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SYNTHESIS AND CHARACTERISATION OF ULTRA-HARD AND LIGHTWEIGHT ALMGB$_{14}$–XTIB$_2$ COMPOSITES FOR WEAR-RESISTANCE AND BALLISTIC PROTECTION

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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 Al and B, whereas Mg was added in the form of a Mg-precursor which liberates elemental magnesium approximately 400 ºC above the melting point of Mg, in this way reducing its evaporation during heating-up. 95 wt % conversion to $AlMgB_{14}$ and 5 wt % to $MgAl_2O_4$ was achieved. 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 microhardness of 29.4GPa 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 particles (d_{50}=4,1μm) was achieved.

Future project milestones necessary for achieving a higher $AlMgB_{14}$ reaction yield, reducing the $MgAl_2O_4$ content and producing sinter-active $AlMgB_{14}$ powder, as well as hot pressed composites processing improvement for gaining maximum hardness are also presented.

Introduction

After their discovery [1], boron-rich compounds that consist of B_{12} icosahedra have been the subject of numerous investigations because of their novel scientific properties and potential technical applications in the fields of nuclear energy, aerospace and military hardware [2]. Recently, researchers at the US Department of Energy's Ames Laboratory discovered an interesting mechanical property of $AlMgB_{14}$. Its hardness reached that of the second hardest material known, cubic BN (c-BN), after small chemical additions; namely addition of TiB_2 gives a GPa hardness of 35-46 and of Si 32-37 GPa [3]. This observation is very intriguing because $AlMgB_{14}$ is far from the

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conventional paradigm for ultra-hard 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 to 7.2 x 10^{-4} Ohm-cm, depending on composition) of these materials, 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 to 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. The stoichiometric amount of boron, in the form of millimetre –sized pieces, was milled for 15 minutes in a vibratory mill. Millimetre-sized pieces of Mg were then added to the vial along with 325 mesh Al powder and the milling was continued for a total of 12 hours in a purified helium atmosphere. As reported [4], at the end of the milling period, the product was a black powder consisting of up to 95 vol. % of $AlMgB_{14}$. Samples with the addition of either elemental silicon or TiB_2, AlN or BN were prepared in the same manner as the stoichiometric "baseline" material, except that silicon was added to the initial powder charge. 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.

As an alternative and cost effective processing route, high temperature synthesis from the elemental constituents was investigated by Okada and co-workers [5], 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 (1673K) 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 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 hours at 1673 K), which is not an easy task, especially on a semi-industrial scale.

In this paper (i) high temperature synthesis from the elemental constituents (aluminium, magnesium and boron), and (ii) 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 as received TiB_2 powder, were hot pressed to near theoretical density. The various samples produced were characterized for microstructure and hardness.

Experimental

In the first set of experiments, the raw materials used were magnesium powder (purity 99%), amorphous boron powder (purity 99.9%) and aluminium powder (purity

99.9%). 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 to 1400 ºC, kept for 2 h and then cooled to room temperature at a rate of about 50 ºC/h.

In the second set of experiments, 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 ºC. The powders were then compacted uniaxially at 100 MPa into a porous preform and heated up as in the first set of experiments.

In the third set of experiments, aluminium powder as the source of aluminium was replaced by an aluminium 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 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 ºC for 2 hours.

In the fourth set of experiments, 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.

All product mixtures fabricated in this study were analysed in the same way, by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). X-ray powder diffraction patterns were collected on a Bruker D4 diffractometer using CuKα radiation in the range from 10 to 60 $^{o}2\theta$. Phase analysis was done with the help of Crystallographica Search-Match software [6] using the PDF-2 database release 2004 [7], while quantitative phase analysis was performed using the Rietveld method, with the program Topas [8]. The structural data were obtained from the ICSD [9]. To account for the differences in the absorption coefficients of the phases present, Brindley [10, 11] 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 1μm 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 estimated that the errors in the quantitative phase analysis did not exceed 5 % relative.

Uniaxial hot pressing was performed in a Degussa vacuum hot press under 106 MPa pressure in an argon atmosphere for 1h at 1400 ºC.

$AlMgB_{14}$-TiB_2 powder mixtures for hot pressing were produced using commercial TiB_2 powder (Alfa-Aesar-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 minutes. After that, the mixed powder was retrieved and loaded into a graphite die for hot-pressing.

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 CuK_α radiation.

