

Chapter 1: Introduction

1.1: Background and Motivation

It has long been accepted that the hardest materials possess covalently bonded three dimensional network crystal structures of high symmetry. The rigidity of the crystal lattice and the inherent strength of the chemical bonds contribute to the hardness of the material. Both diamond and cubic boron nitride (c-BN), have cubic crystal systems and simple unit cells. Both diamond and c-BN have hardness values above 40 GPa that place them firmly in the category of ultra-hard materials.

Materials based on boron compounds have been researched for many decades. Boron displays exceptional properties with respect to the chemical bonding, crystal structure and phonon and electron conduction. As a result boron materials or borides have applications in fields as diverse as reducing agents for fine chemical syntheses, semiconductors, hard materials and abrasives.

One major interest in boride materials is fuelled by the ongoing development and understanding of technical ceramics. For a successful economic application, boride based ceramics must be produced by relatively simple methods, display high reliability, long lifetime and of course they should be available at a competitive price.

Most boron-based ceramics are not very competitive industrially. In particular, densification of the powder-derived parts is difficult. This is a consequence of the high degree of covalent bonding in boron, which results in poor diffusion mechanisms. Additionally, oxide formation by boron is highly favourable and oxide impurities on the surface and grain boundaries create undesired and unexpected microstructural effects. Furthermore, boron's high affinity for oxygen limits its application at higher temperatures and in oxidising environments.

In spite of this, the high melting points and high hardness of boride-based materials (c-BN and B₄C) have long been utilised for industrial applications¹. The hardness of

pure nanocrystalline AlMgB₁₄ has been reported to range between 32-35 GPa. Recently, studies by Cook and Russell working at the Ames Laboratories in Iowa, showed that AlMgB₁₄ could be made harder still by small additions of silicon and titanium diboride, TiB₂². When Si or TiB₂ are added to AlMgB₁₄ in amounts of 5 and 30 wt.% respectively, the hardness has been found to increase to 35-46 GPa. These new materials may be used as a wear resistant material or coatings on various substrates².

Nonetheless, there exists a lot of unanswered questions concerning the AlMgB₁₄ based materials. For example, the mechanism by which the hardness increases as a result of the addition is unknown. How does the hardness vary with respect to composition? In their publication Cook *et al.* did not specify the load at which the hardness was measured and as shall be seen in the literature review, chapter 2, the load at which hardness is measured is an important parameter to specify when reporting hardness values. Thus, it is difficult to reproduce their results without knowing the load at which their hardness was determined. Additionally no fracture toughness measurements were reported for any of the AlMgB₁₄-based materials.

The crystal structure of AlMgB₁₄ is based on B₁₂ icosahedral units bonded together with Al and Mg³. Computational results on AlMgB₁₄ suggest that the high hardness of the material is a result of the intrinsic hardness of the B₁₂ icosahedral units and is not related to the linkage of the B₁₂ icosahedra by Al and Mg⁴.

No complete phase diagram for Al-Mg-B exists⁵⁻⁶. An understanding of the Al-Mg-B ternary phase diagram would form the basis for the reproducible preparation of AlMgB₁₄.

Based on this short overview, it is clear that materials based on AlMgB₁₄ could potentially be suitable materials for wear applications. However, the existing data regarding the synthesis, composition, structure and properties of these materials does not provide a basis for the reproducible preparation of these materials. The aim of this thesis is to provide a fundamental understanding of the preparation, microstructure and properties of AlMgB₁₄ based materials.

1.2: Project Overview

This thesis deals with the synthesis and study of AlMgB₁₄ based materials. The high hardness of AlMgB₁₄ is surprising. Unexpectedly, the hardness of AlMgB₁₄ is further increased by the addition of 5 wt.% Si and 30 wt.% TiB₂, as reported by Cook *et al*². The latter addition elevates the hardness of AlMgB₁₄ into the category of ultra-hard materials. Chapter 2 deals with the literature leading up to and following on from this discovery and discusses the preparation, microstructure and properties of the AlMgB₁₄ materials. The data is contrasted against other ultra- and high-hardness materials.

Chapter 3 describes the experimental techniques and the equipment used.

The Al-Mg-B ternary phase diagram is addressed in Chapter 4 in order to establish the foundations that will ultimately lead to the optimum composition and processing conditions for the preparation of AlMgB₁₄. Due to the possibility of an Al liquid phase present during hot-pressing the Al-rich area of the phase diagram was investigated at various temperatures with respect to the composition AlMgB₁₄ in the Al-Mg-B ternary phase diagram. Furthermore, it was necessary to determine the possible secondary phases in the AlMgB₁₄ materials.

A major setback in boron-based ceramics is the positive oxidation potential of elemental boron. Most synthetic strategies employed thus far involve the meticulous preparation of the compacts in inert atmospheres. This is laborious and often difficult and expensive to implement in industry. Chapter 5 introduces a novel strategy to limit the formation of oxide phases during the synthesis of AlMgB₁₄.

The major interest in AlMgB₁₄ is due to its high hardness. Chapter 6 largely assess the role of various additives to AlMgB₁₄. Strategies developed to synthesise, densify and lower the porosity of the material are presented. The hardness and fracture toughness is measured using Vickers indents and the values obtained are rationalised with respect to the resultant microstructures. The conclusions and necessary future work are presented in chapter 7.