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Determining the applicability of liquid alloy nitriding in fabrication of Al-AlN particle composites

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Abstract

One of the possible techniques of the fabrication of dispersion-hardened composites is by *in situ* reaction between the liquid alloy and gas. The study presents the results of the research on nitriding of liquid aluminium alloy containing Mg and Ti as alloying elements under the conditions of high pressure comprised in the range of 150-1000hPa at the temperature of up to 1100^{o}C. It has been stated that under the applied conditions of the synthesis it is possible to obtain the AlN nitride, but it is formed on the liquid alloy surface and as a deposit on the surface of the crucible. Some results of the analysis of the phase constitution obtained in the fabricated products were presented along with the structure of these products.

Keywords: Aluminum alloys, In situ composites, Aluminum nitride

1. Introduction

Aluminium-based metal matrix composites (AlMMC) are the family of materials which, owing to their unique properties, are more and more popular as a material for modern engineering structures. Composites reinforced with ceramic particles (Al_2O_3, SiC) are gradually implemented in current production in the automotive industry, electronics and aircraft, the reason for their spreading popularity being their excellent tribological properties. Fabrication of composites characterised by high mechanical properties is possible in the case of dispersion hardening of the composite structure when the size of the respective particles is less than 1 μm. Reinforcement of this type can be produced due to an *in situ* reaction that takes place between the reagent and the matrix material. One of the possibilities to obtain dispersion phases is the reaction in liquid metal – gas system [2]. The composite material is formed in the process in which three successive stages can be distinguished: the dissociation of reactive gas, the synthesis of reinforcing phases, and the kinetics of their growth [2-6]. In this process, the dispersion particles, i.e. carbides or nitrides, are formed as a result of reaction that takes place between the gas bubbles and alloying additions [7,8]. Thus formed dispersion reinforcing phase is thermodynamically stable and chemically pure [2-7]. An important advantage of this method is the possibility of using some casting technologies for shaping of products.

Temperature range of 588-566^{0}C, in the time of 104s. Long time of solidification (t=258s) was registered for alloy with the magnesium, titanium and boron modifiers in the temperature range of 586-539^{0}C. The time of solidification for the 226D alloy modified with 0,03% strontium average 208,5s. These material solidified in the temperature range of 573-557^{0}C. The highest temperature of crystallization beginning (T=591^{0}C) used for the aluminium alloy containing 0,5%Ti+0,1%B+0,03%Sr modifiers, with the time solidifying for 248,5s in the temperature range of 591-557^{0}C.

2. Test materials

The base test material was Al99,7% aluminium made by the IMN OML Institute of Non-Ferrous Metals, Light Metals Division, Skawina. As modifiers of the alloy matrix composition, the additives of magnesium, titanium and boron were used. The carriers of the alloying elements were master alloys of AlMg25, AlTi75 and TiBAl, made also by IMN OML Skawina. The chemical composition of the aluminium and of its modifiers is given in Table 1.

Table 1.
Chemical composition of aluminium and alloying elements, %

	Fe	**Si**	**Cu**	**Zn**	**Ti**	**Mn**	**Al**
Al99.7	0.10 -0.16	0.05 -0.11	0.002 -003	0.021 -0.022	0.004 -0.006	0.003 -0.004	99.77 -99.92
	Fe	**Si**	**Mg**	**V**	**Ti**	**B**	**Al**
AlMg25	0.16	0.14	25.3				74,4
AlTABTi75					73.5 -76.5		23.5 -26.5
TiBAl	0.20	0.10			4.8	1.0	93,9

Nitrogen phases were produced with nitrogen 5.0 of 99,999% purity, nitrogen 7.0 of 99,99999% purity (Linde Gas) and argon 5.0 of 99,999% purity (Messer Polska).

Alloys of Al+5%Ti+3%Mg, Al+5%Ti+5%Mg, and Al+3%Mg served as a matrix.

3. Experimental

The selected alloys were subjected to nitriding at various nitrogen pressures and at different temperatures comprised in the range from 850°C to 1100°C. The pressure from 150hPa to 1MPa and the nitriding time from 1 to 5 hours were applied.

