

Understanding AlN Obtaining Through Computational Thermodynamics Combined with Experimental Investigation

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Abstract. Basic material concept, technology and some results of studies on aluminum matrix composite with dispersive aluminum nitride reinforcement was shown. Studied composites were manufactured by „in situ” technique. Aluminum nitride (AlN) has attracted large interest recently, because of its high thermal conductivity, good dielectric properties, high flexural strength, thermal expansion coefficient matches that of Si and its non-toxic nature, as a suitable material for hybrid integrated circuit substrates. AlMg alloys are the best matrix for AlN obtaining. Al_2O_3 –AlMg, AlN– Al_2O_3 , and AlN–AlMg binary diagrams were thermodynamically modelled. The obtained Gibbs free energies of components, solution parameters and stoichiometric phases were used to build a thermodynamic database of AlN– Al_2O_3 –AlMg system. Obtaining of AlN with Liquid-phase of AlMg as matrix has been studied and compared with the thermodynamic results. The secondary phase microstructure has a significant effect on the final thermal conductivity of the obtained AlN. Thermodynamic modelling of AlN– Al_2O_3 –AlMg system provided an important basis for understanding the obtaining behavior and interpreting the experimental results.

1. Introduction

There are more than 50,000 materials available to engineers for the design and manufacturing of products for various applications. These materials range from ordinary materials (e.g., copper, cast iron, brass), which have been available for several hundred years, to the more recently developed, advanced materials (e.g., composites, ceramics, and high-performance steels). Due to the wide choice of materials, today’s engineers are posed with a big challenge for the right selection of a material and the right selection of a manufacturing process for an application [1].

The development of composites is given by the possibility of taking advantage of particular properties of the constituent materials to meet specific demands. It can say that a composite is a material made with several different constituents intimately bonded. Composites definition is very large, and includes a lot of materials such as the Roman ways (constituted of different layers of stones, chalk and sand), wood, human body etc. Industries and materials scientists use a more restrictive definition: a composite material consists of elements produced via a physical combination of pre-existing ingredient materials to obtain a new material with unique properties when compared to the monolithic material properties [2]. This definition distinguishes a composite from other multiphase materials which are produced by bulk processes where one or more phases result from phase transformation (“in situ” composites).



Composite materials have been utilized to solve technological problems for a long time but only in the 1960s did these materials start capturing the attention of industries with the introduction of metallic-based composites. Since then, composite materials have become common engineering materials and are designed and manufactured for various applications including automotive components, sporting goods, aerospace parts, consumer goods, and in the marine and oil industries [3]. The growth in composite usage also came about because of increased awareness regarding product performance and increased competition in the global market for lightweight components.

Among all materials, composite materials have the potential to replace widely used steel, and many times with better performance. Replacing steel components with composite components can save 60 to 80% in component weight. Today, it appears that composites are the materials of choice for many engineering applications.

2. Materials and methods

Fabrication techniques of metal matrix composites are depending on whether they are aimed at continuously or discontinuously reinforced MMC production. According to whether they are primarily based on treating the metal matrix in a liquid or a solid form, the techniques can further be subdivided. An important influence on the type of component to be produced, on the micro-structures, on the cost and the application of the MMC is given by the production factors. Special classes that will be discussed in this paper are the “in situ” composites.

2.1 Materials Selection

The most popular matrix for the metal matrix composites (MMCs) is aluminum. The Al alloys are quite attractive due some characteristics: low density, capability to be strengthened by precipitation, good corrosion resistance, high thermal and electrical conductivity, and high damping capacity. Aluminum matrix composites (AMCs) have been widely studied since the 1920s and are now used in automotive industries, electronic packaging, armors and sporting goods. They offer a large variety of mechanical properties depending on the chemical composition of the Al-matrix. They are usually reinforced by Al_2O_3 , SiC, SiO_2 , B, BN, B_4C , AlN. The aluminum matrices are in general Al-Si, Al-Cu, Al-Mg, 2xxx or 6xxx alloys [4].

