**A study of selected properties and applications
of AlMgB₁₄ and related composites: Ultra-hard materials**

by

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This research presents a study of the hardness, electrical, and thermal properties AlMgB₁₄ containing Al₂MgO₄ spinel. This research also investigated how much Al₂MgO₄ spinel consistently forms with AlMgB₁₄, if AlMgB₁₄ materials can be produced by hot isostatic pressing (HIP), what effects TiC and TiB₂ have on this composite material, and the importance of mechanical alloying. Included also is a study of the variation in hardness measurements and how they relate to SI units. Heretofore, all ultra-hard materials (hardness > 40 GPa) have been found to be cubic in structure, electrical insulators, and expensive; the behavior of AlMgB₁₄, which in certain specimens and compositions can have hardness values greater than 40 GPa, is therefore quite unusual since it is non-cubic, conductive, and moderate in cost. This offers an opportunity to investigate the relationship between hardness, thermal, and electrical properties from a new perspective. The main purpose of this project was to characterize the different properties of the AlMgB₁₄ materials and to demonstrate that this material can be made in bulk. The technologies used for this study include microhardness measurement techniques, scanning electron microscopy, energy dispersive spectroscopy, x-ray diffraction spectroscopy, x-ray diffraction spectroscopy at different temperatures, optical microscopy, thermomechanical analysis, differential thermal analysis, 4-point probe resistivity, density techniques, Seebeck Effect, and Hall Effect. This research may lead to use

of this material for applications where high abrasion resistance along with electrical conduction is needed. Also this research gave more information about a material that could have a great impact on industrial applications.

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CHAPTER 1: INTRODUCTION

1.1 General Background

One material that has been introduced in the last thirty years and has potential to revolutionize the abrasives industry is the ternary boride intermetallic AlMgB_{14} . AlMgB_{14} is a material that has reached ultra-hard status and may be a cost-effective abrasive material. One source estimates the raw materials cost of AlMgB_{14} to be less than \$700 per pound [Cook, et al., 2000]. Research performed prior to this study showed that AlMgB_{14} has limited reaction with iron at elevated temperatures, can attain hardness values up to 45 GPa when certain additives are added, and have some interesting electronic properties, which may even allow its use as a semiconductor. Since the AlMgB_{14} crystal structure is quite different from those of other ultra-hard materials, it may offer valuable scientific insights into the relation between crystal structure and hardness. Table 1 shows properties of various hard materials: density, hardness, bulk modulus, melting point, crystal structure and resistivity. The values shown in Table 1 come from the experimental research, "C.E.S Software Selector," "Handbook of Chemistry and Physics," "Handbook of Modern Electronics and Electrical Engineering," and Dr. Bruce Cook at Iowa State. The values in Table 1 are based on bulk material properties. Most of the other ultra-hard materials, diamond, boron carbide (B_4C), cubic boron nitride (CBN), tungsten carbide (WC), silicon carbide (SiC), and titanium carbide (TiC) all have simple, small unit cells of high symmetry, usually the same crystal structure as diamond. The TiB_2 unit cell is a slight tetragonal distortion of a cubic unit cell containing only three atoms [Cook, et al., *Scripta mater.* 42, 2000] and Si_3N_4 is amorphous. The AlMgB_{14} structure is based on four B_{12} icosahedra units positioned within an orthorhombic unit cell (space group Imam) containing 64 atoms [Collie, 1981], and this structure will be explained in more detail in a later section. Figure 1 shows a model constructed by Bruce Harmon of Iowa State of the crystal structure.

Table 1: Density, hardness, and moduli of selected materials.

Material	Density (g/cm ³)	Hardness (GPa)	Bulk Modulus (GPa)	Average Melting Temp. (°C)	Resistivity (Ohm-m)	Crystal Structure
C (diamond)	3.52	70	530-548	NA	10 ¹²	Cubic
BN (cubic)	3.48	45-50	400	2730	10 ¹¹	Cubic
AlMgB ₁₄ + TiB ₂	3.14	30-46 \$	NA	NA	10 ⁻³ \$	Orthorhombic + Tetragonal
AlMgB ₁₄ + Si	2.71	25-40 *\$	NA	NA	10 ⁻⁴ \$	Orthorhombic
B ₄ C	2.52	38-44	218-271	2450	1	Rhombohedral
AlMgB ₁₄	2.66	25-35 \$	NA	NA	10 ⁻⁵ -30 \$	Orthorhombic
AlMgB ₁₄ +TiC	3.52	25-35 \$	NA	NA	10 ⁻⁶ \$	Orthorhombic
TiB ₂	4.50	30-33	244	2899	(1-2)*10 ⁻⁷	Tetragonal
TiC	4.93	28-29	241	3140	1.05*10 ⁻⁶	Cubic
SiC	3.22	24-28	167-269	2700	(1-2)*10 ⁻⁶	Cubic
WC	15.77	23-30	421	2630	5*10 ⁻⁷	Hexagonal
Al ₂ O ₃	3.98	21-22	137-324	2050	10 ¹⁶	Hexagonal
TaC	13.9	13-24	220-231	3880	(2-3)*10 ⁻⁷	Cubic
Si ₃ N ₄	3.44	17-21	120-241	1900	10 ¹¹	Amorphous
Al ₂ MgO ₄ Spinel	3.6	15.7-17.3	201-211.5	2135	10 ¹⁰	Cubic

NA-Stands for those values not found, measured or applicable.

