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Microstructural evolution and mechanical properties of AlMg/AlN composite materials obtained "in-situ"

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In this paper characteristics of an AlMg/AlN composite produced "in-situ" and processed in a flowing N_2 atmosphere is investigated. Some critical parameters such as the manufacturing process temperature, the percentage of the magnesium consumed, the flowing reactive gas flow and the time for completing the manufacturing are considered as variables for the parametric investigation. Moreover, the effect of different amount of Mg employed has been also investigated, since Mg acts as a catalyst at the surface both for the gas/liquid and solid/liquid systems. Traditional methods were used for the basic characterization of the composite. The microstructure of the composite was investigated by optical and scanning electron microscopy (OM, SEM). SEM analysis was performed in order to observe the microstructural evolution as a function of the Mg content and to identify some reasons of the presence of porosity or any irregularities within the metal matrix. The evolution of mechanical properties, in terms of microhardness, at different percentage of Mg were monitored. By EDS technique the distribution of the elements was obtained. Furthermore, employing an optimization process, uniform dispersion of the strengthening (AlN) particles in the metal matrix with homogeneous properties along the composite material is obtained. Based on the aforementioned statements, it can be concluded that the reactions between Al, Mg and the N_2 atmosphere induce spontaneous infiltration in the metal matrix. The complete mix of properties and experimentally assessed parameters can be used for industrial purpose manufacturing design and development.

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Keywords: Metal matrix composite, Reactive Gas Injection (RGI), Aluminium alloys, "in-situ", Nitrides

1. Introduction

In the present economic context when oil and natural gas dependency controls almost every aspect of our lives, a better assessment of their efficient usage is required. High industrial demand on performing but less expensive metal matrix composite materials implies the development of economical and ecological processing methods (Cup ed altri, 2000; Litvinon ed altri, 2002). Aluminum metal matrix composite (AlMMC) with high mechanical and friction wear properties in corrosive and high temperatures environments constitutes a valuable property of such materials. Especially, the particulate-reinforced MMCs are more interesting due to their ease of fabrication, low costs, and isotropic properties.

It has been determined that the AlMMCs properties are controlled by reinforcement size and volume fraction as well as by the characteristics of the matrix-reinforcement interface (Cup ed altri). In order to obtain a viable combination of mechanical properties (high tensile strength corroborated with high temperature stability and good machinability), the composite material needs to contain fine and thermodynamically stable ceramic particles, evenly dispersed in the matrix (Cup ed altri, 2000; Aguilar-Martinez ed altri, 2007). Particulate AlMMCs are well known for their application as wearing parts (large particles sizes) or structural parts (small particle sizes). However, usually, smaller size (less than 10μm) particles are considerably more difficult to be obtained and incorporated in metal matrix composites through traditional processing technologies and are much more expensive than larger size ones.

Among the several available techniques to synthesize AlMMCs, the Reactive Gas Injection (RGI), in which the reinforcing particles are formed in situ in the molten alloy by gas-liquid exothermal reaction, is especially attractive due to its simplicity, economy, flexibility and the small particle size distribution in the final composite. RGI method is described by the process of injecting a reactive gas (e.g. methane, nitrogen, ammonia) in a molten alloy to produce the composite material by the means of chemical reactions at gas bubble-alloy interface. Previous research work mentioned the successful obtaining of Al-Si/SiC (Wu and Reddy, 2002), Al-TiN (Zheng and Reddy, 2003), Al/TiC (Khatri and Koczak, 1993) and Al/AlN (Tjong and Ma, 2000; Kumari ed altri, 2011) composites by the RGI method.

2. Physico-chemical and transfer processes at the nitrogen gas - liquid alloy interface

During nitrogen gas bubbling process with liquid aluminum alloy at interface nitrogen atom transfer from gas to liquid occurs. For modeling this process it was taken into account that the total transfer resistance is due to a thin static film. Pursuant to static film theory gas bubble with radius R_1 reacts with aluminum alloy at gas-liquid interface.

$$2N_2 + 4Al \rightarrow 4AlN \qquad (1)$$

$$2N_2 + 6Mg \rightarrow 2Mg_3N \qquad (2)$$

Reactions (1) and (2) are slow and depends on the free enthalpy variation with temperature. At temperatures below 700 °C free enthalpy variation is positive, so the reactions take place from right to left. As the temperature increases free enthalpy variation becomes negative and increases in module, which means growth of reaction speed.