The aluminum matrix composites may offer specific advantages (and disadvantages) compared to unreinforced Al alloys, to ceramic matrix composites and to polymer matrix composites. An overview is given in table 1.

Table 1. Aluminum Matrix Composites comparison of Advantages and Disadvantages.

ADVANTAGES	DISADVANTAGES
<i>Compared to un-reinforced aluminum alloys:</i>	
- higher specific strength	- lower toughness and ductility
- higher specific stiffness	- more complicated and expensive production method
- improved high temperature creep resistance	
- improved wear resistance	
<i>Compared to ceramic matrix composites:</i>	
- higher toughness and ductility	- inferior high temperature capability
- ease of fabrication	
- lower cost	
<i>Compared to polymer matrix composites:</i>	
- higher transverse strength	- less developed technology
- higher toughness	- smaller data base of properties
- better damage tolerance	- higher cost
- improved environmental resistance	
- higher thermal and electrical conductivity	
- higher temperature capability	

This article is concerned with metal matrix composites and more specifically on the aluminum alloys matrix composites (AMCs). In AMCs one of the constituent is aluminum alloy (AlMg), which forms percolating network and is termed as matrix phase. The other constituent is embedded in this aluminum alloy matrix and serves as reinforcement, which is usually non-metallic and commonly ceramic such as AlN and Al₂O₃.

Aluminum Nitride, formula AlN, is a newer material in the technical ceramics family. While its discovery occurred over 100 years ago, it has been developed into a commercially viable product with controlled and reproducible properties within the last 20 years. Aluminum nitride has a hexagonal crystal structure and is a covalent bonded material. The use of sintering aids and hot pressing is required to produce a dense technical grade material [5]. The material is stable to very high temperatures in inert atmospheres. In air, surface oxidation begins above 700°C. A layer of aluminum oxide forms which protects the material up to 1370°C. Above this temperature bulk oxidation occurs. Aluminum nitride is stable in hydrogen and carbon dioxide atmospheres up to 980°C. The material dissolves slowly in mineral acids through grain boundary attack, and in strong alkalis through attack on the aluminum nitride grains. The material hydrolyzes slowly in water. Most current applications are in the electronics area where heat removal is important. This material is of interest as a non-toxic alternative to beryllium. Metallization methods are available to allow AlN to be used in place of alumina and BeO for many electronic applications [5]. Aluminum nitride engineering properties are given in table 2.

Table 2. AlN Engineering Properties.

<i>Properties</i>	<i>Units of Measure</i>	<i>SI/Metric</i>
<i>Mechanical</i>		
Density	gm/cc	3.26
Porosity	%	0
Elastic Modulus	GPa	330
Compressive Strength	MPa	2100
Hardness	Kg/mm ²	1100
<i>Thermal</i>		
Thermal Conductivity	W/m•°K	140–180
Coefficient of Thermal Expansion	10 ⁻⁶ /°C	4.5
Specific Heat	J/Kg•°K	740
<i>Electrical</i>		
Volume Resistivity	ohm•cm	>10 ¹⁴

Table 3. 99.5% Al₂O₃ Engineering Properties.

<i>Properties</i>	<i>Units of Measure</i>	<i>SI/Metric</i>
<i>Mechanical</i>		
Density	gm/cc	3.89
Porosity	%	0
Elastic Modulus	GPa	375
Compressive Strength	MPa	2600
Hardness	Kg/mm ²	1440
<i>Thermal</i>		
Thermal Conductivity	W/m•°K	35
Coefficient of Thermal Expansion	10 ⁻⁶ /°C	8.4
Specific Heat	J/Kg•°K	880
<i>Electrical</i>		
Volume Resistivity	ohm•cm	>10 ¹⁴

