

Microstructural and mechanical behavior of mechanical alloying intermetallic compounds between aluminum, magnesium and boron

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In this paper, we employ a novel method of field activated and pressure assisted synthesis to prepare ultra-hard, super-abrasives from the elemental constituents (aluminum, magnesium and boron). Under the conditions in the present work, the simultaneous synthesis and consolidation of such intermetallic compounds can be achieved at 1500 °C with a pressure of 60 MPa. The prepared compounds show a hardness of 32.5 GPa, which is consistent with the hardness of AlMgB₁₄ prepared by hot uniaxial pressing, and the average density was 2.62 g/cm³. Furthermore, it is found that such compounds are not produced from the elemental constituents in the present condition.

Key words: Hardness, Mechanical properties.

Introduction

Hardness is a function of both the strength of the interatomic bonding and of the rigidity of the lattice framework. Diamond is the hardest known bulk material, due to strong covalent sp³ bonding in a tetrahedral lattice configuration. The cF8 structure of diamond is also found in many of the other ultra-hard materials such as cubic-BN and several of the tetravalent metal carbides. The search for new hard materials for use in cutting tools, heat sinks, abrasives, and coating applications has in the past few decades focused on compounds based on the light elements B, C, and N [1, 2]. Boron-rich compounds containing B₁₂ icosahedral clusters are of great technological interest because of their high hardness. A variety of compounds have been made by doping metal/carbon species in the void space between the boron icosahedra. Among these, the AlMgB₁₄-type compounds are simple, and many experimental studies have been carried out in recent years³. The discovery by Cook et al.[4] of an exceptionally high hardness in AlMgB₁₄ has generated renewed interest in boron-rich compounds as hard materials [5, 6].

The boride AlMgB₁₄ has been prepared by several methods. Okada et al.[7] and Higashi et al.[8] prepared single crystals of AlMgB₁₄ from metal salts and characterized them. The boride has also been prepared by high-energy milling of the elements followed by hot-pressing or sintering [9]. Takeda et al.[10, 11] employed the pulsed electric current sintering method (PECS) for the preparation of AlMgB₁₄. In addition, thin films of this boride have been synthesized by pulse

laser deposition (PLD)[12] and sputter deposition [13]. Although these methods 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 impurities, complicated processing and a waste of energy resources.

In this paper we report a novel combined field activated and pressure assisted in situ synthesis (FAPAS) method, which was used for the preparing ultra-hard, super-abrasive AlMgB₁₄ from the elemental constituents (aluminum, magnesium and boron(vacuum annealed 1500 °C). The samples produced were characterized for their microstructure and hardness.

Experimental

In the first set of experiments (route no. 1): the raw materials used were magnesium powder (purity 99.99 %, 200 mesh), amorphous boron powder (1–2 μm) and aluminum powder (purity 99.99%, ≤ 5 μm). All materials were obtained from Shanghai crystal pure industrial limited company. Boron powders were annealed in a vacuum furnace for 2 h at 1500 under an ambient pressure of approximately 6.7×10^{-3} Pa to reduce the oxygen contamination¹¹. Magnesium, aluminum and boron powders were mixed in a 1 : 1 : 14 molar ratio, because oxygen contamination of the preliminary powders was the main concern in producing a single-phase product (i.e., devoid of the spinel phase MgAl₂O₄), the storing and handling of powders were done in a glove box under an argon atmosphere. The powders (total mass, 12 g) were subjected to a planetary mill ((DQM-0.4I)). The jars were Sialon-lined and the balls were zirconia. A charge ratio (ball to powder mass ratio) of 10 was used. The powders were introduced into the jars inside the glove box.

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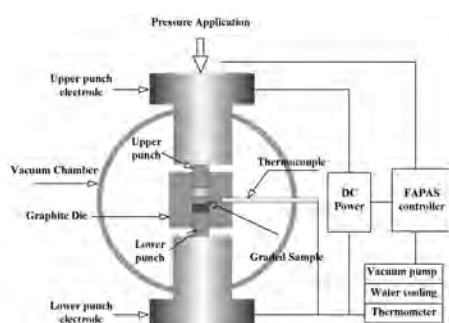


Fig. 1. Schematic diagram of the FAPAS apparatus.

The jars were then sealed with parafilm and electrical tape and placed in the planetary mill, which was then operated at a rotation speed of 250 rpm for 10 h milling time. In the second set of experiments (route no. 2): Magnesium powder as the source of magnesium was replaced by MgH_2 powder. The MgH_2 powder, aluminum powder and boron powder were mixed in a 1 : 1 : 14 molar ratio, followed as in the first set of experiments (route no. 1).

After the milling was completed, the powders were removed from the jars inside the glove box and placed in a graphite die, and then placed in a zip-sealed plastic bag. The milled powder mixtures were compacted into a porous pre-form (20 mm in diameter, 1-2 mm high, a relative density of 60 percent) in a graphite die. The simultaneous synthesis and consolidation of AlMgB_{14} from powder mixtures was performed in a FAPAS apparatus (shown in Fig. 1).