*-Hardness values from Ames Lab study [Byrnes and Kramer, 1994].

\$ -Measured in this research study.

All AlMgB₁₄ materials shown in this table have small amount of Al₂MgO₄ spinel.

Figure 1: Atom positions of AlMgB₁₄. Shows Al, Mg, and B atom positions. Modeled by Bruce Harmon [Cook, 2000].

1.2 AlMgB₁₄ Materials Containing Other Phases

AlMgB₁₄ is quite complex in comparison with other materials. No other material of great hardness has a unit cell of such complexity and low symmetry. Boron itself has a complex crystal structure, but it does not have the same ultra-hard characteristics. One important observation in this particular study is that magnesium aluminum oxide (Al₂MgO₄ spinel) can form along with the AlMgB₁₄ if oxygen is allowed to contact the precursor powders during processing. Thus all the material properties shown in Table 1 for AlMgB₁₄, and in this research were actually the properties of a combination of AlMgB₁₄ and intermetallic of Al₂MgO₄ spinel. The volume percent of the spinel in these specimens is on average was 20 vol% or less, and this will be described in more detail in a later section. It is not surprising that Al₂MgO₄ spinel would form. Oxygen can be introduced into the material simply by contact with the atmosphere and some O₂ impurity are present in all the B, Al, and Mg used to make the samples. Great care is required to prevent high purity Al and Mg from oxidizing, which would include having glove box systems that would contain less than 1 PPM of oxygen in the box's atmosphere. Depending to some degree on the process used, Al₂MgO₄ spinel forms readily when producing AlMgB₁₄. The enthalpy formation of AlMgB₁₄ has not been measured, but the enthalpy formation at 298K for Al₂MgO₄ spinel is – 551 kcal/mol [Stull, 1971]. In the procedures used in forming AlMgB₁₄, elemental Al, Mg, and B are heated, held under pressure at temperature for a certain time, and then cooled. When temperatures reach the melting points of Mg and Al, but below the melting point of B, the O impurity that is either dissolved in the constituents, on oxidized surfaces and present in the atmosphere react with the Al and Mg and form Al₂MgO₄ spinel. Boron, aluminum, and magnesium melt under standard conditions at 2300°C (B), 660°C (Al), and 649°C (Mg), respectively.

Figure 2 shows phase diagrams for MgO-Al₂O₃ [Shackelford, 1996] and Mg-Al [ASM, 1986]. These two phase diagrams show that under equilibrium conditions Al and Mg will form intermetallics, and if oxygen is present, an intermetallic spinel phase can form. An intermetallic compound contains a distinct formula that appears in a phase diagram as an intermediate phase that exists at a specified stoichiometry or over a range of compositions

Figure 2: Left Diagram is MgO-Al₂O₃ [Shackelford, 1996]. Right phase diagram is Al-Mg [ASM, 1986].

[Callister, 1997]. The observed properties of AlMgB_{14} containing spinel differ from those of single phase AlMgB_{14} . Measurements of single crystals of the AlMgB_{14} showed a hardness range from 2790-2890 Vickers, a density of 2.59 g/cm^3 , and a resistivity of 50 ohm-m [Werheit et al., 1993]. Werheit's measured values for single-phase, single crystal AlMgB_{14} differ from those shown in Table 1 for AlMgB_{14} containing $\sim 10\%$ Al_2MO_4 spinel. The AlMgB_{14} and spinel material displays variable hardness, ranging from 2500 to 3500 Vickers, a density of 2.66 g/cm^3 , and a maximum resistivity of 27 ohm-m . The relationship between Vickers and GPa will be explained in later sections, but 1000 Vickers equals roughly 10 GPa. A simple rule-of-mixtures (ROM) calculation for AlMgB_{14} and 10% spinel predicts a density of 2.69 g/cm^3 , which is close to the actual density observed. However, the ROM values for resistivity (55.6 ohm-m) and hardness (2700 Vickers) are not observed in the AlMgB_{14} samples containing spinel. Resistivity values were sensitive to small variations in impurity content in semiconductors, so the drop in resistivity may be a dopant effect. The variability in hardness, however, is less easily explained and may result in part from the very fine grain size of the AlMgB_{14} and spinel specimens. It seems strange that Al_2MgO_4 spinel would have this kind of effect on AlMgB_{14} , because Table 1 showed Al_2MgO_4 spinel having a hardness range from 1500-1700 vickers, a density of 3.6 g/cm^3 , and a resistivity of $10^{10} \Omega\text{-m}$. Thus, one would assume having a material combination between AlMgB_{14} and Al_2MgO_4 spinel would give low hardness values, higher densities and resistivities, which is not true for this research.