Alumina is one of the most cost effective and widely used materials in the family of engineering ceramics. The raw materials from which this high performance technical grade ceramic is made are readily available and reasonably priced, resulting in good value for the cost in fabricated alumina shapes. With an excellent combination of properties and an attractive price, it is no surprise that fine grain technical grade alumina has a very wide range of applications [6]. Aluminum oxide, commonly referred to as alumina, possesses strong ionic interatomic bonding giving rise to its desirable material characteristics. It can exist in several crystalline phases which all revert to the most stable hexagonal alpha phase at elevated temperatures. Alpha phase alumina is the strongest and stiffest of the oxide ceramics. Its high hardness, excellent dielectric properties, refractoriness and good thermal properties make it the material of choice for a wide range of applications.

Aluminum Oxide, Al₂O₃ engineering properties are given in table 3.

2.2. “In situ” processing of AlMg-AlN composites

There are several different processes that would fall under this category including liquid-gas, liquid-solid, liquid-liquid and mixed salt reactions. In these processes refractory reinforcement are created in the aluminum alloy matrix. One of the examples is directional oxidation of aluminum. In this process the alloy of Al–Mg is placed on the top of ceramic preform in a crucible. The entire assembly is heated to a suitable temperature (1000°C) in the atmosphere of free flowing nitrogen bearing gas mixture. Al–Mg alloy soon after melting infiltrates into the preform and composite is formed.

Gas–liquid reaction (eq. 1 and eq. 2) is also utilized to produce AlN reinforced aluminum matrix composites:



A major limitation of “in situ” technique is related to the thermodynamic restrictions on the composition and nature of the reinforcement phase that can form in a given system, and the kinetic restrictions on the shape, size and volume fraction of the reinforcement that can be achieved through chemical reactions under a given set of test conditions.

3. Experimental procedure

The matrix (AlMg15) was prepared from aluminum and magnesium of high purity (>99.9%) by conventional casting technique. Metals were melted in graphite crucibles at 1000°C under argon gas to reduce any contamination. The experiments were carried on in a sealed reaction chamber which was placed in a vertical electrical furnace. After closing the cover, argon was forced into the chamber. Afterwards, the gas was pumped out from the chamber using a vacuum pump, thus lowering the pressure below atmospheric. In order to create a protective atmosphere in the chamber this process was repeated twice. After the matrix had been melted, argon was pumped out at a temperature of 850°C and nitrogen was introduced into the chamber. The matrix alloy was heated at 1000°C and held for 1 hour.

The growth of AlN is predominantly based on capillary mass-transfer phenomena, which occur through a network of micro-channels developed in the empty space among the AlN (columnar crystals) as well as the hollows inside these crystals [7]. N₂ diffusion in the liquid matrix is the rate-determining steps of the process. Mg and Mg₃N₂ resulting after nitridation maintain a very low partial pressure of oxygen during the entire process and favor the AlN formation.

The shape, the orientation of AlN crystals with the liquid metallic droplets at the top of the crystals indicate that mass transfer of liquid matrix through the network of micro-channels is the key point of the entire process, as schematically depicted in figure 1.

According to figure 1, after the formation of the first AlN crystals, capillary forces govern the transfer of liquid matrix to the surface through the micro-channels. In the opposite direction, nitrogen diffuses into the liquid matrix. The Al mass transfer may also occur via surface diffusion mechanism on the AlN walls, which at the investigated temperature, may also result in a significant Al mass transfer towards the reaction front. However, the occurrence of capillary phenomena should be beyond any doubt because at the investigated temperature the viscosity of the matrix should be very low while the size of the micro-channels fits well the size of capillaries [6]. This claim is supported in conjunction with the fact of the good wetting regime observed between the molten alloy and the ceramic crystals of AlN.

