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Cost-effective synthesis of $AlMgB_{14}$–$x$$TiB_2$

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Abstract

As an alternative to mechanical alloying, high temperature synthesis (HTS) of ultra-hard, super-abrasive $AlMgB_{14}$ was performed under normal pressure. The reaction mixture consisted of elemental aluminium and boron, whereas magnesium was added in the form of a Mg-precursor which liberates elemental magnesium approximately 400 °C above the melting point of magnesium, in this way reducing its evaporation during heating-up. The composition after the conversion was 95 wt.% of $AlMgB_{14}$ and 5 wt.% of $MgAl_2O_4$. The synthesized $AlMgB_{14}$ baseline powder, as well as mixtures of $AlMgB_{14}$ consisting of 30, 50 and 70 wt.% of TiB_2, were hot pressed to near theoretical density. The various samples produced were characterized for microstructure and hardness. A micro-hardness of 29.4 GPa in hot pressed $AlMgB_{14}$ and a maximum Vickers hardness of 30.2 GPa in hot pressed samples of $AlMgB_{14}$ reinforced with 70 wt.% of TiB_2 were achieved.

Keywords: Sintering; Electron microscopy; Hardness; Mechanical properties; $AlMgB_{14}$

1. Introduction

After their discovery, boron-rich compounds that consist of B_{12} icosahedra have been the subject of numerous investigations because of their interesting properties and potential technical applications in the fields of nuclear energy, aerospace and military hardware.[1] Recently, researchers at the US Department of Energy's Ames Laboratory discovered an interesting mechanical property of $AlMgB_{14}$. Its hardness, after the addition of some secondary phases, reached that of the second hardest material known, cubic BN (c-BN); namely addition of TiB_2 gives a Vickers hardness of 35–46 GPa and of Si 32–37 GPa.[2] This observation is very intriguing because $AlMgB_{14}$ is far from the conventional paradigm for ultrahard materials, lacking the usual high symmetry, small unit cell, and small bond lengths. Still another apparent departure from the previous paradigm of ultra-hard materials is the good electrical conductivity of these materials ($(1.2–7.2) \times 10^{-4}\ \Omega$ cm, depending on composition), in sharp contrast to the electrically insulating properties of other ultra-hard materials. Scientifically, it might provide a good model for investigating how hardness can be enhanced by microstructural complexity and chemical doping. It might also prove very useful because it may replace the expensive c-BN in technical applications. Much of the Ames Laboratory work performed to date has been devoted to development and optimisation of a suitable method for preparing $AlMgB_{14}$ with no other elements added ("baseline" material), as well as the baseline material combined with 5–30 mol.% additives (such as Si, TiB_2, AlN and BN). Mechanical alloying (MA) was selected as the initial route to baseline material formation because of its ability to convert the elemental constituents into a sinterable, near nano-scale powder. Although mechanical alloying resulted in a high yield of the final product, it also introduced several limitations such as a difficult and costly production scale-up, as well as significant contamination with iron.[3]

As an alternative and cost-effective processing route, high temperature synthesis from the elemental constituents was investigated by Okada et al.,[4] resulting in a product mixture of various borides ($AlMgB_{22}$, α-AlB_{12}, AlB_2, $AlMgB_{14}$). It was demonstrated that a high processing temperature (1400 °C) facilitates the formation of the B_{12} icosahedral framework, and consequently the ternary boride compound $AlMgB_{14}$. However, due to the high vapour pressure of Mg, scaling up of high temperature processing of the baseline material from the elements also poses numerous challenges. The main difficulty is in obtaining a high yield (>75 vol.%) of $AlMgB_{14}$ phase without the presence of

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other borides (such as $AlMgB_{22}$, α-AlB_{12}, AlB_2) and $MgAl_2O_4$ impurities. In order to achieve this target, it is necessary to assure a sufficient amount of highly volatile reactants (magnesium and aluminium) throughout the conversion process (typically for 5 h at 1400 °C), which is not an easy task, especially on a semi-industrial scale.