Assuming that the boundary between the liquid and gas bubbles forms a static gas film of thickness $R_2 - R_1$ by which gaseous nitrogen must diffuse at interphase surface, and AlN and Mg_3N_2 reaction products broadcast in reverse. To determine radial molar flow, $J_{A,r}$, through the film, the continuity equation expressed in spherical coordinates is used (Carcea, 2008). Moreover, let's suppose that $R_2 \geq r \geq R_1$. In this case, we have:

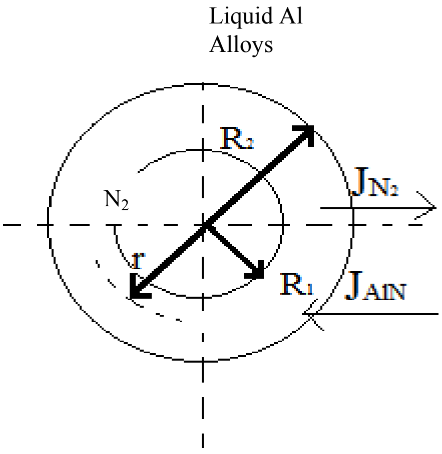


Fig. 1. Diffusion scheme through double layer formed at the alloy-nitrogen interface

$$\frac{d}{dr}\left(r^2 J_{A,r}\right) = 0 \qquad (3)$$

From the above reactions they result:

$$2J_{N_2,r} = -4J_{AlN,r} \qquad (4)$$

$$2J_{N_2,r} = -2J_{Mg_3N_2,r} \qquad (5)$$

Pursuant to molar flow definition for reaction (1) is valid next relationship:

$$J_{N_2,r} = -CD_{N_2-AlN}\frac{dX_{N_2}}{dr} + X_{N_2}\left(J_{N_2,r} - \frac{2}{4}J_{N_2,r}\right) \qquad (6)$$

respectively:

$$J_{N_2,r} = -\frac{CD_{N_2-AlN}}{1-0{,}5X_{N_2}} \cdot \frac{dX_{N_2}}{dr} \qquad (7)$$

and for reaction (2):

$$J_{N_2,r} = -CD_{N_2-Mg_3N_2}\frac{dX_{N_2}}{dr} \qquad (8)$$

where:
C- gas molar density
D_{N_2-AlN} or $D_{N_2-Mg_3N_2}$ - diffusion coefficients

Replacing the molar flux in equation (3) for the case when $R_2 \geq r \geq R_1$ we have:
-for eq. (1)

$$\frac{d}{dr}\left[\frac{r^2 \cdot CD_{N_2-AlN}}{1-0{,}5X_{N_2}} \cdot \frac{dX_{N_2}}{dr}\right] = 0 \qquad (9)$$

-for eq. (2)

$$\frac{d}{dr}\left[r^2 CD_{N_2-Mg_3N_2} \cdot \frac{dX_{N_2}}{dr}\right] = 0 \qquad (10)$$

respectively when CD_{N_2-AlN} or $CD_{N_2-Mg_3N_2}$ are constant (and different from 0), eq. (9) and (10) become:

$$\frac{d}{dr}\left[\frac{r^2}{1-0{,}5X_{N_2}} \cdot \frac{dX_{N_2}}{dr}\right] = 0 \qquad (11)$$

$$\frac{d}{dr}\left[r^2 \cdot \frac{dX_{N_2}}{dr}\right] = 0 \qquad (12)$$

In reaction (1) in which $m = 1 - \frac{2}{4} = 0{,}5 \neq 0$ equation (11) can be integrated within the limits:
Enforcing the boundary conditions:
$X_{N_2} = X_{N_2}{}'$ - nitrogen concentration for $r = R_1$
$X_{N_2} = X_{N_2}{}''$ - nitrogen concentration for $r = R_2$
It will be obtain:

$$\frac{dN_{N_2}}{dr} = \frac{R_2}{0{,}5R_1}\,\frac{1-0{,}5X_{N_2}}{R_1 - R_2}\ln\frac{1-0{,}5X_{N_2}{}'}{1-0{,}5X_{N_2}{}''} \qquad (13)$$