AlN crystals should be precipitated immediately after the concentration of the dissolved N₂ in the AlMg matrix reaches the saturation point, since thermodynamics (at 1000°C, $\Delta G^\circ_{\text{f,AlN}} = 179,84 \text{ kJ/mol}$ [8]) and experimental results indicate high chemical affinity between Al and N and fast reaction kinetics, respectively.

The formation of AlN evidently enriches the liquid matrix in the doping metals. The experimental results showed, however, that Mg is rapidly and intensively evaporated.

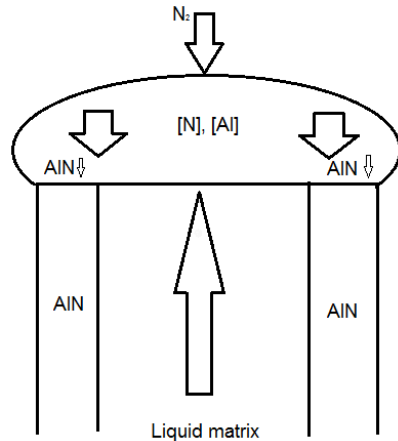


Figure 1. Schematic representation of the mechanism of the AlN crystals production and growth during “in situ” process of AlMg/AlN composite.

4. Results and discussion

4.1. Thermodynamic modeling of AlMg/AlN system

The development of thermodynamic databases presents an increasing demand. A simple model is based on speculation about ionic structure of the phases [9]. The thermodynamic data storage, retrieval and manipulation require accurate analytical representation of thermodynamic properties of solutions. Values of the standard Gibbs energies, G° , of each component are entered and stored in the solution database along with parameters which define the Gibbs energy of mixing according to Kohler/Toop polynomial model. The ternary excess Gibbs energy was calculated from a binary data interpolation. Binary terms of the polynomial expansion for G^E were entered as Redlich–Kister or Legendre polynomials due to their simplicity and the fact that their functional form is consistent with the empirical observations of solutions behavior [10].

The effect of doping elements from Al alloy matrix during its melting and nitridation was clarified through many investigations [11]. The presence of magnesium lowers the melting point of Al from 660°C to 635°C. This temperature decrease is reflected by the formation of solid solution between Mg and Al. During the melting of this material, the molten alloy was covered with an oxide film. Magnesium vaporized and its vapor caused rupture of the protecting oxide film [12]. Accordingly interruption of the oxide film would expose molten metals at the surface to N_2 atmosphere and nitridation took place successfully. Also, [13] indicated that the presence of Mg deoxidized the particles surfaces above 400°C to allow Al surfaces to react with N_2 . The presence of doping elements (Mg) enhanced the nitridation reaction of Al in the matrix alloy. Also the presence Mg can reduce the surface tension of molten aluminum on the gas-liquid surface. The enhancement depends on the formation of nonprotective catalytic nitride (Mg_3N_2) which donates its nitrogen to aluminum in molten state to form AlN. Thermodynamically, nitridation of either Al or Mg is very favorable and strongly exothermic [14]. Also, AlN has higher thermal stability than magnesium nitride over the entire temperature range and thus molten aluminum reacts with Mg_3N_2 to form the more stable phase AlN. The reaction mechanism it is described through the following reactions:



4.2. X-Ray Diffraction of AlMg-AlN composites

Samples of the ingot were taken for X-Ray examinations. Phase analysis was performed using the JDX-7S diffractometric 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 graphite monochromatic. Phase identification was supported by PCSIWIN computer program, based upon the JCPDS-International Centre for Diffraction Data 2000 file.

The X-Ray diffraction pattern (figure 2) confirmed the presence of Al- α solid solution and AlN. The formations of oxide phases were due to the reaction between the metals and residual O₂ gas present in the reaction atmosphere. However no Mg₃N₂ phase was detected in the final product.

Also the X-Ray analysis indicates that AlN forms from the very beginning of the process but the overall crystalline state of the alloy changes over increasing reaction time. In particular, the peaks of Al registered at short reaction times (1 h) were totally vanished in the prolonged experiments (10 h).