Vickers microhardness and Vickers hardness of hot pressed and polished (down to 1 μm) samples were measured using a Fischerscope H100C microhardness tester and a Vickers tester with load of 1000 g.

Results and discussion

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 outside 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) [12-14]. The icosahedra are arranged in distorted, close-packed layers, with atoms between the icosahedra [12]. 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 [15]. In addition, recent studies performed by Bedekar et al. [16] 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 $AlMgB_{22}$ [5]. 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 $AlMg_{0.5}B_{14}$ [12], 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 $AlMg_{0.5}B_{14}$ [12] 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.

High temperature synthesis (HTS) of $AlMgB_{14}$. In Table 1, the concentration of $AlMgB_{14}$ and $MgAl_2O_4$ in various product mixtures obtained by HTS is correlated with the temperature of synthesis. As evident and also reported in the literature [17], 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. The role of the precursor is to liberate elemental magnesium at temperatures as high as 800 ºC above the melting point of Mg, in this way preventing Mg losses caused by evaporation. After heating such a preform for 2h 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.

Table 1. Concentration of $AlMgB_{14}$ and $MgAl_2O_4$ in product mixtures obtained by HTS at different temperatures. Al:Mg:B molar ratio in the reaction mixtures was 1:1:14

Sample	Temperature (ºC)	Time (h)	$AlMg_{0.5}B_{14}$ (wt %)	$MgAl_2O_4$ (wt %)	$Al_{1.67}B_{22}$ (wt %)	N.I.* (wt %)
1	1200	2	40	9	0	15**
2	1400	2	88	6	0	6
3	1500	2	27	9	48	16

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

the top and the bottom of the preform, 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 Al ingot as the source of Al, was found to be about 50 vol %. The rate limiting step in that case is most probably infiltration of molten Al 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 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.

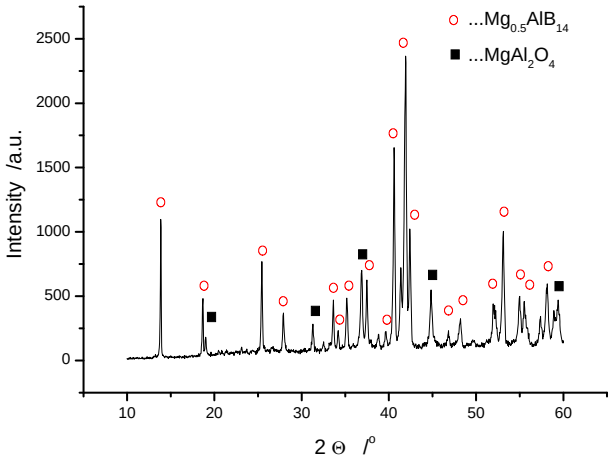

Fig.1. X-ray diffraction patterns for the product mixture obtained in the second set of experiments

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. However, only 15-25% conversion of reactants to $AlMgB_{14}$ was achieved (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.

Experiments, under the same temperature and time conditions, in which Al powder in the preform was replaced by an Al compact placed on

Table 2. Percentage of phases detected in the product mix obtained from a MgB_2 and AlB_{12} reaction mixture

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 %) N.I.* (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 %) N.I.* (22 wt %)**

* Not included in the model (amorphous and all non-identified crystalline phases).
** 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 "N.I." phases.

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 ºC, depending on the over pressure in the reaction chamber.

SEM micrographs 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.

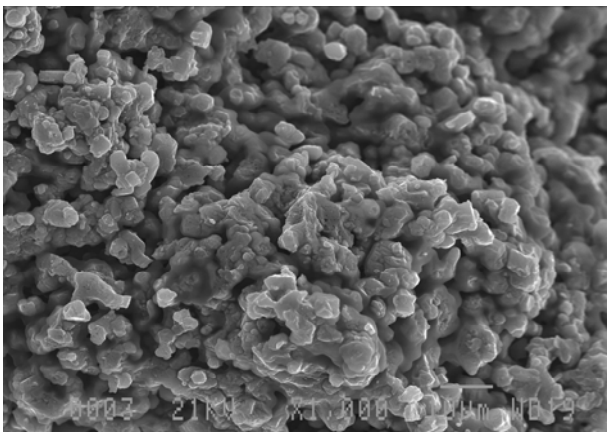

Fig.2. SEM micrograph of high temperature synthesized $AlMgB_{14}$ powder.

Microhardness and Vickers 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 particles in the size range of 1-3 μm and larger aggregates with an average particle size of about 20-30 μm, are dispersed, creating a discontinuously reinforced $AlMgB_{14}$ composite.