When the double layer film thickness (R_2-R_1) is much smaller than R_1, replacing in eq. (7) the concentration gradient results to be:

$$J_{N_2,r} = \frac{CD_{N_2-AlN}}{0{,}5(R_2 - R_1)}\ln\frac{1-0{,}5X_{N_2}{}''}{1-0{,}5X_{N_2}{}'} \qquad (14)$$

Using equation (14) the nitrogen flow to the nitrogen - liquid aluminum alloy interface could be determined. This is possible if diffusion control the entire mass transfer which will allow us to determine the rate of formation of nitrides AlN or Mg_3N_2 on route and during the movement of gas bubbles in the liquid alloy column.

2.1. Minimum oxygen part-pressure required by the nitridation reaction of Al alloys

The chemical affinity between oxygen and Al or Mg is larger than that between nitrogen and Al or Mg, Therefore, less oxygen in the reaction room will react with Al or Mg to form compound Al_2O_3 or MgO (Zeng ed altri, 2002). Consequently, the composition of the resulting products will change. Thus, minimum oxygen content or the critical oxygen part-pressure must be considered and controlled in order to make the nitridation reaction perform fully.

When temperature ranges from 1100K to 1500K, the reactions proceed as follows:

$$4Al + 3O_2 \rightarrow 2Al_2O_3, \quad (15)$$
$$4Al + 2N_2 \rightarrow 4AlN,$$

$$6Mg + 3O_2 \rightarrow 6MgO, \quad (16)$$
$$6Mg + 2N_2 \rightarrow 2Mg_3N_2.$$

The following equation can be deduced from eq. (15):

$$2Al_2O_3 + 2N_2 \rightarrow 4AlN + 3O_2. \quad (17)$$

Eq. (15) describes the stabilization effect which occurs: AlN can be synthesized in very low oxygen content.

2.2. Decrease of oxygen content by Mg element

When Al-Mg alloys are melted at elevated temperature, the volatilized Mg made molten alloys activate everywhere. Thus, on one hand, the nitridation reaction of Al is easily achieved; on the other hand, the Mg stream gas reacted more easily with oxygen so as to decrease the oxygen content. Moreover, it is well known that the Mg vapor pressure increases with temperature (Cholewa ed altri, 2007).

2.3. Dynamics analysis of nitridation reaction

AlN is synthesized by the combination of Al atom and N atom. Therefore, we can apply thermo-gravity (TG) to perform the dynamics analysis (Zhang ed altri, 2009). Here, the thermo-gravity analyzer connected to the computer has been used to collect the reaction data. Additionally, the translation ratio of reaction (α) has been applied, namely the ratio of actual change of reaction to theoretical one, to substitute the actual change of mass when the thermo-gravity analysis was utilized to depict the process of the nitridation reaction.

Fig. 2 shows TG curves for the nitridation reaction of Al-Mg alloys and pure Al (Bello ed altri, 2012). It can be observed that the nitridation reaction of Al-Mg alloys has been achieved more easily than that of pure Al, and the translation ratio is higher in this case. Therefore, it can be safely conclude that Mg facilitates at improving the AlN synthesis starting from Al and N.

