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## MICROSTRUCTURE AND MICROHARDNESS OF BALL MILLED/HOT PRESSED ALUMINIUM WITH $Mg_3N_2$ ADDITION

## MIKROSTRUKTURA I MIKROTWARDÓŚĆ MIELONEGO/PRASOWANEGO NA GORĄCO ALUMINIUM Z DODATKIEM $Mg_3N_2$

The microstructure and microhardness of a ball milled and hot pressed aluminium powder with 10 vol.% of magnesium nitride ( $Mg_3N_2$ ) were investigated. It was expected that the addition of a  $Mg_3N_2$  as an nitrogen-bearing substrate would allow to obtain an in situ reaction leading to a formation of an aluminium nitride (AlN) strengthening phase. The powders were milled in a high energy planetary ball mill for up to 40 h and then compacted in vacuum at 400°C/600 MPa. The material was investigated by means of X-ray diffraction measurements (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and microhardness tests. The performed investigations showed that the composite preparation method provided a significant structure refinement of the material - the average matrix grain size of composite compact was about ~140 nm. Energy Dispersive Spectrometry (EDS) analysis of Al/ $Mg_3N_2$  compact combined with X-ray diffraction (XRD) technique indicated a presence of  $Mg_3N_2$  as well as Mg-Al-O phase, which were probably formed during hot pressing. Microhardness tests showed nearly 40% increase in the hardness of Al/ $Mg_3N_2$  composite over the non-reinforced aluminium compact.

*Keywords:* aluminium matrix composites, high energy ball milling, magnesium nitride

W niniejszej pracy przedstawiono wyniki obserwacji mikrostruktury i pomiarów mikrotwardości kompozytu o osnowie z aluminium z dodatkiem 10% objętościowych azotku magnezu wytworzonego drogą wysokoenergetycznego mielenia połączonego z prasowaniem na gorąco. Zakładano, że dodatek  $Mg_3N_2$  jako substratu azotonośnego pozwoli na uzyskanie reakcji in situ prowadzącej do wytworzenia fazy wzmacniającej w postaci azotku aluminium. Proszki poddano mieleniu w wysokoenergetycznym młynku kulowym przez okres 40. godzin, a następnie sprasowano w próżni pod ciśnieniem 600 MPa w temperaturze 400°C. Przeprowadzone obserwacje mikrostruktury materiału wykazały, że zastosowana metoda wytwarzania kompozytu pozwala na uzyskanie znacznego rozdrobnienia struktury materiału – średnia wielkość ziaren osnowy wynosiła ~140 nm. Pomiary składu chemicznego techniką EDS w połączeniu z analizą XRD wskazały na obecność zarówno azotku magnezu, jak również fazy Mg-Al-O w wyprase kompozytowej. Pomiary mikrotwardości wykazały natomiast 40%-owy wzrost twardości kompozytu Al/ $Mg_3N_2$  w porównaniu z wypraską z niezbrojonego aluminium.

### 1. Introduction

Aluminum matrix composites (AMCs) due to a light weight combined with a higher stiffness, elastic modulus and strength, as well as a better thermal stability, wear, creep and corrosion resistance compared with conventional alloys [1-9], have gained a considerable interest mainly in automotive and aerospace industry. Among these composites, most of the attention, so far, has been paid to  $Al_2O_3$  [1-3] and SiC [3-5] reinforced aluminium composites, and some of them are now well developed and have been already commercialized. However, in order to meet the increasing demands for advanced structural materials, constant efforts are being made to improve existing materials and to design new ones.

Lately, increasing attention is being paid to aluminium nitride reinforcement. The AlN, with its good physico-chemical, mechanical and thermal properties, may enhance the modulus, strength, hardness, wear resistance and high temperature performance of aluminium alloy matrix [6-9]. The aluminium

nitride stands out from commonly applied in AMCs reinforcing phases due to its good bonding to aluminium matrix, a higher wettability in aluminium, as well as a stability of aluminium/aluminium nitride interface [9-11].

