷ 6 hours. Gas flow was measured by a flow meter and maintained at a value between 0.6 and 0.8 liters / min.

After the elaboration of composite was completed the samples was cooled at room temperature. Composites total weight was about 270 g.

3. Experimental studies

3.1. Atmosphere role

Creating an atmosphere devoid of moisture and oxygen [16, 17] is a necessary condition, but not enough for AlN development.

In order to form aluminum nitrides, rather than oxides, the oxygen partial pressure has to be reduced.

For the equation 1 the Gibbs free energy has the value $\Delta G_f^o = 908$ kJ/mol.

$$\text{Al}_2\text{O}_3 + \text{N}_2 \rightarrow 2\text{AlN} + \frac{7}{6}\text{O}_2$$

If the equilibrium shifts to the right, the AlN becomes a stable phase. The oxygen equilibrium partial pressure is:

$$p_o^2 = \left[\frac{\alpha_{\text{Al}_2\text{O}_3}}{\alpha_{\text{AlN}}} \exp \left(\frac{-\Delta G_f^o}{RT}\right)\right]^{2/3}$$

At 1000 °C, $p_{N_2} = 1$ and the critical partial pressure for nitride obtaining is set below $10^{20}$ Pa. But the formation of nitrides is observed long before these pressures kinetics data. Just above the
alloy surface, a vapor cloud it is formed but only if in the matrix alloy is sufficient magnesium [18]. The Pourbaix diagram (figure 2) demonstrate that magnesium oxidizes at very low partial pressure \( p_{O_2} = 10^{30} \text{ Pa} \).

Thus magnesium serves as local agent of catalysis, and creates in the molted matrix favorable conditions for the development of nitride particles.

### 3.2. Alloyning additions
Magnesium is an essential dopant. In the absence of this element of the surface a stable nitride layer appears and stumble the development of aluminum nitrides throughout the melt [16].

Specific volume of nitride layer \( V_{AlN} / V_{Al} = 1.26 \) is greater than one unit, which makes the nitride layer to transforms in a protective one.

The work of Schoiz and Greil [18] reveals that magnesium has a catalytic effect on the formation of nitride so that it favors the transfer reaction surface in a reaction volume. Thence, for the other alloying elements the concentration remaining fixed, by varying the magnesium, were proposed three reaction mechanisms: the formation of a dense nitride surfaces; aluminum nitride is dispersed into the matrix through a volume reaction, and complete conversion of aluminum in AlN by heterogeneous combustion.

![Figure 1](image1.png)  **Figure 1.** Experimental plant for AlMg/AlN composite obtained “in situ”.

![Figure 2](image2.png)  **Figure 2.** Pourbaix diagram (at 1000 °C) for the Al-N-O and Mg-N-O systems [18].

![Figure 3](image3.png)  **Figure 3.** Pressure and temperature curves (function of time delineating reaction domains) [19].

### 3.3. Temperature and pressure
In nitridation, temperature is an important parameter, as was seen by the direct link between the atmosphere and alloying elements. At temperatures above 700 °C between nitrogen and aluminum reactions occurs.

While in pure aluminum matrix is formed a stable nitride layer at surface, alloying with other elements such as Mg favors the development of nitride particles continuously, fact conditioned by the atmosphere and temperature.

By increasing the temperature to values of 800-1050 °C, composites microstructure becomes finer and shows predominantly ceramic phases. This provides the flexibility to produce composites with both metal and ceramic matrix.

Konidela and Schweighofer [19] varied temperature values. Thus, they determinate the critical temperature which led to almost instantaneously change of the reaction rate, leading to changes in the reaction mechanism. Transition temperature is presented in figure 3 as \( T_2 \), when the changing of mechanism to the surface by volume occurs, which is presented as a rapid growth of the reaction heat. Volume reaction acceleration occurs over \( T_1 \), the reaction becomes thermodynamically unstable favoring a heterogeneous combustion, this leads to a sudden drop of nitrogen pressure.
3.4. Microstructure

The optical micrographs of the AlMg/AlN composite obtained “in situ” at 1000 °C by bubbling high purity N\textsubscript{2} gas (gas flow rate 0.6 lpm) for 4 h are shown in figure 4. It can be seen easily that in the matrix the AlN formed is uniformly distributed. By image analysis is revealed the AlN volume fraction which was found to be 4%. The particles average size has values ∼4 μm (average of particles in microstructure eight fields).