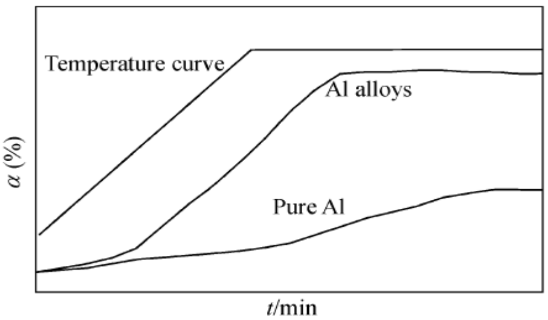


Fig. 2. TG curve of the translation ratio vs time

3. Manufacturing and processing

Experimental procedure for obtaining composite materials such AlMg / AlN is based on the "in-situ" technique and consist of introduction of reactive gas (nitrium) into the melt (AlMg alloy melt). Reinforcing

particles (AlN) are formed from the reaction between molten metal and bubbling gas.

Table 1 presents the material and process parameters that have been tested in experiments on the formation of "in situ" AlN reinforcement particles.

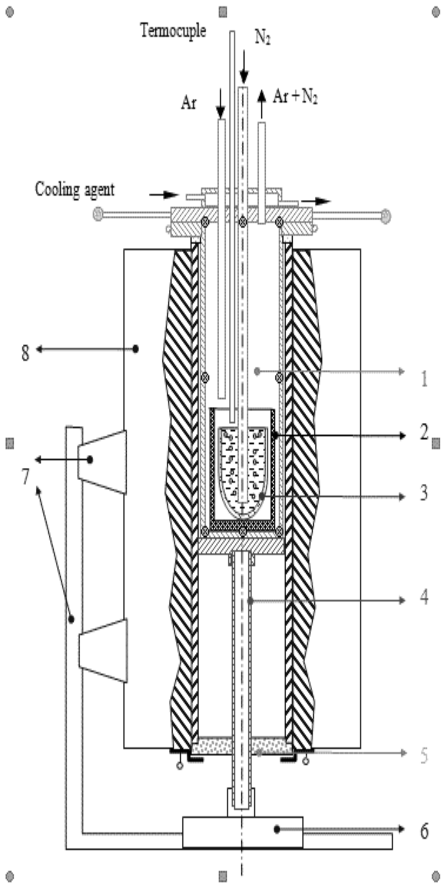


Fig. 3. Experimental installation. 1) melting chamber, 2) graphite crucible, 3) alumina crucible, 4) adjustable pillar, 5) insulation lid, 6) frame base, 7) L - shape frame, 8) furnace (Soare ed altri, 2010).

The experiments have been carried out in an enclosed reaction chamber heated from outside by a vertical tube furnace (Fig. 3). The aluminum alloy(260 g, 99,9% pure Al and 99,9%pure Mg) has been introduced in an alumina crucible (3), which has been placed in a graphite larger crucible (2), inside a closed box melting chamber (1) made out of high grade stainless steel. The entire assembly has been introduced into the furnace (8) supported by an L-shape frame (7) which also holds the closed box supporting and adjustable pillar (4).

Table 1 Experimental parameters.

Composite material type	Temperature, ºC	Mg percentage %gr.	Gas flow, l/min.	Bubbling time, min.
AlMg15/AlN	1000	15	0,6	3600
AlMg10/AlN	1000	10	0,6	3600
AlMg5/AlN	1000	5	0,6	3600

The furnace has been provided with a bottom end cover and sealed at the top side by the chamber cover and the refractory material between the chamber and the furnace. The chamber cap has been water-cooled to room temperature and supplied by several tubes for water and argon circulation.

4. Results and discussion

Chemical analysis , SEM microstructure observation and compositional analysis (EDS) graphs presented in this paper have been carried out on AlMg5/AlN , AlMg10/AlN and AlMg15/AlN composites. SEM microstructures and EDS graphs indicated with a) are composite AlN without reinforcing and in those marked with b) points of interest are aluminum nitride .