The reinforcement phase, which is usually prepared separately, prior to the composite fabrication, may be introduced into the matrix via powder metallurgy [3,6-9], spray deposition, stir casting techniques [2,4,5], etc. These referred to as ex-situ techniques have one major disadvantage - weak bonding between the reinforcements and the matrix. A possible solution for this problem are in situ techniques, in which the reinforcement is produced directly in the metallic matrix e.g. by chemical reactions between elements or between elements and compounds, providing a strong reaction bonded reinforcement [10-13]. As a result, a good interface contact between matrix and the reinforcement is achieved, which is a key for the efficient load transfer from the matrix to the reinforcement.

In recent decades, mechanochemical alloying realized mainly via mechanical milling and followed by hot consol-

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idation process has emerged as a useful technique for production of a wide range of novel materials, such as amorphous alloys, nanostructured alloys, supersaturated solid solutions, intermetallic compounds, ceramic materials, as well as metal matrix composites [14-23]. As it has been suggested, it's the unique combination of a mechanical energy and the formation of fresh reactive surfaces by the shearing action of the steel balls that allows to overcome thermodynamic constraints of the reaction of the starting materials [15]. Despite the fact that, in most cases, the principles governing reactions which occur during mechanochemical alloying are only partly understood and system-specific, the formation of many compounds prepared by mechanochemical reactions, e.g., borides, nitrides, carbides and oxides has been reported [16-23].

So far, aluminium nitride reinforcing phase in metal matrix composites have been obtained in situ using mechanochemical alloying, via ball milling of elemental metal powders in nitrating atmospheres ( $N_2$ ,  $NH_3$ ) [21-23]. However, in most of these cases it was required to apply a post-reaction annealing in order to achieve a desired phase and even though the amount of the formed reinforcement was not sufficient and/or hard to control [21,22].

In this study, an attempt of in situ fabrication of an aluminium matrix composite reinforced with dispersed aluminium nitride (AlN) via high energy ball milling/hot pressing of aluminium with magnesium nitride ( $Mg_3N_2$ ) addition has been made. The  $Mg_3N_2$  has been selected as a nitrogen-bearing substrate due to two reasons – firstly, it has been reported that in situ synthesis of AlN in liquid Al is promoted by Mg addition in the Al melt and is realized through the formation of an intermediate  $Mg_3N_2$  phase [11], secondly, a reaction byproduct in the form of magnesium can be favorable, as it serves as an alloying element which markedly increases the strength of aluminum without decreasing its ductility.

## 2. EXPERIMENTAL PROCEDURE

An aluminium powder (-325 mesh, 99.5%, Alfa Aesar) was mixed with a 10 vol.% of an  $Mg_3N_2$  powder (-325 mesh, 99.6%, Alfa Aesar). Then, the powders were subjected to high energy ball milling in the planetary Fritsch mill Pulverisette 5 for up to 40 hours in tool steel containers filled with argon. The amount of 40 g of powder per container, rotational speed of 200 rpm, bearing steel balls of 10 mm diameter and ball-to-powder weight ratio of 10:1 were utilized. Subsequently, the unsieved powders were compacted in a VEB 40 hydraulic uniaxial press in a mould placed in a vacuum and heated using a high frequency generator. A pressure of 600 MPa and a temperature of 400°C were applied. The structural changes after milling/hot pressing were monitored by BRUKER D2 PHASER diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The microstructure of the hot compacted materials was characterized using an FEI Quanta 3D scanning electron microscope and a Tecnai G2 F20 (200kV) transmission electron microscope equipped with an integrated EDAX system. Thin foils for TEM investigations were prepared by dimpling with a Gatan Dimple Grinder (Model 656) and final Ar ion milling with a Leica EM RES101 system. Mi-

