



# Aluminium matrix composites reinforced with AlN particles formed by in situ reaction

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## ABSTRACT

**Purpose:** Ultrafine reinforcement particles are formed as product of reaction between reactive components. Those kinds of materials have good mechanical properties (higher yield stress and creep resistance). Via in situ reaction between liquid metal and reacting substance (solid or gas) is possible to obtain aluminium matrix composites similar to SAP composites by casting methods. Presented results of researches concerning possibilities of obtaining ultrafine aluminium nitride particles via in situ reaction between aluminium alloys (with addition of Mg) and nitrogen.

**Design/methodology/approach:** The experiments were performed in a reaction chamber, heated in a sylvite furnace where the 0.3 MPa pressure of nitrogen were obtained and autoclave furnace at gas pressure of 1 MPa. Samples were heated at 1000°C and held at that temperature for 1 hour at the suitable gas pressure.

**Findings:** The research has shown, that vaporization of Mg and indirect nitridation depend on gas pressure in reaction chamber. At high pressure (1 MPa) of N<sub>2</sub> in situ reaction proceed in limited scope.

**Practical implications:** Using the in situ reaction in order to form AlN dispersion reinforcement in the aluminium alloy matrix seems possible but the control of the reaction is difficult.

**Originality/value:** During the liquid-phase process, the following factors determine the possibility of controlling the process of the dispersion reinforcement phases' formation: the matrix alloy composition, the temperature, the reactive gas pressure and the time of synthesis.

**Keywords:** Composites; In situ reaction; Aluminium nitride

## MATERIALS

### 1. Introduction

Composites with an aluminium alloy matrix (AlMMC) are a group of materials which due to their properties (high specific elasticity modulus, high stiffness) are more and more frequently used in modern engineering constructions. Composites reinforced with ceramic particles (Al<sub>2</sub>O<sub>3</sub>, SiC) are gradually being implemented into production in automotive, electronic or aircraft industries, first and foremost due to high resistance to friction wear. However, obtaining a material with increased mechanical properties requires an application of dispersion reinforcement which is thermodynamically stable, less susceptible to cracking and because of lack of intermediate layers, well bound to the

matrix [1]. Obtaining such type of reinforcement is possible thanks to the in situ reaction which takes place between the reacting substance and the matrix material [2-4]. A reaction in a gas-metal system offers one of possible ways to obtain dispersive phases. The composite material is formed in a process consisting of three stages: reactive gas dissociation, synthesis of reinforcing phases and kinetics of their growth [3]. Reinforcement particles – carbides or nitrides - are created as a result of a reaction of gas cavities with metal alloying additions. Non-ferrous metals (Al, Cu, Mg, Ni or Ti) are most often used as a matrix material. The dispersive reinforcement phase so created is thermodynamically stable and chemically pure. A significant advantage of this method is the possibility of applying casting techniques for forming the products.[5, 6] However, it has some constraints,

namely a small reinforcing phase fraction, which has a tendency to sedimentation. The possibility of a reinforcement phase formation is limited to systems, where carbon (a mixture of CO+CO<sub>2</sub>+CH<sub>4</sub> can be introduced as the reactive gas) or nitrogen is the reactive substance, and the reaction requires a temperature of 1200°C and is conducted in a protective atmosphere [7].

Due to its properties, such as: high strength and hardness (HV<sub>0,5</sub> 11 GPa), thermal conductivity of 80-260 Wm<sup>-1</sup> K<sup>-1</sup> and a thermal expansion coefficient of 4.5·10<sup>-6</sup> K<sup>-1</sup>, aluminium nitride (AlN) is more and more often used as a dispersive reinforcement phase in the aluminium alloy matrix [8]. An advantage of these phases is also a lack of reaction between aluminium and AlN, on the contrary to the Al-SiC system, where an Al<sub>4</sub>C<sub>3</sub> phase may be created [9]. Methods of obtaining nitric phases are based mainly on the carbothermal reaction, where Al<sub>2</sub>O<sub>3</sub> or Al(OH)<sub>3</sub> is reduced by carbon in a N<sub>2</sub> atmosphere at a temperature of 1300°C or in a reaction of aluminium powder with nitrogen or ammonia [10]. Also, other reactions are used, e.g. those during low-pressure or pressure infiltration of a liquid metal with gas, nitriding reactions with the use of plasma or by mechanical alloying (MA) methods or sintering in a nitrogen or ammonia atmosphere [11]. Nitriding reactions in those two cases can be written in the following way:



At 700°C, the process enthalpy for reaction (1) amounts to -658.99 kJ/mole, while free enthalpy amounts to -429.87 kJ/mole; for reaction (2), the enthalpy value (-549.23 kJ/mole) is higher, while free enthalpy is lower (-547.09 kJ/mole). For reaction (2), the enthalpy and free enthalpy values are similar. Ammonia is more active than nitrogen, which results from its dissociation in high temperatures [12]. Thermodynamically, aluminium nitriding is an exothermic process and is quite energetically favourable throughout a wide range of temperatures. AlN phases in an aluminium matrix may be obtained with a direct or indirect method. Direct nitriding, consisting of introducing reactive gas, e.g. nitrogen, cavities into a liquid aluminium alloy is made difficult with favourable process thermodynamics from the point of view of kinetics of the process. Aluminium is subject to covering with a compact passivation layer of nitrides and the nitriding reaction may be hindered. The indirect method requires the use of a Mg addition in the liquid metal and it consists of indirect forming of the Mg<sub>3</sub>N<sub>2</sub> nitride, followed by an exchange reaction with the formation of AlN. In this case, the kinetic conditions of indirect nitride creation and then, of the exchange reaction, are favourable. The Mg fraction in the alloy leads in the initial phase to the formation of a compact passivation layer of nitrides on the alloy's surface, which is split by the evaporating Mg and next, a volume reaction takes place, where AlN is distributed throughout the matrix, and at the third stage, a complete conversion of Al into AlN takes place [13-15].

## 2. Experimental studies

An aluminium alloy with a 3% Mg addition was used in the study. Nitrogen 5.0 of 99.999% purity and argon 5.0 of 99.999%

purity provided by Messer were used in the reaction. Samples of weight of 160 g were placed in corund crucibles.

The experiments were performed in a reaction chamber, heated in a sylvite furnace. After closing the cover, argon was forced into the chamber, thus creating overpressure of 30 kPa. Afterwards, the gas was pumped out from the chamber using a vacuum pump, thus lowering the pressure to 0.003 MPa (pressure below atmospheric). This process was repeated twice in order to create a protective atmosphere in the chamber. After the matrix had been melted, argon was pumped out at a temperature of 850°C and nitrogen was introduced into the chamber, thus obtaining a gas pressure of 0.03 MPa. The matrix alloy was heated to 1000°C and held at that temperature for 1 hour. In co-operation from Technische Universität Dresden, Institute für Leichtbau und Kunststofftechnik the same nitridation process were performed in autoclave furnace at gas pressure of 1 MPa. In both experiments the material was cooled down in the chamber in the conditions of increased gas pressure.

In case the process was carried out of the pressure 0.03 MPa, the reaction has a clearly superficial nature; in the upper part, a layer of reaction products was formed. After opening the reaction chamber, a yellowish deposit (Figs. 1, 2) was noticed on the surface of the crucibles.



Fig. 1. Reaction chamber interior after 1 hour nitriding process

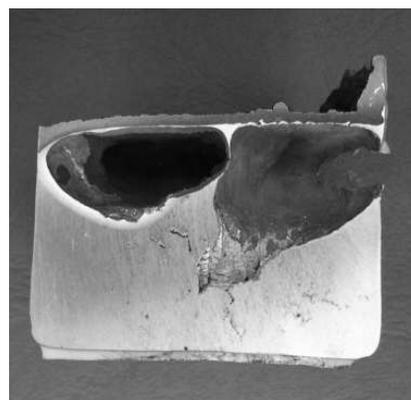


Fig. 2. Cross section of sample



Fig. 3. Ingot after 1 MPa nitriding process

The authors [15] observed a similar phenomenon and identified the product as magnesium nitride,  $Mg_3N_2$ . Presence of this phase on the sample's surface confirms the indirect course of the reaction between aluminium and nitrogen with a fraction of Mg.