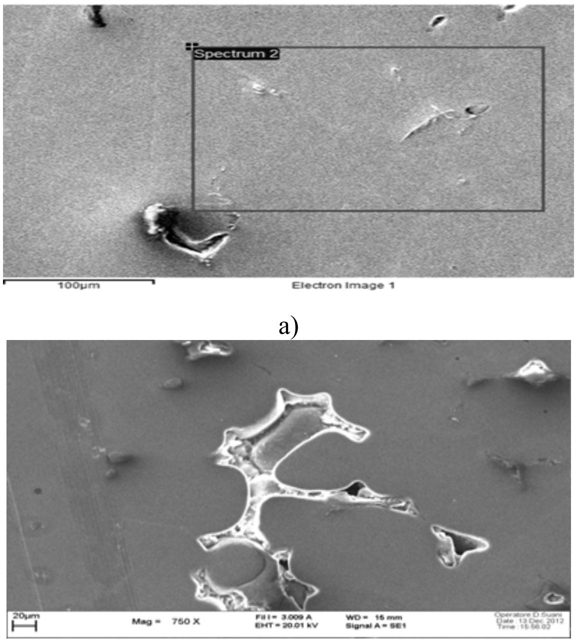
4.1 SEM/EDS Microstructure of AlMg5/AlN composite

The microstructure of the AlMg5/AlN composite samples consists of primary aluminium grains with isolated particles distributed in the matrix, as shown in Fig. 4a. The composition of the isolated particles (SEM images in Fig. 4b) was analyzed by EDS (results in Fig.5). The results revealed that these particles containe mainly Al, Mg, and N, along with a small amount of C, as shown in Table 2.

The Fig. 6 showed the composite microsture, table 4 reports the content of composite.

4.2 AlMg10/AlN composite

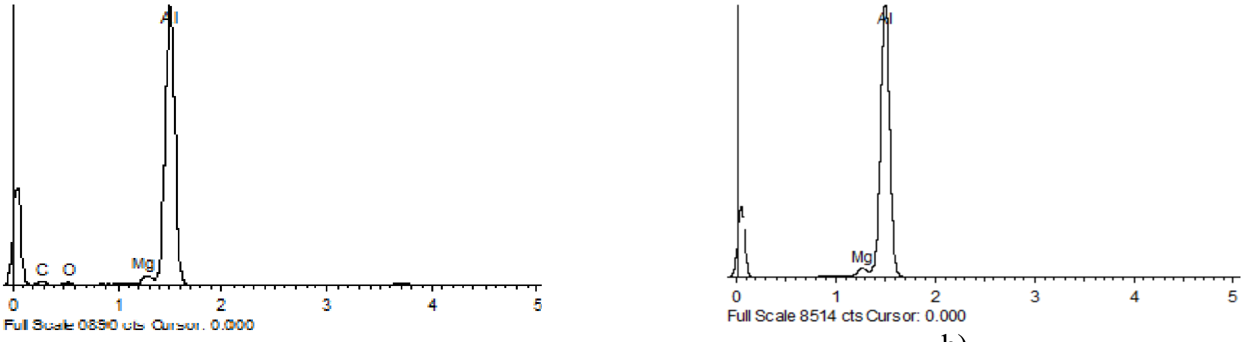
The SEM micrographs for the AlMg10/AlN composite samples are shown in Fig. 7. Compared to theAlMg5/AlN composite samples, a greater amount of particles were formed with significant segregation. The particles, (Figure 7b) had irregular shapes with a maximum size of a few microns. The EDS analysis showed that the composition of these particles is similar to that of the particles in the AlMg5/AlN samples.



a)

b)

Fig. 4. SEM micrographs of the AlMg5/AlN composite: a) AlMg5/AlN composite, point of interest: basic composite; b) AlMg5/AlN composite, point of interest: AlN



a) b)

Fig. 5. EDS analysis of the composite AlMg5/AlN. a) AlMg5/AlN composite, point of interst: basic composite; b) AlMg5/AlN composite, point of interest: AlN.

Table 2. Chemical composition of AlMg5 composite, point of interest: based composite.

Element	Weight%	Atomic%
Mg	3.24	3.58
Al	96.76	96.42
Totals	100.00	100.00

Table 3. Chemical composition of AlMg5/AlN composite, point of interest: AlN.