In this work high temperature synthesis from the elemental constituents (aluminium, magnesium and boron) and a novel high temperature synthesis route for the baseline material are reported. The synthesized $AlMgB_{14}$ baseline powder, as well as mixtures of $AlMgB_{14}$ consisting of 30, 50 and 70 wt.% of TiB_2, were hot pressed to near theoretical density. The various samples produced were characterized for microstructure and hardness.

2. Experimental

In the first set of experiments (route no. 1): the raw materials used were magnesium powder (Kemika, Zagreb, purity 99%), amorphous boron powder (Alfa Aesar, <5 μm) and aluminium powder (Aldrich, purity 99%). Mg and B were weighed at nominal compositions in the atomic ratios B/Mg = 0.5–10.0 and Al metal was added to each mixture at a mass ratio of 1:15. The mixture was placed in a high density alumina crucible and heated in a static argon atmosphere. The temperature of the furnace was raised to1200, 1400 and 1500 °C, kept for 2 h and then cooled to room temperature at a rate of about 50 °C/h. In the second set of experiments (route no. 2): the Mg-precursor, boron and aluminium powders were magnetically stirred with acetone for uniform mixing in a 1:1:14 molar ratio, followed by drying at 100 °C. The powders were then compacted uniaxially at 100 MPa into a porous preform and heated up as in the first set of experiments (route no. 1). In the third set of experiments (route no. 3): aluminium powder as the source of aluminium was replaced by an aluminium powder compact, whereas the Mg-precursor and boron powders were mixed in a molar ratio of 1:14. The homogenized reaction mixture of Mg-precursor and boron was then compacted to a porous preform. $AlMgB_{14}$ was fabricated by the reactive infiltration of the porous preform with molten aluminium. For infiltration, the preform sandwiched with an aluminium powder compact on the top and the bottom of the assembly was placed in an alumina crucible. The infiltration trials were performed in a static argon atmosphere, under normal pressure, at 1400 °C for 2 h. In the fourth set of experiments (route no. 4): as an alternative, the high temperature synthesis of $AlMgB_{14}$ from MgB_2 and AlB_{12} powders mixed in a molar ratio of 1:1 was also investigated. For that purpose, the AlB_{12} and MgB_2 powder mixture was pressed into a preform and heated up as in the first set of experiments (route no. 1).

Uniaxial hot pressing of dense material was performed in a vacuum hot press (Degussa, Germany) under 106 MPa pressure in an argon atmosphere for 1 h at 1400 °C.

$AlMgB_{14}$–TiB_2 powder mixtures for hot pressing were produced using commercial TiB_2 powder (Alfa-Aesar-325 mesh—99.5% purity). The baseline $AlMgB_{14}$ powder was weighed out along with the desired fraction of TiB_2 and sealed in a hardened steel vial with chrome steel milling media. The powder mixtures were then milled for an additional 30 min. After that, the mixed powder was retrieved and loaded into a graphite die for hot pressing.

X-ray powder diffraction patterns were collected on a Bruker D4 diffractometer using Cu Kα radiation in the range from 10 to 60° 2θ. Phase analysis was done with the help of Crystallographica Search-Match software[5] using the PDF-2 database release 2004,[6] while quantitative phase analysis was performed using the Rietveld method, with the program Topas.[7] The structural data were obtained from the ICSD.[8] To account for the differences in the absorption coefficients of the phases present, Brindley[9,10] correction was applied. The particle diameter was set to 1 μm as determined from the SEM image of the microstructure of the material. The phase quantification was done in two steps. In the first, the mass ratio of the identified phases was determined from the Rietveld refinement of the pattern of powdered as-made material. In the second, the samples were mixed with a known amount (40.0 wt.%) of corundum with particle size of 1 μm and the data collection and refinement were repeated. Due to the presence of material not included in the Rietveld refinement model (amorphous or non-identified crystalline phases), the calculated wt.% of corundum was in all cases larger than 40.0%. Dividing the actual (40.0%) by the calculated value of the wt.% of corundum, a factor was determined which was used to multiply the relative weight fractions of the identified crystalline phases, derived in the first step, to obtain the "absolute" weight fractions. The R_{wp} factors of the refined patterns were in the range between 13 and 15%. Cross-checking with the as-made and corundum-added samples showed good agreement and we estimate that the errors in the quantitative phase analysis did not exceed 5% relative.