crohardness Vickers measurements were performed using a CSM-Instruments tester.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of the as-milled Al/ $Mg_3N_2$  composite powder and the material after hot pressing at 400°C. Magnesium nitride diffraction lines are clearly visible in both diffraction patterns, but their intensity decreases in the hot compacted sample. In the diffraction pattern of the compact, some additional diffraction peaks can be distinguished, which are an evidence of a new phase formation during hot pressing at 400°C. These diffraction peaks can be assigned to an orthorhombic  $Mg(Al_2O_4)$  spinel phase. It is believed that a precursors of this phase were formed by the reaction between  $Mg_3N_2$  and the aluminium powder oxide surface layer during mechanical alloying, and then the precursors were transformed into  $Mg(Al_2O_4)$  at 400°C. No diffraction lines coming from aluminium nitride phase were distinguished neither in the as-milled powder nor in the consolidated composite sample. It may suggest that the amount of AlN phase was not sufficient for the detection by means of XRD or the formation of metastable cubic AlN phase occurred, whose diffraction lines are overshadowed by Al diffraction peaks.

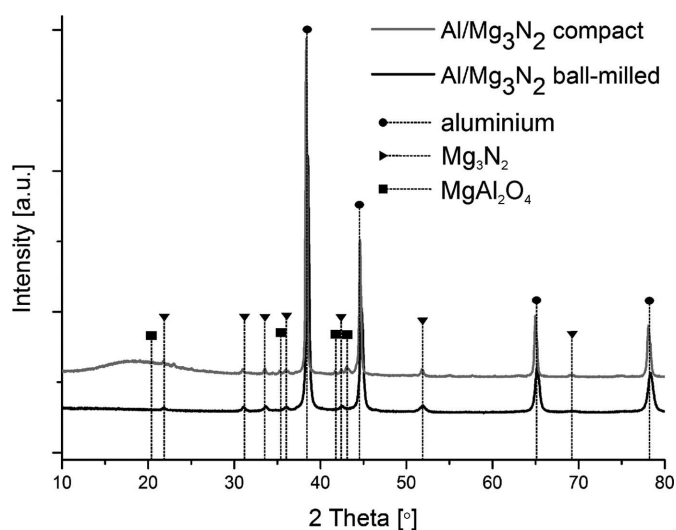


Fig. 1. X- ray diffraction patterns of Al/ $Mg_3N_2$  ball milled powder and Al/ $Mg_3N_2$  compact

The microstructure examinations of the Al/ $Mg_3N_2$  compact using scanning electron microscopy combined with EDS analysis showed that particles characterized by a slightly darker than the matrix contrast consisted of aluminium, magnesium, nitrogen and/or oxygen and were evenly distributed in the composite matrix (Fig. 2). The matrix contained a lot of fine intermetallic particles represented by a bright contrast. The above identification was also confirmed using EDS technique, which allowed recognition of Fe, Mg and Al in the intermetallic phases. The presence of iron in the sample can be explained by a wear of the steel milling tools (container and balls), which is a common problem during the milling process [9,23]. A presence of voids of a regular oval shape and size comparable to the ceramic particles is probably due

to their extraction from the aluminium matrix during sample preparation process (grinding, polishing).