Al_2MgO_4 spinel is a close-packed oxygen sublattice that has both octahedral and tetrahedral sites filled within a FCC system [Chiang, 1997]. A single unit cell of Al_2MgO_4 spinel has eight FCC oxygen subcells in a cubic array. Al^{3+} ions form octahedral structures and fill up half of the possible octahedral sites. Mg^{2+} ions form tetrahedral structures and fill up one-eighth of the possible tetrahedral sites. A total of 56 ions are in a unit cell that has 8 Mg^{2+} , 16 Al^{3+} , and 32 O^{2-} ions. The Mg^{2+} tetrahedrons are coordinated by four O^{2-} ions and the Al^{3+} octahedrons are coordinated by six oxygens. Figure 3 shows a three-dimensional pictorial of a spinel structure and single tetrahedron and octahedron substructures. As a naturally occurring mineral, Al_2MgO_4 spinel has a highly ordered structure resulting from

Figure 3: A three-dimensional schematic of an Al_2MgO_4 spinel. Also showing atomic layers parallel to the (001) plane in the spinel [Chiang, 1997].

slow crystallization over many years. Synthetic Al_2MgO_4 spinel is disordered to some degree and the Al_2MgO_4 spinel that occurs with AlMgB_{14} is very likely to be disordered to some degree. This disorder comes from the exchange of the various cations and by the process of producing them. In these processes, the cooling is just too fast to allow enough time for the spinel to fully crystallize [Chiang, 1997].

Al_2MgO_4 spinel may play an important role in the properties of these AlMgB_{14} materials, but the size of the grains and particles clearly have a major effect. Figures 5-9 and Table 1 indicate that the AlMgB_{14} contained Al_2MgO_4 spinel. Figure 5 shows scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) scans that has only elements of Al, Mg, and O. EDS cannot pick up reliably any elements lighter than Carbon. Figure 5a shows an SEM micrograph in backscattered mode at 1000X of specimen that contained very low impurities other than the Al_2MgO_4 spinel. Picture (a.) shows a white phase dispersed through a dark phase matrix. Picture (b.) and picture (d.) shows the dark

phase having only Al, and Mg. This was assumed to be the AlMgB_{14} . Picture (c.) and picture (e.) shows the bright phase to have Al, Mg, and O. This phase was assumed to be Al_2MgO_4 spinel. The reason that the dark phase looks so “dark” is because in backscattered mode smaller atomic number compounds appear dark and larger atomic number compounds appear whiter or “lighter.” This is also true for EDS. Backscattered mode is better SEM mode then secondary electron mode because all the samples have to be polished to fine micron grades to measure the various properties. Figure 4 shows an SEM micrograph in secondary electron mode, showing little information except the surface roughness. Secondary electron mode is best for imaging surface topography. Backscattered mode is best to view compositional change between various phases as shown in Figure 5. Figure 5 also shows that the phases,

Figure 4: SEM Micrograph of polished sample AlMgB_{14} composite material in secondary electron mode. Mag. 1000X, 15 kV, and working distance of 23mm.

and particles were submicron size. Generally, the smaller the microstructures the higher the hardness of the material. X-ray diffraction was also used to analyze this material. Figure 6 shows the x-ray diffraction pattern of AlMgB_{14} , and Figure 7 shows the x-ray diffraction pattern of Al_2MgO_4 spinel phase. AlMgB_{14} has a total of 76 peaks, which are shown in Figure 6. The range of diffraction angles that give the most information of this material is from 12° to 44° . These peaks are the most intense and give the d-spacing of the first lattice planes. The lattice parameters for this orthorhombic material are $a=5.8480 \text{ \AA}$, $b=8.1120 \text{ \AA}$, and $c=10.3120 \text{ \AA}$ [International Centre For Diffraction Data, Card # 39-0459, 1997]. Table A1 in Appendix A show the d-spacing, diffraction angle using a copper x-ray tube, intensity, and the corresponding lattice plane. Previous research results from the literature are

Figure 5: SEM micrographs and Energy Dispersive Spectrums of AlMgB_{14} material from Sample 83 in Back Scattered Electron Mode. (a.)-Shows Sample 83 at 1000X. (b.)-shows the various microstructures and location of EDS scan in picture (d). (c.)-shows the various microstructures and location of EDS scan in picture (e).

presented in Chapter 4. This gives further information about this diffraction pattern and the crystal structure. Figure 7 shows the 15 peaks of Al_2MgO_4 spinel that appear within 2θ diffraction angles between of 15° and 90° for Cu target x-rays. This material is cubic with a lattice parameter of $a=8.0831 \text{ \AA}$ [International Centre For Diffraction Data, Card # 21-1152, 1997]. Table A2 in Appendix A shows the d-spacing, diffraction angle using a copper x-ray tube, intensity, and the corresponding lattice planes for this material.

Figure 6: Diffraction pattern of pure AlMgB_{14} phase without spinel peaks [International Centre For Diffraction Data, Card # 39-0459, 1997].

Figure 7: Diffraction Pattern of Al_2MgO_4 spinel phase [International Centre For Diffraction Data, Card # 21-1152, 1997].

Many of the samples used in this research and in the past have had some form of mechanical alloying in the processing used to produce AlMgB_{14} . A detailed description of mechanical alloying will be presented in Chapter 4. In most cases, iron impurities introduced into the Al-Mg-B specimen through mechanical alloying, and while these particles may help increase hardness, they also decrease the resistivity of the composite material. Figure 8 shows a SEM backscattered micrograph of AlMgB_{14} material with some Al_2MgO_4 spinel (shown by Arrow 1), a bright white phase-iron oxide (Arrow 2), and dark phase matrix- AlMgB_{14} (Arrow 3). Picture (b.) shows an area within picture (a.) at high magnification containing oxide impurities. Picture (b.) in Figure 8 shows the white phase and the location of the EDS scan. Picture (c.) shows the EDS scan and shows high intensity peaks of

Figure 8: SEM micrographs and EDS of a normal baseline AlMgB_{14} Sample 80 using intense mechanical alloying in processing in backscattered electron mode. (a.)-shows microstructures at 1000X. (b.)-shows the various microstructures at 10000X and location of EDS scan in picture (c.).

iron, with oxygen, aluminum and magnesium. All three forms of iron oxide; Iron (I) Oxide, Iron (II) Oxide, and Iron (III) Oxide, have appeared in these AlMgB_{14} composite materials, but the most common iron oxide is Iron (III) Oxide (Fe_3O_4). These forms of iron oxide were observed from x-ray diffraction. Fe_3O_4 is a cubic structure that has a density of 5.18 g/cm^3 , melting point of 1595°C [Weast, 1988], and has the same crystal structure to Al_2MgO_4 spinel.