The process was conducted in a specially designed and manufactured retort (Fig.1). The test billet of alloy matrix weighing 300 g was placed in a corundum crucible and enclosed in the reaction retort fixed in a resistance furnace. Next, the air was evacuated from the retort and replaced with argon forced into this retort. The operation was repeated twice to ensure oxygen-free atmosphere in the retort chamber. After melting down of the matrix, at the temperature of 780°C, argon was pumped out and replaced with nitrogen introduced to the chamber at an appropriate pressure and raising the temperature to a required level. With the process of nitriding completed, the retort was cooled with furnace to room temperature.

The obtained material was evaluated in terms of its reaction degree, and its phase constitution and microstructure were examined.

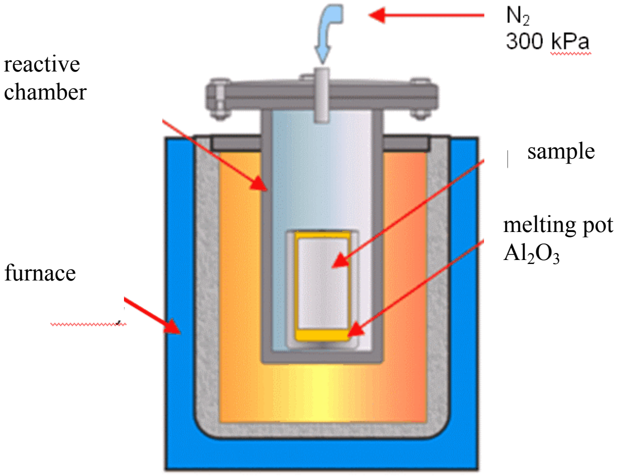

Fig. 1. Schematic representation of the stand for direct nitriding of liquid aluminium alloy

4. The results and discussion

The concept of producing in liquid metal the dispersion phases of AlN was based on the feasibility of a reaction between magnesium and nitrogen, on the instability of thus formed magnesium nitride at high temperature leading to the formation of atomic nitrogen, and on the tendency of this nitrogen to enter into reaction with aluminium and other alloying additives. The individual stages of this scenario were anticipated basing on a model proposed in [2]. The results of the investigations are presented in [3-8]; the thermodynamic calculations are plotted in Fig. 2.

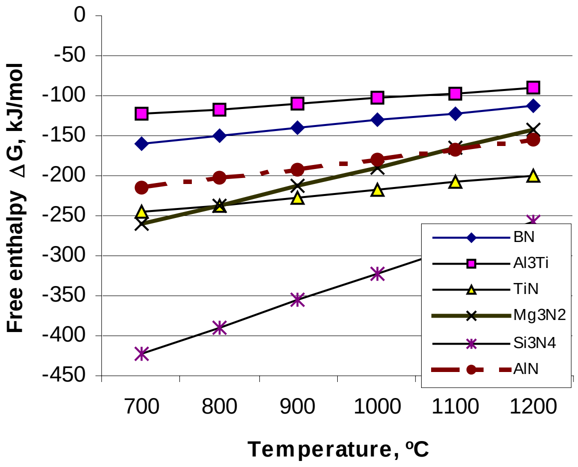

Fig. 2. Changes in free enthalpy during formation of nitrides; calculations carried out in a HSC program

Yet, it has turned out that the process of nitriding was proceeding by its own route, different from the expected one, and - depending on the type of the base alloy used and on the conditions under which the synthesis was conducted - it resulted in either partial or complete reaction with molten aluminium alloy, followed by the formation of nitride phases..

The attempts to obtain an alloy with the dispersion particles distributed evenly in the matrix ended in failure. Some selected results of the technological investigations have been presented in this study. Figure 3 shows the effect of the reaction of synthesis proceeding in alloys of Al.+5%Ti+3%Mg (a) and Al+3%Mg (b) at the temperature of 1100°C during one hour, keeping the same parameters of melting, nitriding and casting cooling as those presented above. It has been observed that under these conditions the reaction was of a strongly exothermic character with very distinct effect of magnesium evaporation and formation of Mg_3N_2 nitride of a typical yellowish colour. The outcome of the reaction was quite clear when the retort was opened, viz. magnesium nitride was present there as well as the products of reaction deposited on the surface of alundum crucible (Fig.3).