Element	Weight%	Atomic%
C	6.51	11.4
N	4.51	6.78
O	12.76	19.95
Mg	2.19	1.89
Al	74.04	59,97
Totals	100.00	100.00

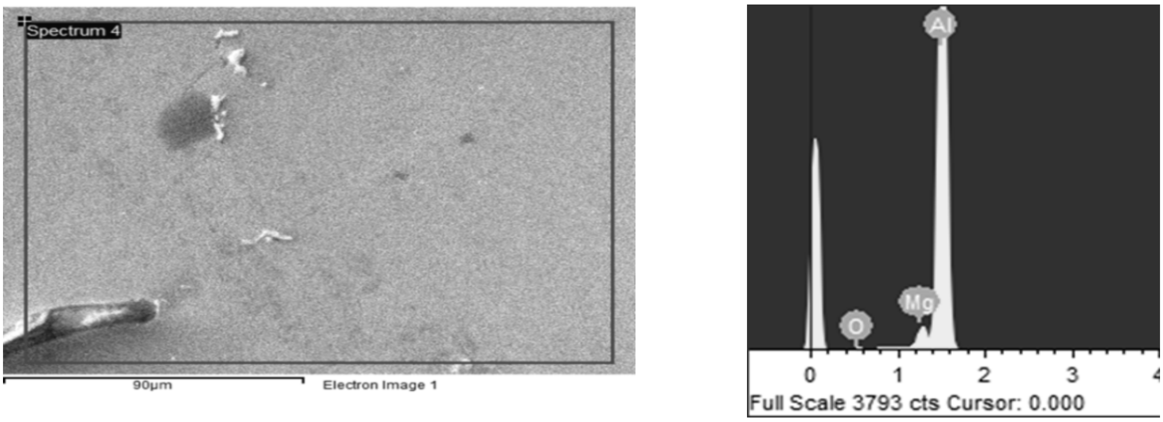
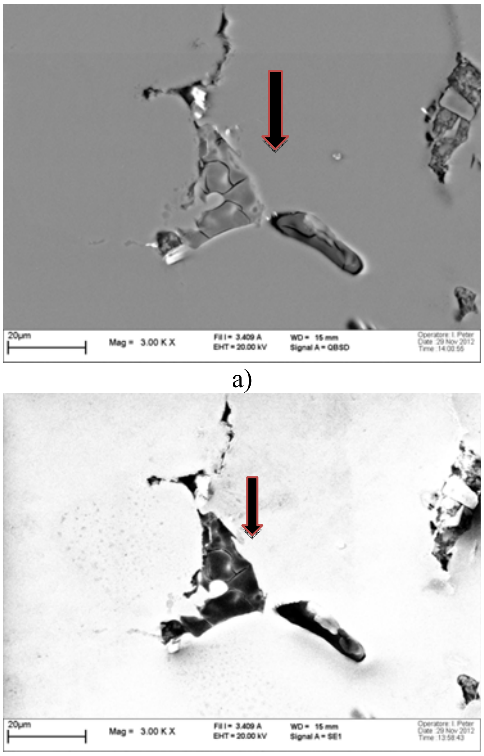


Fig. 6. SEM and EDS microscopy of AlMg5/AlN

Table 4. Chemical composition of AlMg5/AlN composite.