Figure 9 shows the diffraction pattern of Fe_3O_4 and how its diffraction pattern compares to Al_2MgO_4 spinel. The top diffraction pattern is Fe_3O_4 and the bottom diffraction pattern is Al_2MgO_4 spinel. The figure shows that the peaks of Fe_3O_4 almost line up perfectly with Al_2MgO_4 spinel, but have different intensities. The Al_2MgO_4 spinel has more peaks than the iron oxide. Fe_3O_4 has a lattice parameter of $a=8.0903 \text{ \AA}$ [International Centre For Diffraction Data, Card # 26-1136, 1997], which is nearly the same lattice parameter as Al_2MgO_4 spinel. Only 9 peaks appear in the diffraction pattern of Fe_3O_4 . Table A3 in Appendix A shows the d-spacing, diffraction angle using a copper x-ray tube, intensity, and the corresponding lattice plane for this material. Since Al_2MgO_4 spinel and Fe_3O_4 diffraction patterns are quite similar it is difficult to separate them from each other unless the signal to

Figure 9: Diffraction Pattern of Al_2MgO_4 spinel and Fe_3O_4 [International Centre For Diffraction Data, Card # 21-1152, 26-1136, 1997].

noise ratio in the diffractometer is quite high. Also found with AlMgB₁₄ materials and Fe is the compound FeB. FeB x-ray diffraction information is shown in Table A5.

1.3 Purpose of Thesis

At the outset of this research project, eight tasks were identified for investigation.

1. To analyze the variation of hardness measurements.
2. To show the various characteristics of AlMgB₁₄ baseline materials.
3. To determine the effects of increasing temperature on AlMgB₁₄. Although this material has a high melting temperature, it is important to know if this material undergoes phase changes and if so, the effect of such changes on hardness at elevated temperatures.
4. To observe the electronic properties of AlMgB₁₄ materials.
5. To observe the amount of Fe₃O₄, FeB and Al₂MgO₄ spinel in various baseline samples.
6. To observe the effects on hardness, electrical properties, SEM microstructures, and thermal expansion caused by TiB₂ and TiC additives to AlMgB₁₄.
7. To determine whether Hot Isostatic Pressing (HIP) can be employed to produce AlMgB₁₄ and if so, to compare the properties of HIP'd material to the material produced by hot uniaxial pressing techniques.

CHAPTER 2: INDUSTRIAL APPLICATIONS

2.1 Possible Applications

AlMgB_{14} materials have potential applications in several industrial processes, especially in applications that deal with cutting and grinding ferrous metals. Ferrous materials are the dominant metal alloys in industry. In the U.S. alone, iron and steel production is 90 million tons, followed by aluminum and aluminum alloys at 4 million tons. AlMgB_{14} , used in sintered cermet tools (composites of hard ceramics and metal binders), may provide a low-cost alternative to cubic boron nitride cutting tools and grinding media for ferrous work pieces.

Materials that reach hardness of 35 GPa or higher are considered ultra-hard. Ultra-hard materials are needed in many different applications where they can minimize undesirable dimensional changes in machine parts by resisting wear and abrasion. They can also improve the efficiency of cutting, grinding, and polishing operations by accelerating dimensional change in the work piece while minimizing dimensional change in the cutting and grinding tools. For example, in the automobile industry, pistons and piston rings in various engines are subjected to friction forces as the pistons move in the cylinders of the engines. These friction forces can eventually cause failures. If these components were made of a material that was abrasion resistant, then both the pistons and the cylinders could run cooler and operating life would be increased, and/or the pistons and cylinders can operate at higher operating temperatures leading to higher efficiencies. Another application for an ultra-hard material is cutting silicon wafers using a diamond saw, as shown in Figure 10. Since silicon is a somewhat abrasive material, normal iron blades are ineffective in slicing silicon wafers. Diamond is the hardest material known, and it is able to cut through the silicon wafer. Silicon wafers are one of the most common materials in the microelectronics industry. The most common and conventional abrasives are SiC and Al_2O_3 , which are used in many cutting and grinding applications, while cubic boron nitride and diamond are the most commonly used superabrasives [Budinski, 1996].

In many polishing techniques, small, irregular shaped abrasive particles with sharp edges are bonded in the form of wheels, cups, disks or cones to act as grinding wheels, which

Figure 10: A diamond saw cutting a 150 mm silicon wafer.

are used for stock removal, finishing and deburring operations. Thousands of different types and sizes of grinding wheels are manufactured and used, but only a small percentage of these are manufactured from superabrasives due to their high cost. The properties important for abrasives are hardness, non-reactivity, low cost, and the ability to incrementally fracture into smaller pieces to self-sharpen during use. If AlMgB_{14} materials demonstrate characteristics that can give effective abrasive/grinding wheel performance at low cost, then AlMgB_{14} materials could have a large market impact by making superabrasive grinding wheels more affordable.