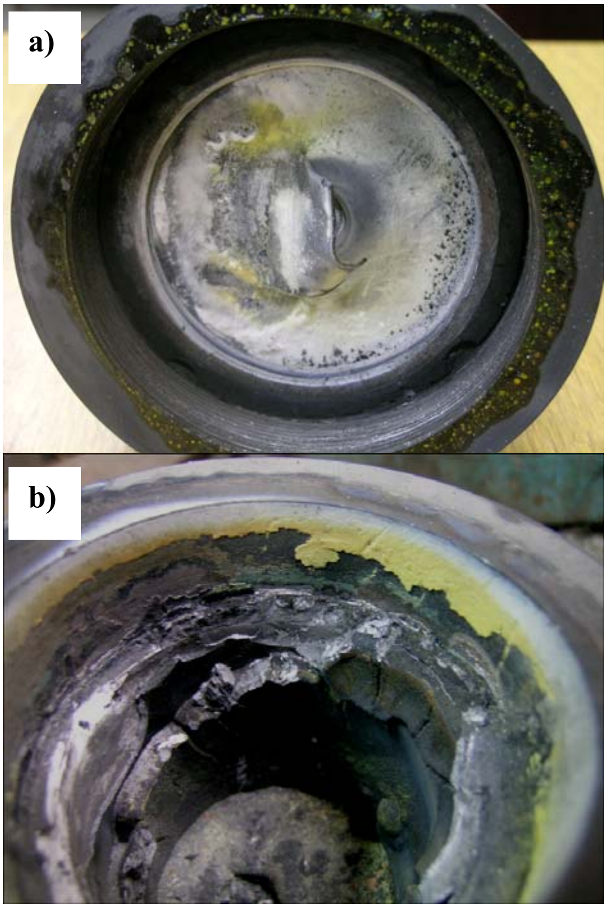

Fig. 3. The interior of reaction chamber after nitriding process carried out at the temperature of 1100°C during 1 hour on alloys of: a) Al.+5%Ti+3%Mg , b) Al+3%Mg

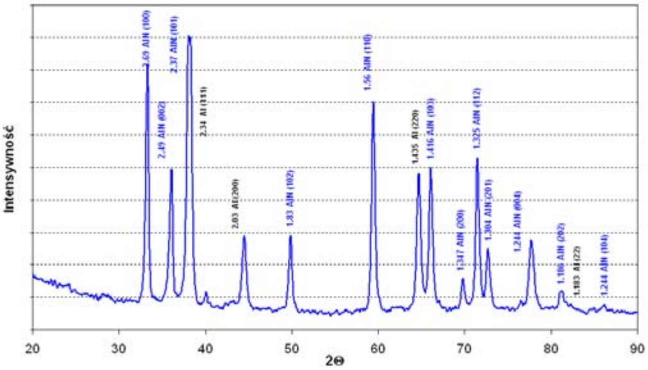

Fig. 4. X-ray analysis of the Al+3% Mg alloy after reaction with N_2 (the temperature of 1100°C, 1 hour, gas pressure of 300 kPa)

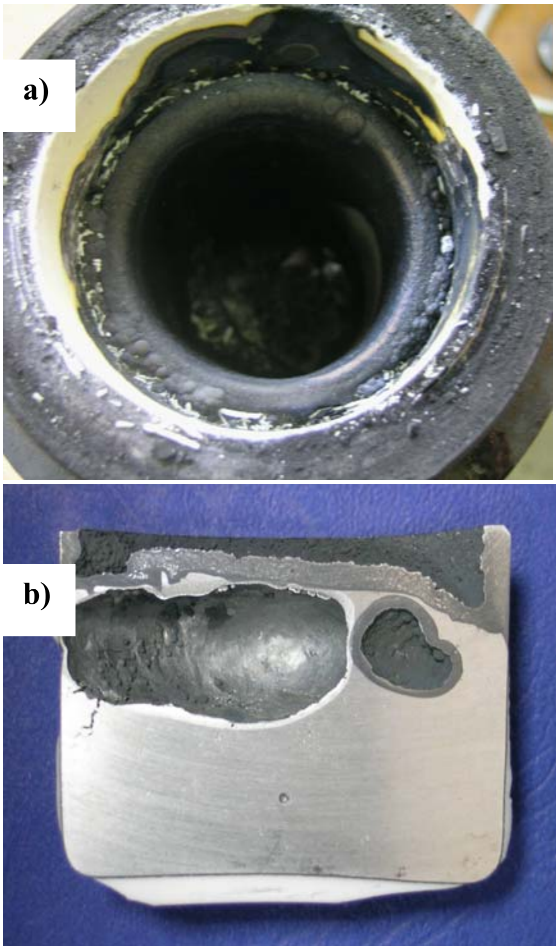

Fig. 5. a) The interior of reaction chamber after the nitriding process of Al.+3%Mg alloy at the temperature of 1000°C during the time of 1 hour, b) cross-section of test billet