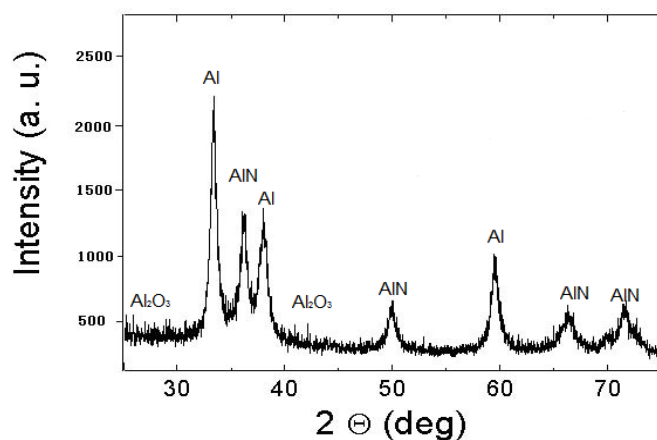


Figure 2. XRD for AlMg15/AlN after reaction with N₂ at 1000°C temperature.

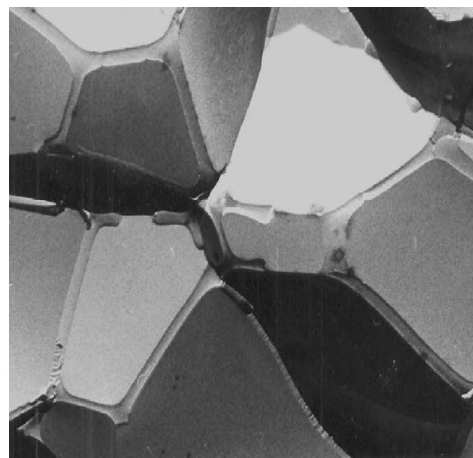


Figure 3. TEM replica of AlN reinforcing element from AlMg/AlN composite.

4.3. SEM Microstructure of AlMg15/AlN composite

The microstructure of the AlMg15/AlN composite has been investigated using a scanning electron microscope. The typical accelerating voltage used was 10–15 kV. The surface micro topography of samples was also observed by a high resolution TEM using Pt/C replicas. The replicas consisted of a thin Pt/C metal film (1–2 nm thick, consisting of 95% Pt and 5% C) and a 15–20 nm thick supporting C film. Replicas were produced from the fractured surfaces of the samples.

Nitrating for one hour at 1000°C, the ceramic reinforcing element, AlN, shows a density of 99%. A TEM micrograph of this sample is shown in Figure 3. This high density is due to the formation of an aluminum oxynitride (Al–O–N) liquid by reaction between Al₂O₃ and AlN. The addition of Mg in matrix composition promotes more extensive liquid formation due to reaction to form a quaternary liquid (Mg–Al–O–N) at lower temperature.

The SEM microstructure of a typical AlMg/AlN composite is shown in figure 4. The grain boundary distribution of the secondary phase is quite different from that of figure 3.

The secondary phase (white) shows up at the grain junctions only and not along grain edges.

The addition of Mg appears to have a further effect of changing the wetting behavior of the liquid phase with respect to the AlN grains. Indeed the dihedral angle of the secondary phase at the grain junction is high (>70°). This has a significant effect on the thermal conductivity (k). [15] suggest that thermal conductivity rises to a maximum and then decreases due to the increase in volume fraction of aluminates with further Mg addition.