The density of hot pressed species was measured using the Archimedes displacement method. The microstructure of the obtained powders and hot pressed species (polished with diamond abrasives down to 1 μm) was characterized by SEM. Phase and impurity determination was largely performed by utilizing the energy dispersive spectroscopy (EDS) capabilities of the SEM. Verification of the phases present was carried out by X-ray crystallography (XRD) to confirm proper phase formation when the processing variables were changed, using a Scintag PadV X-ray diffractometer with Cu Kα radiation.

Vickers micro-hardness and Vickers hardness of hot pressed and polished (down to 1 μm) samples were measured using a Fischerscope H100C micro-hardness tester and a Wilson Tukon Vickers tester with load of 1000 g. Five measurements were made for each composition.

3. Results and discussion

3.1. The chemical formula of $AlMgB_{14}$

The crystal structure of $AlMgB_{14}$ is a body-centered orthorhombic arrangement, space group Imam, with lattice constants $a = 0.5848$ nm, $b = 1.0312$ nm, and $c = 0.8112$ nm. The unit cell contains 64 atoms and is based on four B_{12} icosahedral units centered at (0, 0, 0), (0, 0.5, 0.5), (0.5, 0, 0), and (0.5, 0.5, 0.5) within the unit cell, while the remaining eight B atoms lie out-

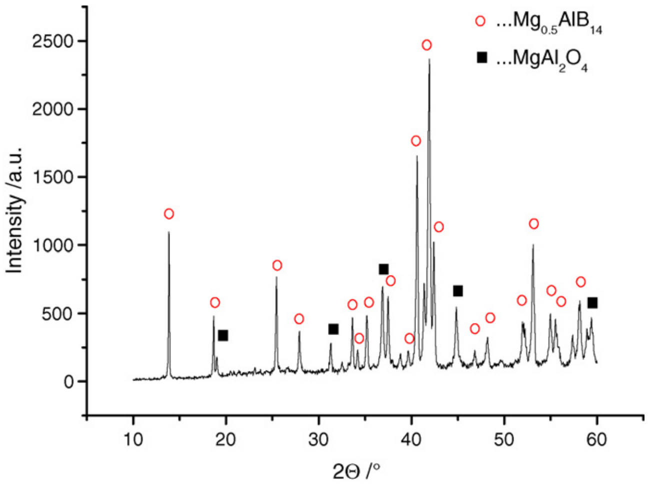

Fig. 1. X-ray diffraction patterns for the product mixture obtained in the second set of experiments (route no. 2).

side the icosahedra, bonding to the icosahedral B atoms and to the intericosahedral Al atoms occupying a four-fold position at (0.250, 0.750 and 0.250) and to the intericosahedral Mg atoms occupying a four-fold position at (0.250, 0.359, and 0).[11–13] The icosahedra are arranged in distorted, close-packed layers, with atoms between the icosahedra.[11] The unusual mechanical and electronic properties of this material are thought to result from complex interactions within each icosahedron (intrahedral bonding), combined with interactions between the icosahedra (intericosahedral bonding).

Crystallographic studies indicated that the metal sites are not fully occupied in the lattice, so that the true chemical formula of the compound obtained by mechanical alloying was proposed to be closer to $Al_{0.75}Mg_{0.78}B_{14}$, which is a necessary consequence of the electron deficiency in the valence band.[14] In addition, recent studies performed by Bedekar et al.[15] also demonstrated that the final compound synthesised by mechanical alloying is not $AlMgB_{14}$ but more probably $Al_{0.5}Mg_{0.5}B_{14}$, written as $(Al,Mg)B_{14}$ to express combination of two non-stoichiometric, metastable borides–AlB_{14} and MgB_{14}.