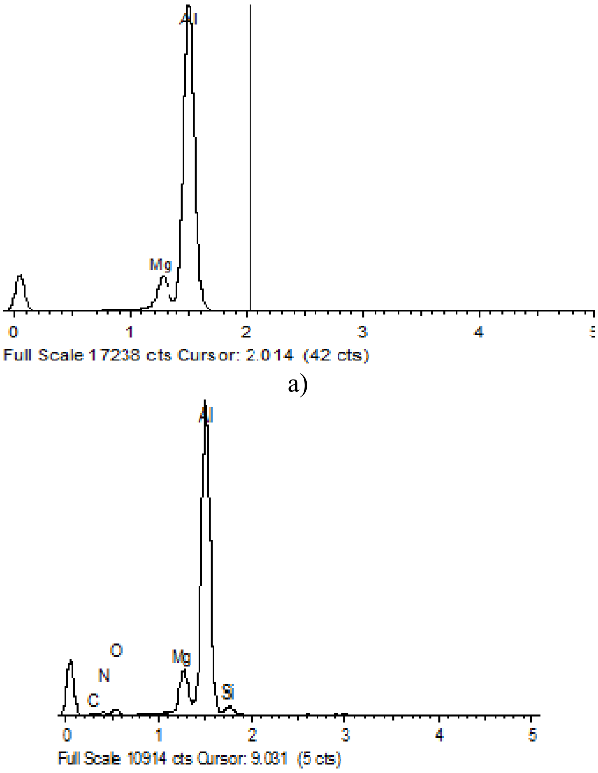
Element	Weight%	Atomic%
C	8.23	16.33
N	1.15	1.95
O	2.29	3.41
Mg	3.07	3.01
Al	85.26	75.30
Totals	100.00	100.00



a)

b)

Fig. 7. SEM micrographs of the AlMg10/AlN composite a) AlMg10/AlN composite, point of interst: basic composite b) AlMg10/AlN composite, point of interest: AlN



a)

b)

Fig. 8. EDS analysis of the composite AlMg10/AlN a) AlMg10/AlN composite, point of interst: basic composite b) AlMg10/AlN composite, point of interest: AlN

Table 5. Chemical composition of AlMg10/AlN, point of interest: based composite

Element	Weight%	Atomic%
Mg	8.78	9.65
Al	91.22	90.35
Totals	100.00	100.00

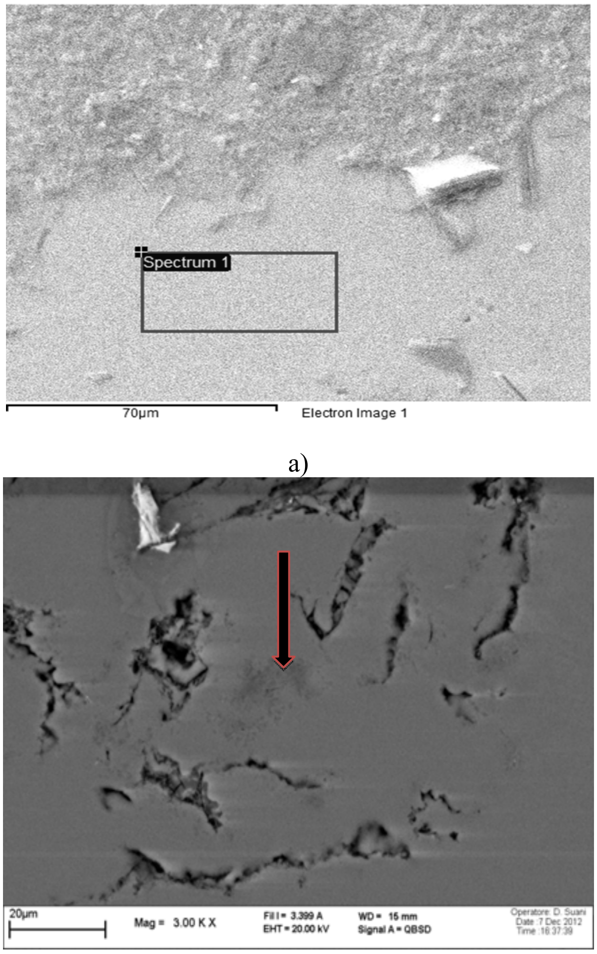
Table 6. Chemical composition of AlMg10/AlN, point of interest: AlN.

Element	Weight%	Atomic%
C	11.59	17.29
N	9.03	11.55
O	18.80	23.46
Mg	10.09	7.44
Al	50.48	40.25
Total	100.00	100.00

4.3. AlMg15/AlN

The microstructure of the AlMg15/AlN composite has been investigated using an optical microscope and EDS/SEM. The SEM micrographs of the sample are given in Fig. 9.