At the temperature of 1100°C and the 300 kPa nitrogen pressure acting on the surface of the liquid Al+3% Mg alloy, the conditions of the reaction have proved to be sufficient for sintering and the formation of AlN phases within the entire volume of the test billet

(Fig.3b). The phase constitution of thus fabricated composite examined by X-ray radiography is shown in Figure 4. The material is mainly composed of AlN and aluminium. The presence of magnesium or magnesium nitride has not been detected in the examined specimen.

Under the same conditions, the reaction between Al+5%Ti+3%Mg alloy with nitrogen was proceeding on the surface without any strong exothermic effect and sintering of the reaction products. The AlN phases were formed in porous regions of an upper part of the test billet (Fig.3a). Probably a fraction of the reaction energy was used for the formation of intermetallic phases of Al_3Ti [9], which must have reduced the effectiveness of the direct reaction between aluminium and nitrogen.

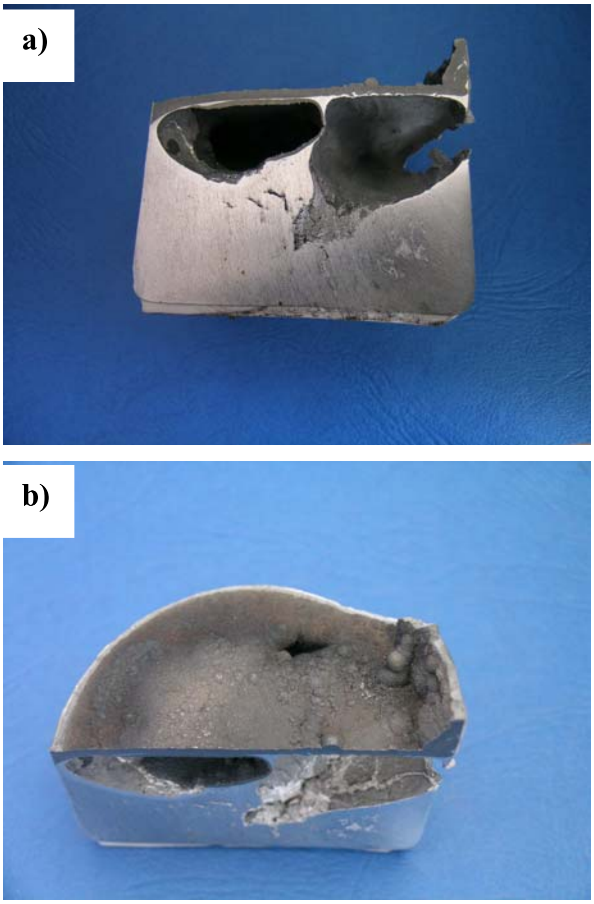

Fig. 6. Cross-section of an Al+3% Mg specimen after nitriding with nitrogen 7.0, b) products of reaction on the specimen surface

The reaction was proceeding on the surface also during nitriding of Al+3%Mg alloy, but this time at the temperature of 1000°C and the nitrogen pressure of 300 kPa (Fig.5). This proves how important is the role of temperature in the formation of nitride phases. Similar effects were obtained during nitriding of Al.+3%Mg alloy at the pressure of 1000hPa and the temperature of 1000^{o}C.

Figure 5a shows the interior of the reaction chamber after the nitriding process. During the process going on for 1 hour, in the upper part of the test billet, a distinctly visible layer of reaction products of a thickness up to about 4 mm has been formed. The matrix also shows the presence of a gas void (Fig.5b) caused by the gas bubbles occluded by the products of reaction at the solidifying metal matrix/reaction products layer interface. The exothermic nature of the reaction is proved by the presence of products which have been deposited on the internal walls of the retort and on the entire internal surface of a corundum crucible. Similar effects were observed in the case of reaction in which high-purity nitrogen was used (nitrogen 7.0 of 99,99999) (Fig.6).