However, the results of an X-ray diffraction (XRD) phase analysis in the product obtained by high temperature synthesis using a starting mixture of Al, Mg and B identified both $AlMgB_{14}$ and $AlMgB_{22}$.[4] Considering the peak match observed in the present study, Fig. 1, the true formula of the material fabricated by high temperature synthesis from the elements may be closer to $AlMg_{0.5}B_{14}$. Further investigation of the true composition will be needed, because the two low-angle peaks of this phase (011 and 110), calculated from the structural model of $AlMg_{0.5}B_{14}$,[11] had significantly too low intensities in all Rietveld refinements performed. The fit improved significantly when the population of Mg on the shared Al,Mg site (Wyckoff position 4e) was allowed to refine. The final values were around 0.4 (in $AlMg_{0.5}B_{14}$[11] the value id 0.5). It has to be noted that an equally good fit could be achieved refining the population of Al on this site, or even both Al and Mg. But these results are not reliable, due to very similar scattering powers of Al and Mg. Therefore, we can only indicate that the overall population of this site is probably less a 0.75 in our samples, and be satisfied with the better Rietveld fits on applying this additional variable (which, on the other hand, had little impact on the final mass ratios), and leave the investigation of the actual variability of the population of this site for the future.

3.2. *High temperature synthesis (HTS) of $AlMgB_{14}$*

In Table 1, the concentration of $AlMgB_{14}$ and $MgAl_2O_4$ in various product mixtures produced by route no. 1 is correlated with the temperature of synthesis. As evident higher temperatures of synthesis facilitate both the formation of $AlMg_{0.5}B_{14}$ and $MgAl_2O_4$.

A further increase of $AlMgB_{14}$ content in the product mixture was achieved by replacing elemental magnesium in the reaction mixture preform with Mg-precursor (route no. 2). The role of the precursor is to liberate elemental magnesium at temperatures as much as 800 °C above the melting point of Mg, in this way preventing Mg losses caused by evaporation. After heating such a preform for 2 h at 1400 °C in a static argon atmosphere, the concentration of $AlMg_{0.5}B_{14}$ was found to be 95 wt.%. The rest was spinel (see Fig. 1).

Experiments, under the same temperature and time conditions, in which Al powder in the preform was replaced by an aluminium powder compact placed on the top and the bottom of the perform (route no. 3), resulted in an almost 50% lower concentration of $AlMg_{0.5}B_{14}$ in the product mixture. The maximum concentration of $AlMgB_{14}$ in the product mixture, obtained using an aluminium ingot as the source of aluminium, was found to be about 50 vol.%. The rate limiting step in that case is most probably infiltration of molten aluminium into the Mg- and B-containing preform, which should be completed before chemical conversion occurs. Although it is often rate limiting, the main advantage of infiltration is in its capability of producing near

Table 1
Concentration of $AlMgB_{14}$ and $MgAl_2O_4$ in product mixtures obtained by HTS (route no. 1) at different temperatures

Sample	Temperature (°C)	Time (h)	$AlMg_{0.5}B_{14}$ (wt.%)	$MgAl_2O_4$ (wt.%)	$Al_{1.67}B_{22}$ (wt.%)	NI[a] (wt.%)
1	1200	2	40	9	0	15[b]
2	1400	2	88	6	0	6
3	1500	2	27	9	48	16

Al:Mg:B molar ratio in the reaction mixtures was 1:1:14.

[a] Not included in the model (amorphous and all non-identified crystalline phases).

[b] The missing 36 wt.% belongs to $Al_{0.5}Mg_{0.5}B_2$ (27 wt.%) and possibly B_2O (9 wt.%). The latter has only one strong characteristic peak and its presence is less certain.

Table 2
Percentage of phases detected in the product mix obtained from a MgB_2 and AlB_{12} reaction mixture (route no. 4)

Run no.	MgB_2:AlB_{12} (molar ratio)	Temperature (°C)	Time (h)	Phases present
1	1:1	1400	2	$AlMg_{0.5}B_{14}$ (20 wt.%); $MgAl_2O_4$ (6 wt.%); $Al_{1.67}B_{22}$ (63 wt.%); NI[a] (11 wt.%)
2	1:1	1500	2	$AlMg_{0.5}B_{14}$ (3 wt.%); $MgAl_2O_4$ (9 wt.%); $Al_{1.67}B_{22}$ (66 wt.%); NI[a] (22 wt.%)[b]

[a] Not included in the model (amorphous and all non-identified crystalline phases).