One of the most promising applications AlMgB_{14} may have is the ability to be a wear resistant coating material. Since neither diamond nor cubic boron nitride can be plasma-sprayed because both are non-equilibrium phases, it is possible that AlMgB_{14} may be the hardest material that is amenable to plasma spraying. Thermally sprayed coatings find extensive applications to reduce machinery wear and corrosion. Revisiting the automotive piston example: a worn aluminum piston could be coated by an abrasion-resistant coating by using thermal spray to return it to its original dimensions. WC-Co and $\text{Cr}_3\text{C}_2/\text{NiCr}$ based cermets are used extensively as thermal spray coatings for protection against abrasive wear environments. The single largest industry that use these kinds of coatings is the aircraft engine industry, where the turbine compressors, mid-span stiffeners and other components are coated to reduce wear and increase component life. Recent developments in the use of

thermal spray coatings for wear resistance include coatings on Al-alloy cylinders for internal combustion engines [Byrnes and Kramer, 1994; Zaluzec, et al., 1994].

AlMgB₁₄ materials might also find use in the microelectronics industry where it is necessary to test microchips to see if they meet electrical specifications. Usually these chips are tested by micro-probes. The micro-probes need to be conductive and also wear resistant, because each time the micro-probe comes in contact with a chip some kind of wearing occurs. If AlMgB₁₄ proves to be a useful conductive material, then AlMgB₁₄ could be a solution to this microprobe wear problem. By using pulsed laser deposition (PLD) technology, which is a new laser deposition technique for thin films, metal wires can be coated with AlMgB₁₄. This coating would be both electrically conductive and highly abrasion-resistant.

Bruce Cook and Bruce Harmon at Iowa State have shown that AlMgB₁₄ is also a semiconductor, which means it could conceivably be used in electronic components. Other research has shown that this material may have unusual thermoelectric properties. Research on both of these topics is presented in more detail in Chapter 4.

2.2 Recent Industrial Studies of the Application of AlMgB₁₄

Until recently, AlMgB₁₄ has been studied primarily from a scientific viewpoint. However, within the past two years, an Iowa State University research group has conducted studies using AlMgB₁₄ materials as grinding and cutting tools. The first study was made in March, 1999, by Steve Batzer, who is a faculty member in the Mechanical Engineering Department at the University of Arkansas. Batzer took AlMgB₁₄-Al₂MgO₄ spinel half-inch diameter disks to Autodie, International and brazed them to an end mill tool holder. The procedure is described more fully in Chapter 4. These disks had the same properties as those described in Chapter 1. Autodie, International's business is mold manufacturing and tool and die forming for the automobile, aerospace, furniture, watercraft, and telecommunications industries. Autodie is located in Grand Rapids, Michigan.

The purpose of the AlMgB₁₄ tool trial was to machine the dies for auto body panel forming presses. The tools were constructed by putting the AlMgB₁₄ disks into holders that

machined to get the right diameter and have an appropriate cutting edge geometry. The diameter of the holders was 1.5 inches, and the depth of AlMgB_{14} disks in these holders was 0.2 mm. Each tool cost about \$1000 dollars to construct [Batzer, 2001]. Figure 11 shows pictures taken by Batzer of AlMgB_{14} tools in action. The tools were placed into Rambaudi high-velocity CNC mills. The tools were tested on cast iron dies at milling rotation rates of 10,000 rpm. The test procedure had the CNC mills plunge the tool down at high milling rate into the gray cast iron die to make the beginning cut. As the tool rotates, it presents the cutting edges to the material. All of the data were qualitative observations made by Batzer and the Autodie tool foreman, who had forty years of machining experience. They observed the tools did not fracture on first plunge, as did many other kinds of tools that had been tried at Autodie, and there was little vibration and noise. They found that the AlMgB_{14} tools did wear faster than c-BN tools and that the lubricity was not as good as cubic boron nitride or silicon carbide, which are the common materials used for this process. The Autodie tool

Figure 11: AlMgB_{14} cutting cast iron materials at an Autodie facility (Photographs by Steve Batzer).

foreman was impressed with the tools, and was convinced that they would work well for this purpose. Currently a more quantitative study is being conducted by Bruce Cook and Joel Harringa at Iowa State University. Their research consists of making tools of AlMgB_{14} (containing several percent Al_2MgO_4 spinel impurity phase) using half-inch diameter disks into metal lathe cutting tools and drill bits. So far they have had successful results in cutting iron, aluminum, Inconel, stainless steel, and concrete.

2.3 Comparison and Information of the Hardest Materials

For most nonferrous polishing, grinding, cutting, and machining operations, the premier tool material is diamond. Diamond is the hardest known bulk material (approximately 70 GPa); the next hardest material is only 2/3 as hard. Table 1 of Chapter 1 shows some of diamond's material properties. Diamond is derived from the Greek word "Adamas," which means unconquerable and indestructible [Leshem Diamond Services Corp., 1997]. The hardness in diamond comes from diamond's crystal structure and strong interatomic covalent bonds. Diamond has a modification of the FCC crystal structure containing four additional interior atoms located at four of the eight tetrahedral interstitial sites [Mangonon, 1999]. The crystal structure of diamond, and diamond-related structures is shown in Figure 12. Diamond's great hardness, high thermal conductivity, and low electrical conductivity would make it an excellent material for cutting or grinding ferrous-based materials. Major disadvantages for diamond, it is expensive and reacts with iron, leading to rapid wear when cutting ferrous and high nickel-content alloys. This is a major problem, since iron and iron compounds are the most used metals in society. The cutting, grinding, and machining of ferrous alloys is a major part of most manufacturing processes. Additionally, the affinity of carbon to titanium also renders diamond tooling unsuitable for machining titanium [Kramer, 1987].