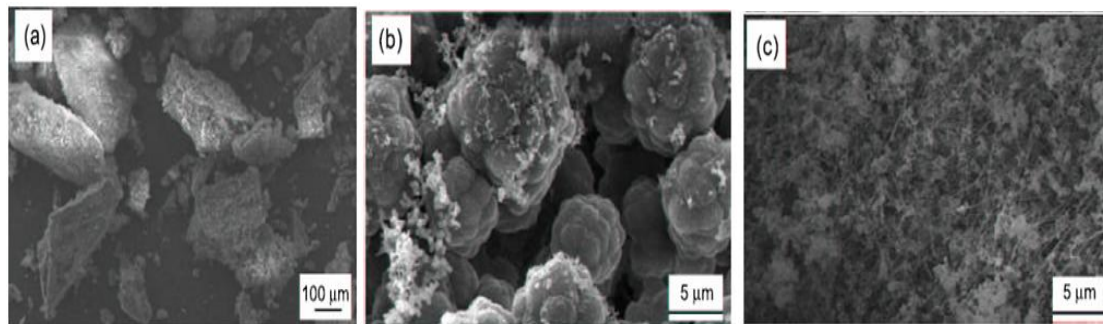


Figure 4. SEM microstructures of AlMg/AlN composite: (a) at higher magnification, 6000 X; (b) at higher magnification, 4000 X; (c) at lower magnification, 500 X.

5. Conclusions

AlN crystals were successfully grown via “in situ” process in an AlMg matrix at 1000°C. From *Thermodynamic modelling of AlMg/AlN system* discussion, it could be said that presence of doping element like Mg during the Al nitridation served as a recyclable catalytic nitrogen carrier. In other words the presence of Mg_3N_2 and/or Mg may serve as an effective nucleation site for the formation of AlN. Mg plays a key role on reducing the partial pressure of oxygen in the furnace chamber during the entire process favouring the formation of AlN and suppressing the formation of Al_2O_3 . The experiments made have corroborated that the reaction between liquid aluminum 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 inhibits 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.

References

- [1] Surappa M K 2003 *Aluminium matrix composites: Challenges and opportunities* **28** Parts 1 & 2 Sadhana Printed in India 319–334
- [2] Mazumdar S K 2002 *Composites manufacturing materials, product, and process engineering*, CRC Press LLC, ISBN 0-8493-0585-3, United States of America
- [3] Medraj M, Drew R A L, Thompson W T 2003 *Can. Metall. Q.* **42**(4) 495–506
- [4] Medraj M, Hammond R, Thompson W T, Drew R A L 2003 *J. Am. Ceram. Soc.* **86**(4) 717–726
- [5] Accuratus Corporation 35 Howard Street Phillipsburg NJ 08865, www accuratus.com
- [6] Jackson T B, Virkar A V, More K L, Dinwiddie R, Cutler B 1997 *J. Am. Ceram. Soc.* **80**(6) 1421–1435
- [7] Burton B, Chart T B, Lukas H L, Pelton A D, Seifert H S P 1995 *Calphad* **4**(19) 537–553
- [8] Chase Jr. M W, Davies C A, Downey Jr. J R, Frurip D J, McDonald R A, Syverud A N *JANAF Thermochemical Tables 3 Part I* American Chemical Society Michigan 131
- [9] Pelton A D, Bale C W, Thompson W T 2006 *F*A*C*T (Facility for the Analysis of Chemical Thermodynamics)*, McGill University/Ecole Polytechnique Montreal
- [10] Farghaly F E 2001 Ph.D. Thesis Ain-shams University Cairo Egypt
- [11] Kondoh K, Takeda Y J 1999 *Jpn Soc. Powder/Powder Metall.* **46**(8) 801
- [12] Liu J, Gao X, Chen J, Wang Q, Shen Y, Gao Q 2005 *Thermochim. Acta* 253–265
- [13] Hou Q H, Mutharasan R, Koczak M 2005 *Mater. Sci. Eng. A*, 195–121
- [14] Florea R M, Peter I, Rosso M, Mitrica M, Carcea I 2013 *JOAM* **15** (7- 8) 833 – 840
- [15] Haibo J, Chen K, Heping Z, Agathopoulos S, Fabrichnaya O, Ferreira J M F 2005 *J. Cr. Growth* **281** 639–645