![Figure 4. AlMg5/AlN composite obtained “in situ” after 4 h reaction (gas flow rate: 0.6 lpm) optical micrographs.](image)

![Figure 5. AlMg5/AlN composite obtained “in situ” after 6 h reaction (gas flow rate: 0.8 lpm) optical micrographs.](image)

AlMg5 matrix optical and SEM micrograph are shown in figure 5 respectively Figure 6. The AlMg5 alloy sample was infiltrated with N\textsubscript{2}, the gas flow rate had the value 0.8 lpm. It is noted that the percentage of AlN particles considerably increases and the size varies from micron, submicron nano to values.

![Figure 6. AlMg5/AlN composite obtained “in situ” after 6 h reaction (gas flow rate: 0.8 lpm) SEM micrographs.](image)

![Figure 7. AlMg5/AlN sample after 6 h reaction XRD pattern.](image)

The particles seem to be interconnected and have the structure of a network of particles in the grain boundaries. Analyzing the image, AlN volume fraction couldn’t be realized because the particles have very small sizes and are presents a network form.

Another microstructure at higher magnification has been taken by SEM (figure 6). In this picture the individual particles are seen.

To demonstrate that the particles are AlN, the composite samples have been analyzed by XRD. figure 7 shows that analyzed particles are AlN.

The SEM microscopy and EDS analysis of AlN particles from AlMg5/AlN composite are shown in figure 8. The picture reveals that the AlN particles have hexagonal morphology.

Further, the nano-size of AlN particles and its hexagonal morphology was confirmed by TEM in figure 9.

AlMg5/AlN composite obtained “in situ” optical and SEM micrographs are given in figures 10 and 11 and shows the composite sample after 6 h reaction (gas flow rate: 0.8 lpm). If the gas flow rate is increased from 0.6 to 0.8 lpm was obtained a higher of fine particles (mostly nano sizes).

Figure 10 (b–d) reveals (by arrows) other phases. Without a detailed investigation, this supposed to be an MgAl\textsubscript{2}O\textsubscript{4} spinel layer.
Figure 8. (a) SEM morphology of the AlN particles from AlMg5/AlN composite obtained “in situ” (b) EDS of Al, N, Mg, C and O elements.

Figure 9. TEM morphologies of hexagonal AlN particles from AlMg5/AlN composite obtained “in situ”.

Figure 10. AlMg5/AlN composite obtained “in situ” after 6 h reaction (gas flow rate: 0.8 lpm) optical micrographs.

Figure 11. AlMg5/AlN composite obtained “in situ” after 6 h reaction (gas flow rate: 0.8 lpm) SEM micrographs.
4. Conclusions
"In situ" methods for obtaining composite materials with ceramic particles were developed in order to overcome some of the inherent problems associated with conventional processes. "In situ" technique allows the variation of parameters in order to obtain composite reinforcing elements with high volume fraction, fact that classifies it as compatible materials used in electronics. The formation of AlN particles strongly depends on temperature of nitridation, Mg presence in the matrix composition, gas flow rate and reaction time.

The nitridation rate and the development of a network with interconnected AlN particles were enhanced by the presence of Mg.

It is a challenge to obtain uniformly distributed AlN particles in the AlMg5 matrix and in this paper the cause was almost reached. Some of the AlN particles appear to be agglomerated and some are distributed in the entire composite surface. For a real success further work is required. One step may by to modifying the melt chemistry, solidification conditions and experimental set-up. Furthermore, for the AlMg5/AlN composites obtained "in situ", correlation of the mechanical properties with the microstructural variables need to be studied in detail.

5. References
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