In the process was carried out of the pressure 1 MPa, the magnesium not initiate reaction. Only top surface of sample reacted with gas, and thin layer of reaction products was obtained (Fig. 3). Probably high pressure of nitride made impossible to vapour Mg and indirect nitridation process was inhibited. However that phenomena need confirmation in the following experiment.

Samples of the ingot were taken for X-ray examinations Phase analysis was performed by X-ray diffraction on polycrystals by using the JDX-7S diffractometer from JEOL. The source of radiation was a lamp with a copper anode, powered by a constant voltage of 40 kV and current of 20 mA. Monochromatisation of the beam was performed on a graphite monochromator. Phasal identification was supported by PCSIWIN computer programme, based upon the JCPDS-International Centre for Diffraction Data 2000 file, whose studies confirmed the presence of AlN phases in both samples (Fig. 4).

### 3. Conclusions

The experiments made have corroborated 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 nitrogen 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 control. Using the *in situ* reaction in order to form AlN dispersion reinforcement in the aluminium 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.

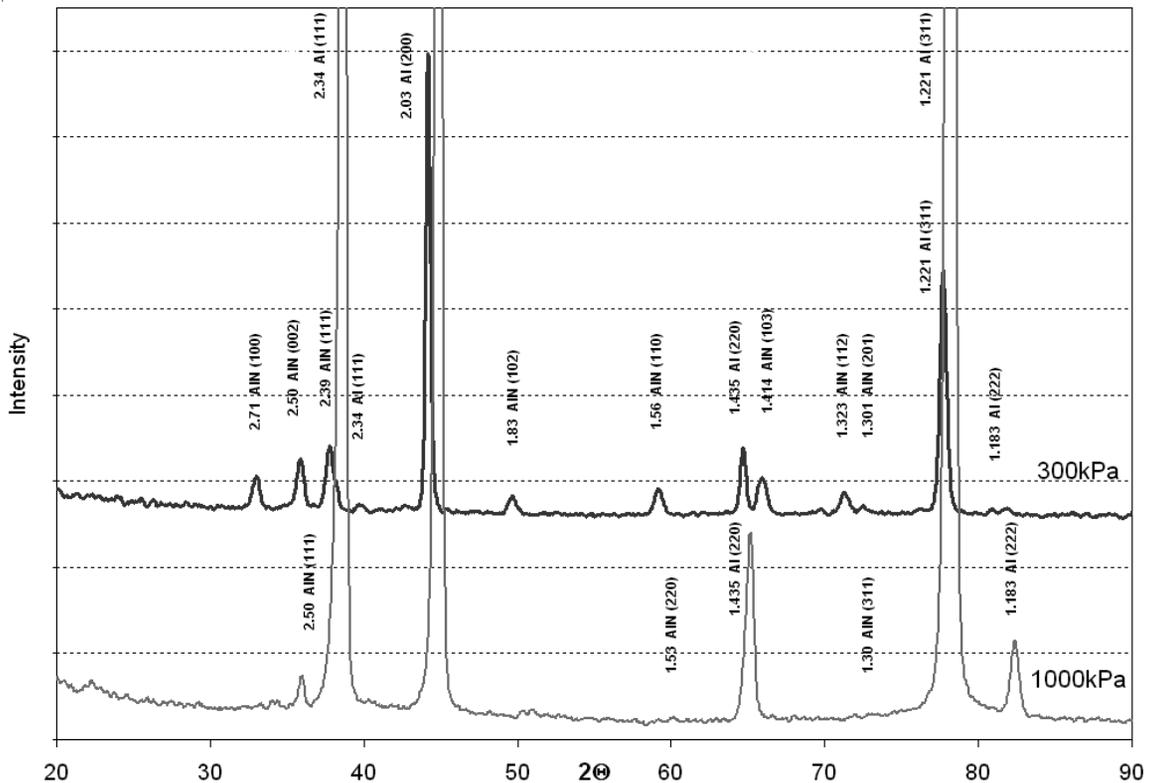


Fig. 4. XRD for Al+3%Mg alloy after reaction with  $N_2$  at 1 000°C temperature

Purity of the gas is of great importance, as well (in subsequent experiments, nitrogen 7.0 was used). In case of a typically superficial reaction, application of the mechanical stirring method should enable a uniform distribution of dispersive phases in the matrix.

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