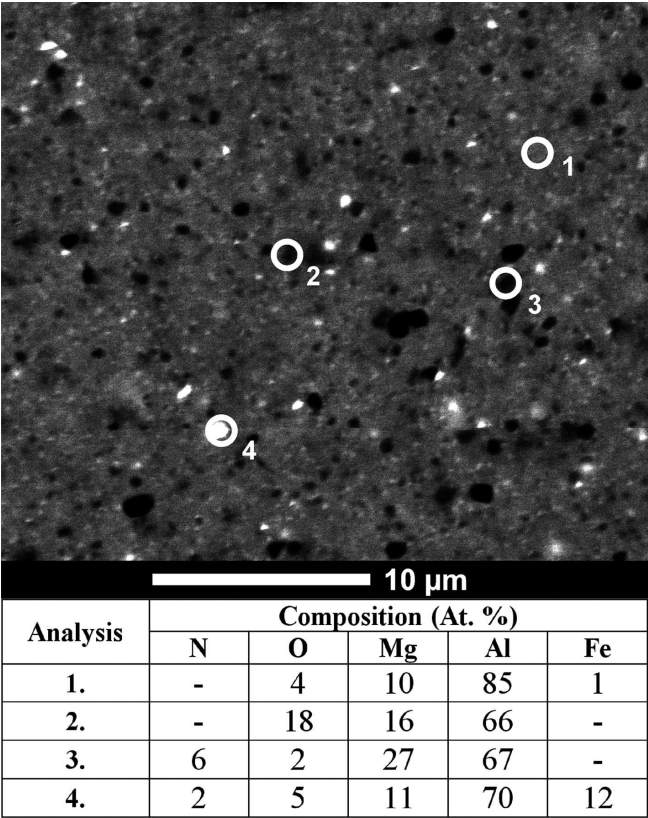


Fig. 2. SEM (BSE) image of microstructure of Al/Mg<sub>3</sub>N<sub>2</sub> compact with EDS analysis results

It is clear from the accompanying transmission electron microscopy observations (Fig. 3, Fig. 4) that the size of the Al grains significantly decreased during ball milling and remained in the submicron range even after applying a hot pressing process. The quantitative measurements performed on the series of BF TEM micrographs showed that the average Al grain size was about ~150 nm, while the present reinforcing phases were in the range of 100-300 nm and were homogeneously distributed in the aluminium matrix.

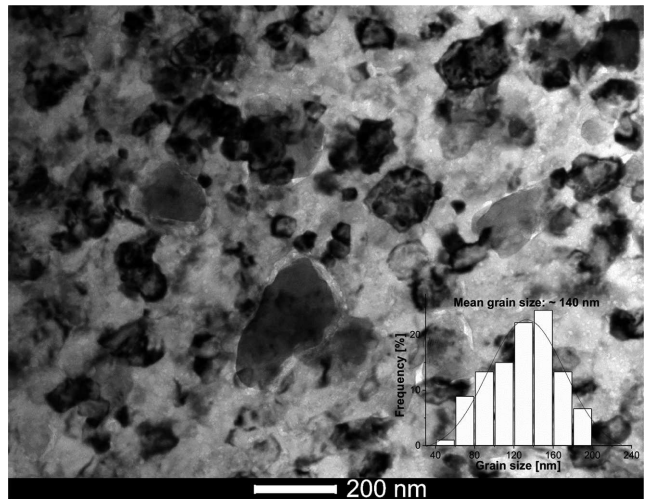


Fig. 3. Bright-field TEM micrograph of Al/Mg<sub>3</sub>N<sub>2</sub> compact with Al grain size distribution

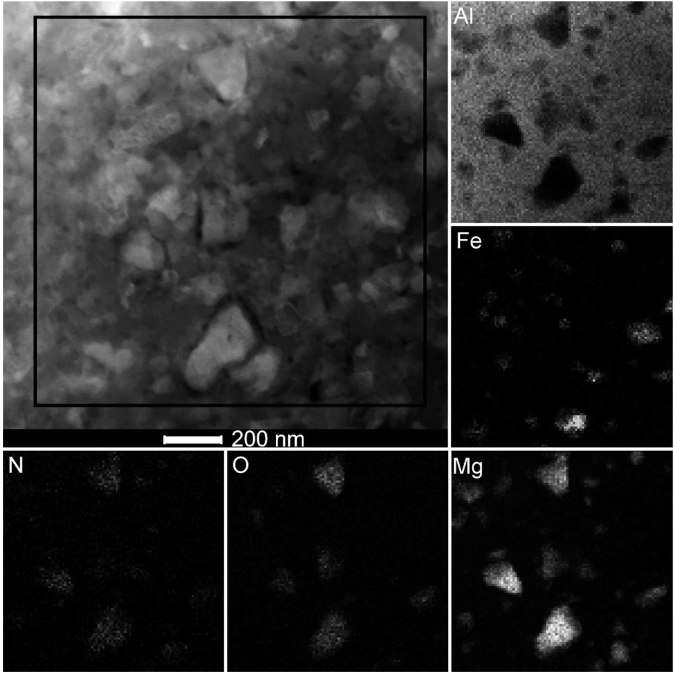


Fig. 4. HAADF STEM micrograph of Al/Mg<sub>3</sub>N<sub>2</sub> compact with EDS elemental mapping