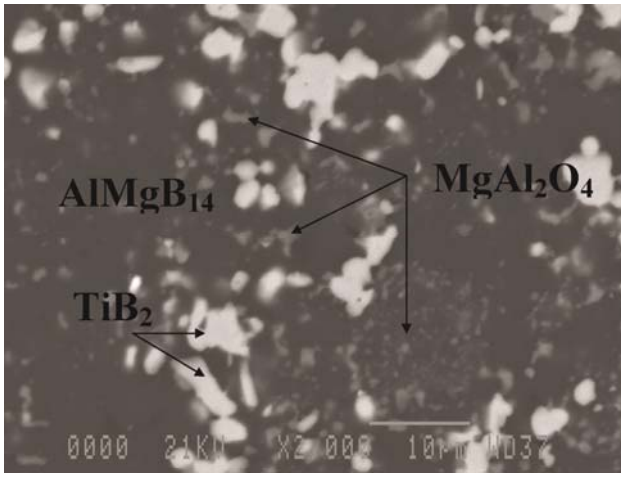

Fig. 3. SEM micrograph showing microstructure of as hot-pressed $AlMgB_{14}$-30 wt% TiB_2 sample.

The microhardness of the individual $AlMgB_{14}$ grains was 29GPa, while the microhardness of the individual TiB_2 grains was 31.5 GPa.

Hardness of $AlMgB_{14}$-TiB_2 composites can be predicted by a simple rule of mixture taking into consideration the volume portion of the main constituents: $AlMgB_{14}$, TiB_2, $AlMgB_{14}$-TiB_2 interface, $MgAl_2O_4$ and porosity.

The typical Vickers hardness of these constituents is listed in Table 3.

Table 3. The Vickers hardness of various constituents of $AlMgB_{14}$-TiB_2 composites

Constituent	**Vickers micro-hardness (GPa)**	**Estimated volume portion in the composite (vol. %)**
$AlMgB_{14}$	29	60-20
TiB_2	31,5	30-70
$AlMgB_{14}$-TiB_2 interface layer	46	3
$MgAl_2O_4$	16,1	5
Porosity	0	2

Based on an average volume portion of these phases found in the hot pressed samples of $AlMgB_{14}$-TiB_2 composites, one can calculate the expected Vickers hardness. These data are presented in Table 4 and compared with experimentally measured values.

Table 4. The Vickers hardness of hot pressed $AlMgB_{14}$ and $AlMgB_{14}$-$xTiB_2$ samples

Composition	**Vickers hardness (GPa)**	
	Measured	Theoretically expected by a rule of mixtures
$AlMgB_{14}$	27,9	29,0
$AlMgB_{14}$ + 30 wt% TiB_2	28,4	29,0
$AlMgB_{14}$ + 50 wt% TiB_2	29,7	29,2
$AlMgB_{14}$ + 70 wt% TiB_2	30,2	30,0

As evident, the Vickers hardness of hot pressed samples of $AlMgB_{14}$ composite reinforced with 50 wt% and 70 wt% of TiB_2 (d_{50} = 4,1μm) slightly exceeds the theoretically expected value.

Planned future milestones. 1) Further improvement in the yield of $AlMgB_{14}$ by applying HTS under overpressure of an inert gas: the main goal is to optimise the liberation of elemental Mg from the Mg-precursor, so that liberation starts at 1400 ºC. 2) $AlMgB_{14}$ morphology development (particle size, agglomeration etc.): an approach for achieving fine (sinter-active) $AlMgB_{14}$ powder by optimising the reaction conditions (temperature and time), as well as the morphology of the boron particles, will be implemented during HTS. 3) Spinel content reduction: ~~in~~ applying liberation of elemental Mg from the Mg-precursor at 1400 ºC, the oxidation of volatile reactants and spinel formation will become even more critical. Hence, further attention will be paid to reducing spinel formation. Research in this area will continue with extensive testing of various Al-Ti-B precursors, the thermal decomposition of which ~~to~~ elemental Al obtained *in situ* could be adjusted to proceed at approx. 1400 ºC. The oxide content in the starting elemental powders will be also reduced. For example, the significant removal of B_2O_3 is expected to be achieved by milling the starting powders in methanol. B_2O_3 reacts with methanol to produce boron ester which volatilise during evaporation of the milling solvent under a reduced pressure.