[b] Sample 2 most probably contained the b form of AlB_{12} (PDF***), but a structural model for this phase is not available in the ICSD,[9] so that its amount (estimated to about 10 wt.%) contributes to the "NI" phases.

net shape bodies. This is particularly important in the case of super-hard materials such as $AlMgB_{14}$, for which machining to close tolerances is almost impossible.

In order to investigate an alternative route of synthesis of $AlMgB_{14}$, trials were made in which we attempted to synthesize $AlMgB_{14}$ from a 1:1 molar ratio mixture of AlB_{12} and MgB_2 (route no. 4). However, only 15–25% conversion of reactants to $AlMgB_{14}$ was achieved. The results of these experiments are presented in Table 2. The main product was spinel. Indirectly, this finding confirms that the initial step in formation of $AlMgB_{14}$ is arrangement of boron atoms into a slightly distorted B_{12} icosahedron. For this reason, the presence of elemental boron is necessary in the reaction mixture.

3.3. Reaction mechanism of HTS and the role of the Mg-precursor

The high temperature synthesis of orthorhombic $AlMgB_{14}$ is initiated by the formation of α-rhomohedral boron consisting of nearly regular B_{12} icoshaedra in an approximate cubic close packed arrangement, with bonds between adjacent icosahedra.

In addition, it seems that the presence of elemental boron at the reaction front is a prerequisite for successful formation of orthorhombic $AlMgB_{14}$. Trials with AlB_{12} and MgB_2 as reactants were unsuccessful, resulting in a maximum of 25 vol.% of $AlMgB_{14}$ in the product mix.

For achieving maximal $AlMgB_{14}$ yield during HTS, a sufficient concentration of highly volatile reactants (particularly magnesium) at the reaction front should be assured. In this respect, the Mg-precursor enables the liberation of elemental magnesium in situ, at temperatures even up to 1400 °C, depending on the over pressure in the reaction chamber.

SEM photographs of high temperature synthesized $AlMgB_{14}$ powder reveal the presence of large aggregates consisted of individual particles with an average particle size of 5–10 μm and with a narrow particle size distribution, Fig. 2.

3.4. Hardness and micro-hardness of hot pressed specimens

As shown in Fig. 3, the microstructure of hot pressed samples is not uniform. In the near theoretically dense $AlMgB_{14}$ matrix, both TiB_2 reinforcing particulates and $MgAl_2O_4$ inclusions, in the form of individual grains in the size range of 1–3 μm and larger aggregates with an average grain size of about 20–30 μm, are dispersed, creating a discontinuously reinforced $AlMgB_{14}$ composite.

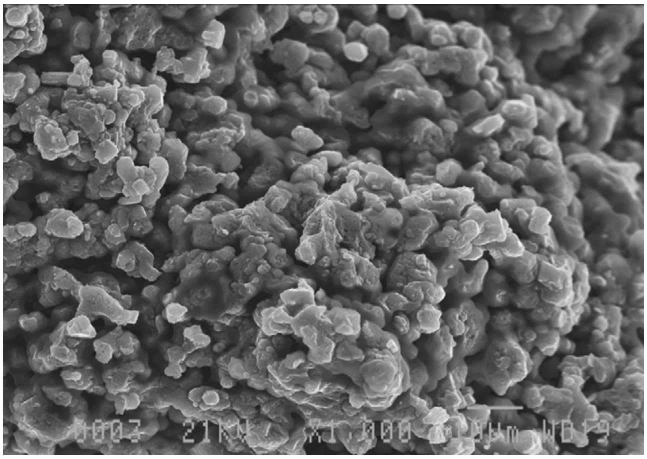

Fig. 2. SEM micrograph of high temperature synthesized $AlMgB_{14}$ powder.