Originally, diamonds were valued for their cosmetic properties, and throughout history they have been fought over, worshipped, incorporated into mythologies and religions, and sought in geological formations throughout the world. In the past 3000 to 4000 years, diamonds have been symbols for many kings, queens, and their subjects. Diamonds have

Figure 12: Lattice Structure of Diamond (Modeled by Theron Lewis).

symbolized wealth, power, love, spirit, and magical powers [Leshem Diamond Services Corp., 1997]. Today, diamonds are still important as jewelry and other aesthetic objects. The DeBeers diamond cartel has pursued a long-term marketing strategy to promote the custom of having the future husband give a diamond ring to his fiancé. This has been the archetypal model for marketing strategies that seek to create a demand by peer pressure where none existed previously.

Generally, quality diamonds are expensive and can cost from \$200,000 per kg to \$500,000 per kg. In exceptional specimens, depending on the size, cut, and history of the diamond, a single diamond can be worth several millions of dollars [CES Selector, 1998].

In industrial applications, the diamonds' appearance is unimportant. Thus, industrial grade diamonds are black or colored, but they are still expensive [Van-Daaz, 2000]. More than 500 million carats (100 metric tons) are produced each year for industry applications. About eighty percent of the diamond production comes from diamond mines, and the other twenty-percent is produced synthetically. Diamond is a fundamental industrial material that is used in myriad operations to cut, grind, and polish. Diamonds are used to fashion stones,

ceramics, metals, and concrete. Diamonds help shape by machining or cutting eyeglasses, gems, and computer chips, as shown in Figure 10. Diamond specialty-uses are growing. These uses include special blades, some used in medical surgery; specialty windows, and heat spreaders [American Museum of Natural History, 1998]. Recently, diamond has been researched as a thin film using growth methods that include vapor phase chemical reactions. The maximum film thicknesses are less than one millimeter, but none of the films have regular crystalline structures [Callister, 1997]. The properties of these films are similar to bulk properties. These thin layer techniques have been used for coatings on loudspeaker tweeters, lenses, drills, dies, and other tools to increase surface hardness [Callister, 1997].

Diamond is a metastable carbon polymorph that is formed by extreme heat and pressure. Diamond's crystallographic stability decreases as temperature increases. At high temperatures, diamond transforms at a rapid rate to the more stable phase, graphite. In nature, at any temperature, diamond is unstable, but at low temperatures the kinetics to transform diamond into graphite and causing diamond to decomposes are such that the material can be considered to be stable, even though it is actually a metastable phase. By increasing the temperature, diamond changes to graphite and the original material properties would change and the hardness would drastically decrease [Gaskell, 1995].

In the last fifty years, diamonds have been made synthetically by scientists who follow the same reactions of the diamonds made in nature. Until recently, these synthetic diamonds were usually darker or yellowish and were slightly less hard than naturally formed diamonds, but they were still hard enough for industrial uses [Van-Daaz, 2000]. In the 1990's synthetic diamond production had been refined to the point that large gem quality diamonds are now being manufactured that are visually indistinguishable from natural gem diamonds. A far-ultraviolet phosphorescence test is now the only known method to distinguish the source of a gem diamond.

Diamond can be naturally formed only in molten rock about 75 to 120 miles below the earth's surface. Volcanic eruptions move the diamond from the depth at which it was formed to the surface through the earth in carrot-shaped cones called "pipes". Usually, diamond forms in a mineral called kimberlite, named after the town of Kimberly, South

Africa. As the diamond crystals move up kimberlite pipes, the crystals usually change into free carbon atoms, vaporize into carbon dioxide, or turn into graphite. To avoid the diamond's conversion into any of those products, diamond crystals must undergo a rapid cooling rate near the earth's surface under stable land plates called "cratons". There are few kimberlite pipes in existence, and not many contain important quantities of diamond [Leshem Diamond Services Corp., 1997]. The first diamonds were found in riverbed alluvial sites in India in about 800 B.C. The volcanic sources for these diamonds were never found, but these alluvial sites had enough diamonds to meet demand until the eighteenth century. Usually diamonds were mined from the soil around rivers and riverbeds, but in 1870 in South Africa the practice of dry digging for diamonds was invented and more sophisticated mining techniques allowed deeper subterranean digging to find more diamonds. The most recent site for diamonds is in western Canada [Leshem Diamond Services Corp., 1997], and it is believed that Antarctica may have a rich source diamonds, because it has large "craton" land plates. Since, international laws prohibit mining in Antarctica, these diamond sources have not been investigated [Leshem Diamond Services Corp., 1997].