Regarding future improvements in microstructure of hot pressed composites, particular attention will be paid in achieving more homogeneous distribution of TiB_2 reinforcement phase and in applying TiB_2 powders with an average particle size less than 1μm. The possibilities of hardness and fracture toughness increasing by other reinforcements such as TiC, Si and combination of TiB_2+WC+B will be also investigated.

Conclusions

$AlMgB_{14}$ 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 ºC. 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 was in the range of 5-10 μm and the average particle size of the applied TiB_2 reinforcement was 4,1 μm, which are at least one order of magnitude higher in comparison with powders obtained by mechanical alloying, a microhardness of 29.4GPa in hot pressed $AlMgB_{14}$, as well as a maximum Vickers hardness of 31,2 GPa in hot pressed samples of $AlMgB_{14}$ reinforced with 70 wt% of TiB_2, were achieved.

The microhardness (29,4 GPa) of hot pressed $AlMgB_{14}$ samples obtained from as received powders prepared by high temperature synthesis is near to the maximum values reported in literature (32-35 GPa) corresponds to samples with submicron-scale grain size. It seams that further particle size reduction of the synthesized $AlMgB_{14}$ powder, which could be in principle achieve by reducing boron particle size in the reactive mixture, would not increase significantly the hardness of the hot pressed composite.

An additional hardness improvement of the hot pressed composite to the range of 35-46 GPa is possible only by the appropriate $AlMgB_{14}$ matrix reinforcement, preferably by the 30-70 vol. % of nano-sized TiB_2 or other particulates.

It is also important to note that the actual decreasing of the composite hardness caused by the presence of 5 wt% of $MgAl_2O_4$ spinel phase is about 0,8 GPa (2,7%).

Hence, further R&D efforts in $AlMgB_{14}$ composites hardness improvement will be directed toward better understanding of the matrix reinforcement mechanism.

References

[1] G.S. Zidanov, N. G. Sevastyanov, Comp. Rend. Acad. Sci. USSR, **32** (1941) 432
[2] A. Russel, B. Cook, IMF Newsletter: Industrial Materials for the Future (2002) 4
[3] B. A. Cook, J. L. Harringa, T. L. Lewis, A. M. Russell, Scr. Mater. **42(6)** (2000) 597-602.
[4] B. A. Cook, J. L. Harringa, A. M. Russell, U.S. Patent 6,432,855 (2002)
[5] S. Okada, K. Kudou, T. Mori, T. Shishido, I. Higashi, N. Kamegashira, K. Nakajima, T. Lundström, Mat. Sci. Forums **449-452** (2004) 365-368.
[6] Crystallographica Search Match, Version 2,1,0,2, Oxford Cryosystems, UK, 2003.
[7] Powder Diffraction File -2, Release 2004, International Center for Diffractiona Data, Newtown, USA, 2004.
[8] TOPAS, Version 2.1, Bruker AXS, Karslruhe, Germany, 2003.
[9] Inorganic Crystal Structure Database, Release 1/2005, FIZ Karlsruhe, Germany and NIST, USA, 2005.
[10] G.. W. Brindley, Philos. Mag., 36 (1945) 347-369.
[11] J. C. Taylor and C. E. Matulis, J. Appl. Cryst., 24(1) (1991) 14-17.
[12] V. I. Matkovich, J. Economy, Acta Crystallogr. Sect B 26(5) (1970) 616-621.
[13] I. Higashi, T. Ito, J. Less Comm. Met. 92(2) (1983) 239-246.
[14] I. Higashi, K. Masayoshi, O. Shigeru, H. Kenya, L. Torsten, J. Less Comm. Met. 128 (1993) 1113-1120.
[15] R., Schmechel, H. Werheit, J. Phys.: Condens. Matter. 11(35) (1999) 6803-6814.

[16] V. Bedekar, D. G. Bhat, S. A. Batzer, L. Walker, L. F. Allard, In: Proceedings of 2003 ASME International Mechanical Engineering Congress-IMECE2003, Paper No. 42374

[17] Y. Tian, A. Constant, C. C. H. Lo, J. W. Anderegg, A. M. Russell, J. E. Snyder, J. Vac. Sci. Technol. A 21(4) (2003) 1055-1063.

[18] J.S. Peters, B. A. Cook, J. L. Harringa, A. M. Russel, paper presented at the International Conference on Powder Metallurgy and Particulate Materials (PM2TEC), Metal Powder Industries Federation, Montreal, Canada, June 2005.