The principle of the FAPAS apparatus is to utilize the Joule heat generated in the sample by the direct current through the graphite molds and the sample blank. Rapid heating of the sample achieved combustion synthesis. It is carried out in the condition of multifields including an electric field, a mechanical field, a thermal field and a chemical field, and has become one of key technologies to prepare functional materials due to its characteristics of high temperature, fast heating-up, efficiency and energy saving [14, 15]. The current is 1600 A, temperature is up to 1500 and the ultimate vacuum is 6.67×10^{-3} Pa. The temperature is arranged in the following manner: from room temperature to 600 in 2 minutes at a pressure of 15 MPa, then from 600 to 1500 the temperature was increased at a rate of 100 K minute, the samples were then held at a higher pressure of 60 MPa for 10-15 minutes, after which the power was turned off and the samples were allowed to cool down.

The density of FAPAS specimens was measured using the Archimedes displacement method. The microstructure of the FAPAS specimens (polished with diamond abrasives down to 1 μm) was characterized by SEM. Phase and impurity determination was largely performed by utilizing the energy dispersive X-ray spectroscopy (EDS) capabilities of the SEM. X-ray powder diffraction patterns were collected using $\text{Cu K}\alpha$

radiation in the range from 10 to 70 (2θ). Phase analysis was done with the help of Crystallographica Search-Match software[16] using the PDF-2 database release 2004 [17]. The product obtained by FAPAS was examined by XRD. Vickers hardness of polished samples was measured using a HXD-1000TM tester with a load of 1000 g. Five measurements were made for each composition.

Results and Discussion

X-ray diffraction patterns

It was found that the MA/FAPAS samples had MgAl_2O_4 and Al_2O_3 XRD peaks in addition to the AlMgB_{14} peaks as seen in Fig. 2 by route no.1 synthesis. The presence of MgAl_2O_4 and Al_2O_3 forms as a result of the oxide phases present in the starting materials and the milling process. Since the XRD patterns for Al_2O_3 in the region of 53° - $56^\circ(2\theta)$ and AlMgB_{14} are nearly identical, it was difficult to distinguish the Al_2O_3 impurity phases by XRD. The presence of AlMgB_{14} can be seen as a broad peak in the region of 41.5° - $43^\circ(2\theta)$ [18]. The major crystalline phase in the sample is AlMgB_{14} , the rest major impurity phases were MgAl_2O_4 and Al_2O_3 .

A further increase of AlMgB_{14} content in the product was achieved by replacing elemental magnesium with MgH_2 (route no.2). The role of MgH_2 is to liberate elemental Mg and H_2 , in this way preventing Mg oxide, also H_2 could prevent O_2 intervention too. But H_2 could form porosity, leading to a less dense sample. In Fig.3 three strong peaks was found to be MgAl_2O_4

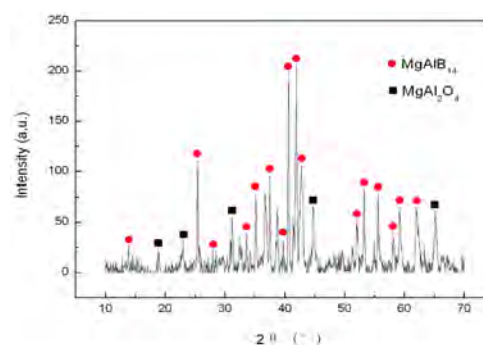


Fig. 2. X-ray diffraction patterns for the product obtained (route no.1).

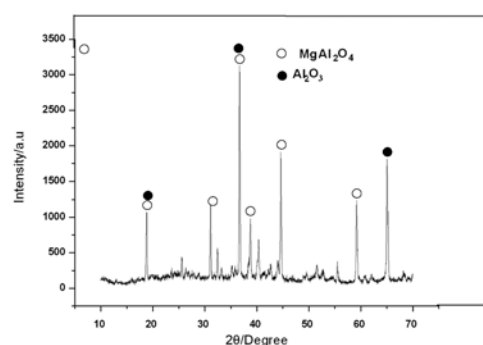


Fig. 3. X-ray diffraction patterns for the product obtained (route no.2).

and Al_2O_3 . AlMgB_{14} was not found by XRD.