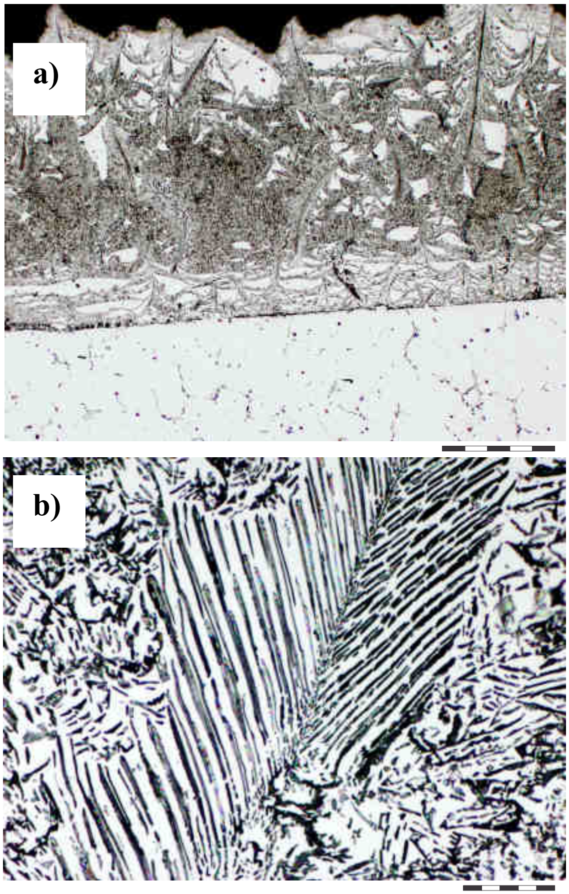

Fig. 7. Structure of an upper part of the Al+3%Mg test billet after nitriding at 1000^{o}C for 1 hour: a) surface layer, b) microstructure in reacted zone

Structure of the top layer obtained in Al+3%Mg alloy was shown in Figure 7, and the results of analysis of the phase constitution in Figure 8.

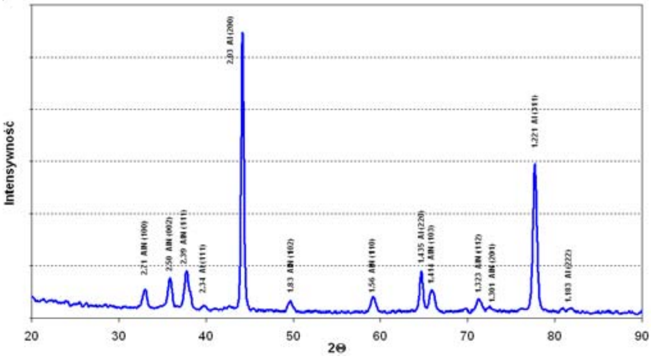

Fig. 8. X-ray analysis of Al+3% Mg alloy after reaction with N_2 (7.0) (the temperature of 1000°C, 1 hour, gas pressure of 300 kPa)

XRD and EDS analyses have confirmed the presence of nitride phases in the surface layer formed in the region of gas/liquid metal interface. It has been observed that the nitride phases are formed in the areas containing magnesium [9], which proves the role played by this element in the process of indirect nitriding. Since it was not possible to determine the composition of nitrogen-containing phases by the method of EDS, these results are to be regarded as supporting data. Indirectly, the results have been verified and confirmed by XRD analysis of the phase constitution of the fabricated composites.

4. Summary

The experiments have proved that the reaction between liquid aluminium and nitrogen under the conditions of high gas pressure results in the formation of AlN phases, while magnesium presence in the matrix accelerates this reaction through indirect nitriding with participation of a metastable Mg_3N_2 phase.

Since the reaction is of an exothermic nature, it is difficult to control and may even result in total overreacting of the alloy. Yet, the reaction products are not as good as expected, mainly because they are condensed only on the surface of the crucible.

Using *in situ* reaction for the formation of dispersion AlN reinforcement in the matrix of an aluminium alloy seems possible mainly through reduced process rate obtained by, e.g. modification of alloy composition, or properly adjusted temperature, gas pressure, reaction time and alloy stirring effect.

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