The second hardest bulk material is cubic boron nitride (sometimes called CBN, or the trade names Borazon, Elborite, or Kubonite). The hardness of CBN is 45 GPa [Cook, 2000]. CBN was introduced to the market in the late 1960s. CBN was needed in industry because the supplies for diamond were quite limited, it was expensive, and no other material was nearly as effective for many cutting and grinding tasks. A statistic often cited in the 1960's was that for every automobile assembled in Detroit, about one and a half carats of industrial diamond was consumed. The accuracy of this statistic is open to debate, but there is no question that diamond is a critical industrial material. CBN made it easier to machine ferrous materials and fully hardened ferrous metals [Ceramics Sources.com, 2000]. Although CBN does not have the cosmetic qualities that diamond has, CBN has been used for many cutting, grinding, and polishing applications where diamond would react with the materials in those applications.

Originally, cubic boron nitride was thought to be a metastable polymorph with the diamond crystal structure in which the carbon atoms of diamond are replaced by boron and

nitrogen and the more stable polymorph is hexagonal boron nitride. Lately, researchers are challenging this assumption. Current research suggests that CBN maybe the more stable polymorph. Figure 13 shows the most recent phase diagram constructed for B-N; this diagram is based only on thermodynamic theory. Empirical studies to confirm or refute this hypothesis are largely lacking. Due to the electronegativity difference of the N and B atoms, the bonding of cubic boron nitride is about 25% ionic and 75% covalent, which results in lower bond strength than the 100% covalent bonding in diamond. CBN exhibits much lower chemical reactivity with iron, but also possesses a significantly lower hardness than diamond [Cook, 2000]. The cubic polymorph of BN can be prepared by placing hexagonal boron nitride in environments that have a combination of high temperatures at 1800°C to 2500°C and pressures of 50,000 atmospheres. The reason such extreme manufacturing conditions are needed to make CBN is that a larger amount of energy is needed to change the bonding from sp^2 to a sp^3 hybrid bonding [McColm, 1990]. The commercial price of CBN can range from \$2,000 per pound to \$7,000 per pound (\$15,000 per kg) depending on grade and purity [Cook, 2000].

Currently boron carbide (B_4C), is the most significant competitor to $AlMgB_{14}$ as the third hardest known material. B_4C has a hardness range from 38-44 GPa (see Table 1 in Chapter 1). This material is commonly used in lightweight body armor. The body armor is made by hot pressing B_4C into hexagonal tile 6 mm thick and mounting it into a backing of glass-fiber-reinforced epoxy resin. When a bullet hits the armor, the bullet impacts the B_4C

Figure 13: Phase p,T-diagram for Boron Nitride. (Solozhanko, et al., 1999).

and shatters the tile, but while the tile shatters, it absorbs the impact energy. Thus, the bullet is prevented from piercing through the under-layer of the glass-fiber-reinforced epoxy resin. Other applications that include B_4C are aircraft armor and strong neutron moderator rods in nuclear reactors. Like $AlMgB_{14}$, B_4C has covalent bonded B_{12} icosahedra. The other structure in B_4C is C_3 chains. The structure is a FCC lattice that has B_{12} icosahedra at the corners and C_3 chains in the center of the faces of each unit cell. Figure 14 shows a piece of the structure of B_4C , where the large atoms are carbon and the small atoms are parts of the boron icosahedra. The bonding between the boron and carbon groups is through sp-sp orbital interactions. Boron carbide is most commonly produced by the reaction of elemental magnesium, boric oxide and carbon in electric furnaces at a temperature of 2500°C. Relation 1 shows the reaction to form boron carbide.

This process gives large amounts of coarse-grained material. One major problem with this material is the difficulty in sintering this powder [McColm, 1997]. The next-hardest abrasive bulk materials are tungsten carbide, titanium diboride, titanium carbide, and silicon carbide; these materials have hardness within the 24 to 35 GPa ranges. Table 1 of Chapter 1 shows the different properties of these selected hard materials.

Figure 14: A schematic of a part of the structure of B₄C; large atoms are carbon and the small atoms are parts of the boron icosahedra [McColm, 1997].

CHAPTER 3: UNDERSTANDING HARDNESS

3.1 Defining Hardness

Hardness is a measure of a material's resistance to an applied compressive load on a small area. Hardness is a function of both the strength of the inter-atomic bonding and of the rigidity (or compliance) of the lattice framework. The term hardness is often confused with "hardenability" and "toughness". Hardenability is the ability of metal to become hardened by applying a particular heat treatment. The term "hardenability" is most commonly used in describing the ease with which martensite, a non-equilibrium microstructure, will form by quenching in ferrous material. Toughness is a measure of a material's ability to absorb energy until it fractures.

The earliest technique in measuring hardness was to observe how well one material scratches a different material. Probably, the most basic, qualitative, and arbitrary hardness scale is the scratch test called Mohs scale. The Mohs scale ranges from 1 to 10 where the hardness of diamond is considered 10 and 1 is the hardness of a soft material such as talc [Callister, 1997]. Mohs scale measures how well one material scratches another material. Many different techniques have been developed for hardness: scratch tests, ploughing test, cutting test, abrasion test, erosion test, damping test, rebound test, and static indentation tests [McColm, 1997]. These tests are defined in Table B1 of Appendix B.