The micro-hardness of the individual $AlMgB_{14}$ grains was in the range of 29–31 GPa, while the micro-hardness of the individual TiB_2 grains was about 36 GPa.

Table 3 shows the Vickers hardness of hot pressed samples as a function of the wt.% of TiB_2 reinforcement. The density of hot pressed samples was over 99% of TD.

As in the case of hot pressed samples of $AlMgB_{14}$–TiB_2 composite powders obtained by mechanical alloying,[1–3] the hardness of hot pressed samples of $AlMgB_{14}$–TiB_2 composite powders prepared by the high temperature synthesis method also exceeds the micro-hardness of the individual constituents $AlMgB_{14}$ and TiB_2, continuing to rise with increase of TiB_2 content.

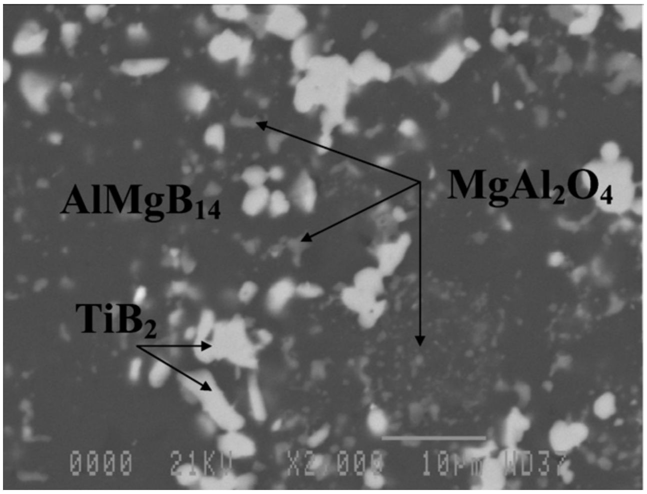

Fig. 3. SEM micrograph showing microstructure of as hot pressed $AlMgB_{14}$–30 wt.% TiB_2 sample.

Table 3
The Vicker hardness of hot pressed $AlMgB_{14}$ and $AlMgB_{14}$–$x$$TiB_2$ samples

Composition	Vickers hardness (GPa ± S.D.)
$AlMgB_{14}$	27.87 ± 0.97
$AlMgB_{14}$ + 30 wt.% TiB_2	27.67 ± 0.60
$AlMgB_{14}$ + 50 wt.% TiB_2	27.92 ± 0.82
$AlMgB_{14}$ + 70 wt.% TiB_2	30.21 ± 0.59

4. Summary

$AlMgB_{14}$ powder was successfully fabricated by high temperature synthesis under normal pressure. Aluminium and boron were added as the elements whereas magnesium was added in the form of a Mg-precursor. The role of the precursor is that, under normal pressure, it liberates elemental magnesium at a temperature above the melting point of magnesium, in this way reducing its evaporation during heating-up. In this regard, under normal pressure, 95 wt.% conversion to $AlMgB_{14}$ and 5 wt.% to $MgAl_2O_4$ was routinely achieved. However, an additional yield increase is planned to be achieved by applying overpressure in the reaction chamber, which will increase the Mg-precursor decomposition temperature to 1400 °C. The presence of elemental boron at the reaction front is necessary for the formation of $AlMgB_{14}$.

The as fabricated $AlMgB_{14}$ powder, prepared by high temperature synthesis, was routinely hot pressed to 99% of TD without sintering additives or further powder processing. A similar density was achieved in $AlMgB_{14}$–TiB_2 composites with 30, 50 and 70 wt.% of TiB_2.

Although the average particle size of $AlMgB_{14}$ powders fabricated by the high temperature synthesis method is in the range of 5–10 μm, which is at least one order of magnitude higher in comparison with powders obtained by mechanical alloying, a micro-hardness of 29.4 GPa in hot pressed $AlMgB_{14}$, as well as a maximum hardness of 30.2 GPa in hot pressed samples of $AlMgB_{14}$ reinforced with 70 wt.% of TiB_2, were achieved.

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