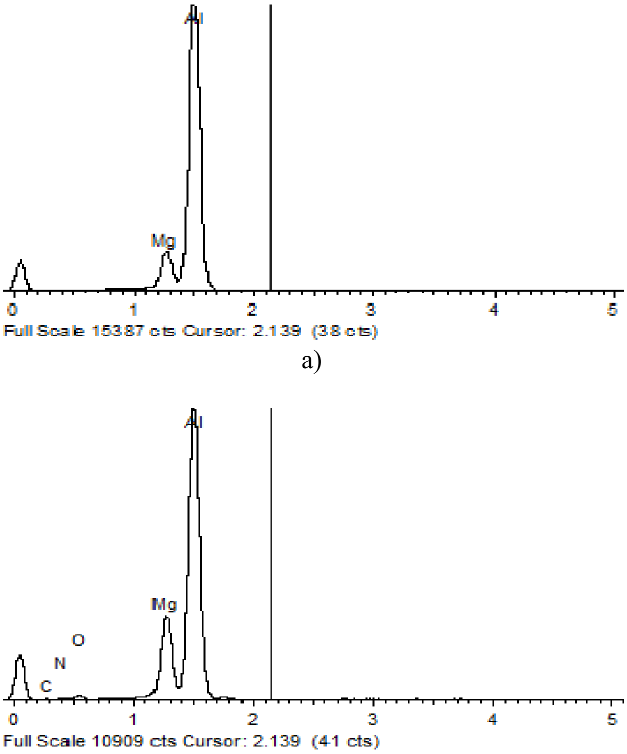
A typical EDS spectrum of the particle and the distribution of the element has been evidenced in Figure 10. Compared with the surrounding matrix, the particle is rich in Al and N, as illustrated by the brighter areas in contrast to the darker ones.



a)

b)

Fig. 9. SEM micrographs of the AlMg5/AlN composite a) AlMg15/AlN composite, point of interst: basic composite b) AlMg15/AlN composite, point of interest: AlN



a)

b)

Fig. 10. EDS analysis of the composite AlMg15/AlN a) AlMg15/AlN composite, point of interst: basic composite b) AlMg15/AlN composite, point of interest: AlN

Table 7. Chemical composition of AlMg10/AlN, point of interest: based composite.

Element	Weight%	Atomic%
Mg	9.22	10.13
Al	90.78	89.87
Totals	100.00	100.00

Table 8. Chemical composition of AlMg15/AlN, point of interest: AlN.

Element	Weight%	Atomic%
N	8.61	14.85
O	3.95	5.97
Mg	9.65	9.58
Al	77.79	69.60
Totals	100.00	100.00

5. Conclusions

The thermodynamics calculation indicates that the Mg element in Al-Mg alloys can decrease the oxygen content in reaction system for realizing the nitridation reaction of Al-Mg alloys.

The dynamics analysis shows that the Mg content can accelerate the nitridation reaction and improve the transformation ratio of nitridation reaction of Al-Mg alloys.

The experiments have comfirmed that the reaction between liquid aluminium and nitrogen in the conditions of an increased gas pressure may lead to the formation of AlN phases, and the presence of Mg in the matrix speeds up the reaction intensity. In the initial stage, the reaction proceeds on the surface. High pressure of nitrogene inhibit vaporization of Mg and reaction between Al and N_2 proceed in limited scope. Since the reaction is of an exothermic nature, it is difficult to be controled. Usingthe „in situ" reaction in order to form AlN dispersion reinforcement in the AlMg alloy matrix seems possible with limited intensity of the process, for example, through lowering the Mg fraction in the matrix or setting an appropriate reaction time.

The high Mg concentration in the Al-Mg alloys improved the nitridation reaction, which resulted in a high nitride growth rate. AlN is the major phase exists in the final product besides MgO, α-Al_2O_3, $MgAl_2O_4$ and residual Al. The presence of the oxide phases indicated the existence of O_2 content threshold in the nitriding atmosphere. A lower heating rate means a longer reaction period is required, thus allowed more conversion of Al to AlN to form Al/AlN composite.

Acknowledgement

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