A Synthesis and Study of $AlMgB_{14}$

Richard Bodkin

A thesis presented to the University of the Witwatersrand in fulfilment of the requirements for the degree of Doctor of Philosophy

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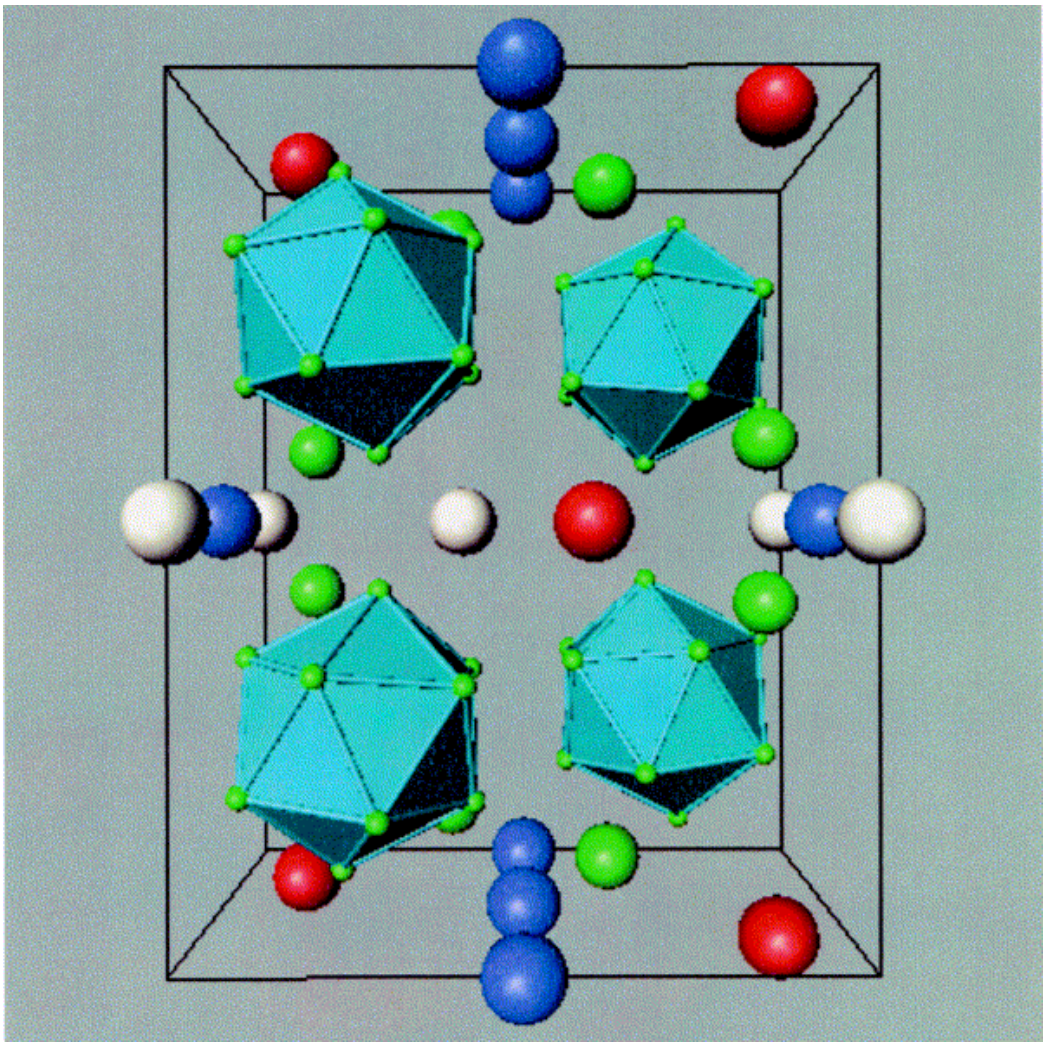

by

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 $MgAl_2O_4$ (≈ 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 $MgAl_2O_4$ can be limited by removal of the B_2O_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^oC, heating rate of 100^oC/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^oC, 20 MPa, 10^oC/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^oC, 75 MPa, 100^oC/min. Samples prepared from the pre-reacted powders contain W_2B_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 $MPam^{½}$ to 9.8 $MPam^{½}$.

Dedication

It is over! Thank God, Mathias and Candice.

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