A Synthesis and Study of AlMgB$_{14}$

Richard Bodkin

A thesis presented to the University of the Witwatersrand in
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A Synthesis and Study of AlMgB\textsubscript{14}

by

Richard Bodkin
DECLARATION

I, Richard Bodkin declare that this thesis is my own work. It is being submitted for the degree of Doctor of Philosophy at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other university.

______________

Richard Bodkin

This ________ day of _________, 2005
Abstract

This project is specifically concerned with the processing, densification and mechanical properties of hot-pressed AlMgB$_{14}$, a hard ceramic material. In order to gain a better understanding of the processing and densification of AlMgB$_{14}$, it was necessary to investigate the Al-Mg-B ternary phase diagram. The study conducted indicated that the continuous solid solution that exists at 900°C between AlB$_2$ and MgB$_2$ recedes towards MgB$_2$ as the temperature is increased from 900°C to 1400°C. The position of the boundary was quantified using X-Ray diffraction and linear regression analysis to estimate the lattice constants. The results obtained using this method were confirmed by a Rietveld method. The final quantification of the solid solution boundary was done using the Rietveld results.

From the phase diagram studies it was shown that aluminium rich compositions of the elemental powders Al, Mg and B could be used to produce AlMgB$_{14}$. Specifically, composites that had a 3 wt.% excess of aluminium were found to produce the densest samples with the lowest porosities. As stated above samples were produced by hot-pressing. Hot-pressing was done on elemental powders of aluminium, magnesium and boron, at various loads between 20 and 75 MPa, temperatures between 900 and 1900°C, soak times of 1 hour and heating rates between 10 and 100°C/min.

It was found that for elemental powders, milled in a planetary ball mill with a WC milling media, of Al, Mg and B in the mole ratio of 1:1:14 did not produce AlMgB$_{14}$ at temperatures of less than 1200°C. For compositions richer in aluminium AlMgB$_{14}$ could be produced at temperatures of 1000°C. This suggests that the presence of the aluminium liquid phase aids with mass transport and thus the formation of AlMgB$_{14}$ is facilitated. Pure AlMgB$_{14}$ was not produced by this method and the predominant impurity was MgAl$_2$O$_4$ ($\approx$ 10 wt.%).

It was found that this impurity phase is formed as a result of the oxide content in the starting elemental powders. The amount of MgAl$_2$O$_4$ can be limited by removal of the B$_2$O$_3$ from the starting powders. This is achieved by milling the starting powders in an
alcohol, specifically, methanol. $B_2O_3$ reacts with the methanol to produce boron esters which volatilise during evaporation of the milling solvent under a reduced pressure. It was also demonstrated that the milling of magnesium and aluminium in a planetary ball mill at 200-250 rpm did not further oxidise the aluminium and magnesium starting powders.

The optimum hot pressing parameters for producing dense AlMgB$_{14}$ were found to be at a temperature of 1600°C, heating rate of 100°C/min, a pushing force of 75 MPa and a soak time of 1 hour. However, samples produced from elemental powders were found to have a preferred orientation perpendicular to the hot-pressing direction. This is not uncommon for hot-pressed materials in which there exists a liquid phase. It was also found that equally dense AlMgB$_{14}$ could also be produced from micron sized pre-reacted elemental powders at the optimum hot-pressing conditions as those for the elemental powders. Pre-reacted powders were produced at 1400°C, 20 MPa, 10°C/min and 1 hour soak time. Compacts produced from the pre-reacted elemental powders were found to have no preferential alignment of homogeneous microstructure after hot-pressing at 1600°C, 75 MPa, 100°C/min. Samples prepared from the pre-reacted powders contain W$_2$B$_5$ as a secondary phase due to wear associated with WC milling media.

Pre-reacted powders were admixed separately with the compounds TiB$_2$, TiC, TiN, Si and WC. Additionally, a compact containing TiB$_2$ and WC was also produced. Because of the reaction of the carbides and nitride with boron containing compounds, additional boron was added to those composites with the added nitrides and carbides in an attempt to minimise the reaction of those nitrides and carbides with the already formed boride phases in the pre-reacted powder. All the composites produced were found to contain only closed porosity (< 3%). The hardness and fracture toughness of these composites were measured from Vickers indents made at a 10 kg loading. The addition of TiB$_2$ (29.5 GPa), TiC (32.1 GPa), TiB$_2$ + WC (29.1 GPa) and Si (31.2 GPa) to the baseline material, AlMgB$_{14}$, were found to increase the hardness of the baseline material (24 GPa). The addition of TiN did not increase the hardness of the baseline material.
WC was found to react with boron and/or boride phases to form platelet-like $W_2B_5$ grains. The formation of $W_2B_5$ was prevalent in all the compacts because of the introduction of WC from the milling media and vessel. In the composites with Ti-based additions a solid solution $(Ti,W)B_2$ formed. In composites produced with $TiB_2$ a core-rim structure was observed by SEM. Composites based on the additions of TiC and TiN or those with additional boron were found to have no core-rim structure.

Composites produced from $TiB_2 + WC +$ additional B increased the hardness of the baseline material from 24.0 GPa to 33.8 GPa and the fracture toughness from 7.7 MPa\text{$m^{\frac{1}{2}}$} to 9.8 MPa\text{$m^{\frac{1}{2}}$}. 
Dedication

It is over! Thank God, Mathias and Candice.
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FIGURE 6.3.20 G: AN SEM IMAGE FOR $\text{PR}_{3\text{CS}} + 30.0 \text{ WT.}\% \text{WC}$, HEATING RATE $100^0\text{C}/\text{MIN}$

FIGURE 6.3.20 H: AN SEM IMAGE FOR $\text{PR}_{3\text{CS}} + 30.0 \text{ WT.}\% \text{WC}$, HEATING RATE $10^0\text{C}/\text{MIN}$

FIGURE 6.3.20 I: AN SEM IMAGE FOR $\text{PR}_{3\text{CS}} + 30.0 \text{ WT.}\% \text{WC}$, HEATING RATE $100^0\text{C}/\text{MIN}$

FIGURE 6.3.20 J: AN SEM IMAGE FOR $\text{PR}_{3\text{CS}} + 30.0 \text{ WT.}\% \text{WC} + 17.7 \text{ WT.}\% \text{B}$, HEATING RATE $100^0\text{C}/\text{MIN}$

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FIGURE 6.3.21 C: AN SEM IMAGE OF $\text{PR}_{3\text{CS}} + 30 \text{ WT.}\% \text{TIB}_2 + 30 \text{ WT.}\% \text{WC}$

FIGURE 6.3.21 D: AN SEM IMAGE OF $\text{PR}_{3\text{CS}} + 30 \text{ WT.}\% \text{TIB}_2 + 30 \text{ WT.}\% \text{WC} + 14.2 \text{ WT.}\% \text{B}$

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