Microstructure analysis

An SEM image of the sample made with annealed boron and sintered at 1500 °C under a pressure of 60 MPa is shown in Fig. 4a

Two different phases can be observed in this micrograph. The EDS spectra from two points (labeled “1” and “2”) on the micrograph are shown in Fig. 4b and c. In Fig. 4b, the darker regions contained primarily Al, Mg, and B, and thus are thought to be predominately AlMgB_{14} [19]. Although B can be detected by EDS, the X-ray emissions from light elements are strongly absorbed, and the relative intensities of the B peaks are not a reliable indication of the abundance of B [19]. EDX spectra from the grey regions (abeled “2”) on the micrograph are shown in Fig. 4c. The grey regions contained primarily Al, Mg, and O. Oxygen resulted from contamination of the preliminary powders and the milling process,

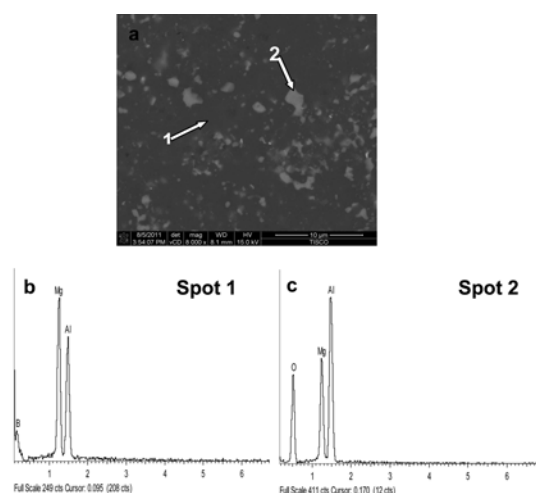


Fig. 4. SEM image of a sample and EDS spectrum (route no.1) a) Back-scattered electron SEM image of a sample containing impurities. b) EDS spectrum from the location labeled 1 on the micrograph in Fig. 4a. c) EDS spectrum from the location labeled 2 on the micrograph in Fig. 4a.

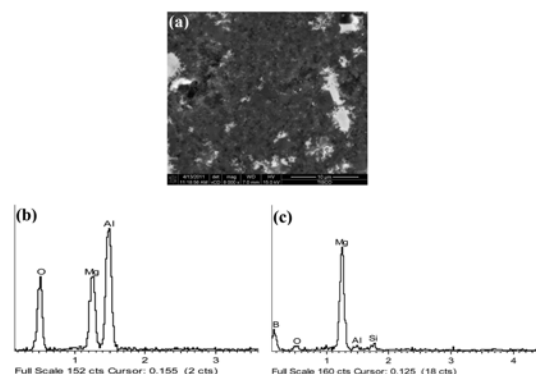


Fig. 5. SEM image of and EDS spectrum (route no.2). Back-scattered electron SEM image of a sample. (b) EDS spectrum from the brighter regions on the micrograph in Fig. 5a. (c) EDS spectrum from the grey regions on the micrograph in Fig. 5a.

indicating the existence of MgAl_2O_4 impurities. Both SEM and XRD showed that the most common impurity in these MA/FAPAS samples was MgAl_2O_4 .

Figure 5a is a SEM micrograph in backscattered electron imaging mode of a sample made by MA/ FAPAS (route no.2). Two major different phases can be observed on this micrograph. EDS spectra from the brighter regions on the micrograph are shown Fig. 5b. The brighter regions contained an enriched Al content, as well as an O content, and thus are thought to contain MgAl_2O_4 and/or Al_2O_3 . EDS spectra from the grey regions on the micrograph are shown Fig. 5c. The grey regions contained an enriched Mg content, as well as Si and O impurities. O came from contamination of the preliminary powders and the milling process. Si is introduced into the material from the milling process, and thus the sample are thought to contain MgAl_2O_4 and/or Si. Therefore, with high MgAl_2O_4 content, AlMgB_{14} are not formed in this condition, which is different from reaction of aluminum powder, magnesium powder and boron powder. In addition, it was confirmed that AlMgB_{14} was not produced under the present condition.

Mechanical properties

Polished samples (route no.1) were analyzed by Vickers microhardness testers. The microhardness was determined for constant loads. The hardness was determined using a load of 10000 g and a dwell time of 15 s. Each hardness value reported is the average of at least five measurements. The average hardness of the sample was 3527.67 HV (32.5 GPa), depending upon the amount and distribution of the Al_2MgO_4 impurity. This hardness is consistent to that of AlMgB_{14} prepared by mechanical alloying/hot uniaxial pressing (30–35 GPa). The average density of the sample was measured using the Archimedes displacement method and the result is 2.62 g/cm³ lower than the theoretical density (2.66 g/cm³).

Conclusions

(1) Ultra-hard material AlMgB_{14} metallic ceramic was successfully fabricated by the MA-FAPAS process. Under the conditions utilized in this work, the simultaneous synthesis and consolidation of AlMgB_{14} can be accomplished at 1500 with a pressure of 60 MPa.

(2) The samples had a hardness of 3527.67 HV (32.5 GPa). This value corresponds to the hardness of AlMgB_{14} prepared by mechanical alloying/hot uniaxial pressing (30 GPa). The average density of sample was 2.62 g/cm³.

(3) AlMgB_{14} was not produced from the elemental constituents (aluminum, MgH_2 and boron) by MA-FAPAS in the present condition.

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