The scanning transmission electron microscopy (STEM) observations using the High Angle Annular Dark Field (HAADF) detector supported by local chemical analysis with the EDS technique allowed the identification of magnesium nitride as well as Mg, Al, O and/or N containing phases (Fig. 4). The MgAl<sub>2</sub>O<sub>4</sub> spinel phases as well as the magnesium oxide phase are very common by-products entering AlMg alloy matrices, especially with alumina reinforcement, produced either via powder metallurgy route or by casting methods [9,11,23]. The presence of oxygen in the Al/Mg<sub>3</sub>N<sub>2</sub> is likely due to the oxygen contamination (mostly surface) of the raw powders, because the milling process was performed in Ar (5.0) atmosphere, hot pressing, on the other hand, was done in vacuum (10<sup>-2</sup> bar). Additionally, a presence of mostly very fine (<100 nm) Fe and Al or Fe, Mg and Al-rich intermetallic precipitates was confirmed by EDS elemental mapping.

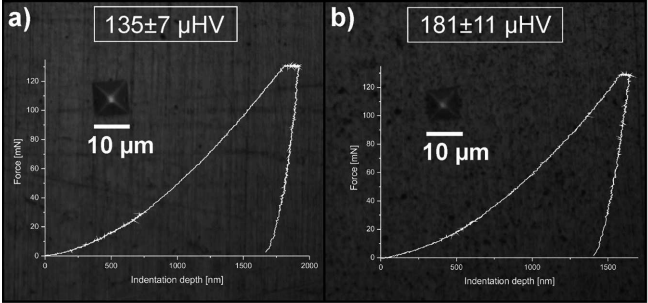


Fig. 5. Vickers microhardness measurements of a) ball milled/hot pressed aluminium b) ball milled/hot pressed Al/Mg<sub>3</sub>N<sub>2</sub>

The examples of Vickers microindentations of both ball milled/hot pressed aluminium and Al/Mg<sub>3</sub>N<sub>2</sub> compact are shown in Fig. 5. Microhardness tests revealed that the addition of 10 vol.% of Mg<sub>3</sub>N<sub>2</sub> increases the hardness from 135 HV (hot pressed ball milled aluminium without reinforcement) up to 180 HV. High hardness of non-reinforced aluminium com-



pact, as well as composite compact can be explained by the fact that not only the reinforcement addition play a role in the material strengthening but also a high structure refinement and a presence of intermetallic precipitates.

#### 4. SUMMARY

The ball milling combined with hot pressing in vacuum of aluminium with addition of  $\text{Mg}_3\text{N}_2$  provided a significant structure refinement of composite powder during milling without a substantial grain growth during hot pressing process. The EDS chemical analysis of  $\text{Al}/\text{Mg}_3\text{N}_2$  compact combined with X-ray diffraction technique indicated a presence of  $\text{Mg}_3\text{N}_2$  as well as  $\text{MgAl}_2\text{O}_4$  spinel phase, which was likely formed during hot pressing. Although the  $\text{AlN}$  phase was not directly detected in the investigated composite material, the presence of reaction products in the form of a spinel phase may suggest that some amount of nitrogen was released and most probably reacted with the aluminium matrix. Microhardness tests showed nearly 40% increase in the hardness of composite  $\text{Al}/\text{Mg}_3\text{N}_2$  sample over the non-reinforced aluminium compact.

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