The most common technique used in industry is the static indentation test. This test consists of an indenter that has a tip shaped like a diamond, ball, cone, or pyramid. The indenter is pressed into a sample's surface causing deformation. The load per unit deformation or impression area is the hardness measurement. Several static indentation tests exist and each test is different depending on the load, the indenter, and the procedure for measuring it [McColm, 1997]. The most common hardness test technique for metals is Rockwell. Brinnell is the second most common test for metals. Within the Rockwell hardness test there are different scales: A, B, C, D, E, F, G, and H. Each scale has a combination of load and type of indenter. Rockwell indenters consists of either a hardened spherical steel ball or a cone-shaped diamond indenter [Callister, 1997]. Both kinds of indenters are shown at the bottom of Figure 15. Rockwell hardness values are direct

measurements of the depth of plastic or permanent deformation, and not on the area of deformation. This direct measurement of permanent deformation makes Rockwell different from other static indentation tests. One major disadvantage to Rockwell static indentation is that it has a scale that can go up to only about a 100 for each mode, and the highest mode is Rockwell C. Rockwell C uses the diamond indenter and has a load of 150 kg. From the ASM Hardness Conversion Charts shown in Table B2 Appendix B, an approximate relationship between Rockwell C and Vickers hardness value can be constructed.

Figure 15: Schematic showing the common types of hardness test geometries [Shackelford, 1996].

This relationship is shown in equation 2.

$$R_c = .000000038 * (V_k)^3 - .00014748 * (V_k)^2 + .1954(V_k) - 16.8756 \quad (2)$$

Where, R_c = Rockwell C value

V_k = Vickers value

The coefficient of determination (correlation coefficient) for this relation was $R^2 = 0.99810$.

The coefficient of determination statistically is a representation of the correlation between the two variables in the relationship. The plot of the relationship between R_c and V_k is shown in Figure 1B, Appendix B. The relationship calculates that 100 Rockwell C would equal about 2140 Vickers. Rockwell C should not be used for materials that have hardness values higher than 2140 Vickers.

Vickers and Knoop hardness are used for very hard materials like diamond, cubic boron nitride, boron carbide, and titanium diboride [McColm, 1997]. Figure 15 shows the Vickers and Knoop indenters. These diamond indenters are pressed into the surface of a specimen under loads ranging from 1 to 5000 grams. The indentations are typically are just a few tens of microns wide and are measured under a microscope [DeGarmo, 1999]. Vickers hardness is shown as either Pa or Vickers Hardness Number. Relationships between Vickers, load and indentation dimensions is shown in the following two relations, the first of which gives hardness in Pa and the second of which gives hardness in Vickers:

$$H_v = \frac{P}{\text{contact_area}} = \frac{0.322 P}{a^2 \sin 136^\circ} = \frac{0.464 P}{d^2} \quad (3)$$

Where, H_v = hardness in Pascals

P = load in Newtons

$a^2 = d^2$ = square of the mean diagonal length of the indentation in microns

The 136° angle is the angle between the faces of the diamond indentation in the surface of the material [McColm, 1997].

$$VHN = \frac{2M}{d^2} \sin\left(\frac{136^\circ}{2}\right) \quad (4)$$

Where, VHN = Vickers Hardness Number

M = mass in kilograms,

d = the mean diagonal length of the indentation in millimeters

Again the 136° angle is the angle between the faces of the diamond indentation in the surface of the material [Callister, 1997]. The direct conversion between Vickers Hardness number and hardness in Pa is:

$$1VHN * \frac{9.8 * 10^6 Pa}{VHN} = 9.8 MPa \quad (5)$$

Thus, 3000 Vickers equals 29.4 GPa. The Vickers technique has many advantages over Rockwell and Brinnell. This technique can accurately measure extremely hard materials and can measure sample areas less than 100 µm in size. This provides greater accuracy in determining the diagonal of a square diamond impression. Other advantages for Vickers are that it is a simple technique, little time is involved, usually very little surface preparation is needed, it is inexpensive, and since the measurement is expressed on a load versus area basis it shows some representation of the material strength characteristics [DeGarmo, 1999].

Most static indentation tests find hardness from the following relationship:

$$H = \frac{P}{\text{contact_area}} \quad (6)$$

H = Hardness

P = Load (N)

contact_area = area of sample surface altered by the indentation

Relationships 6 and 7 shows hardness is related to the bonding of atoms and molecules, shape of crystal structure, lattice energy, the molar volume and the dependence of whether the material's bonding and crystal structure is in extension or compression [McColm, 1997].

The derivation of relationship 7 is shown in Table B3 of Appendix B.

$$H_{th} = \frac{nmU_LK}{(n-m)V_m} \left[\frac{1}{b_2} \left\{ \left(\frac{m+1}{n+1} \right)^{(m+1)/(n-m)} * \left[\left(\frac{m+1}{n+1} \right)^{1/(n-m)} - 1 \right] \right\} + \frac{1}{b_1} \left(\frac{m+1}{n+1} \right)^{(m+1)/(n+m)} \right] \quad (7)$$

Where, n and m = values based on bonding

b₁ and b₂ = values based on shape of crystal structure

U_L = lattice energy

K = structure factor related to atomic coordination z ,

V_m = the molar volume

z = atomic coordination

In the brackets of the relation there are two parts that are related to the extension and compression within a crystal structure. The part that has $1/b_2$ as a multiple factor is the extension part of the expression, and the part that has the $1/b_1$ as a multiple factor is the compression part. Depending on the material, either the extension or compression part will be the dominating part and the non-dominant part would be dropped from the expression. For example, silicon would have the extension term as being dominant, which would give a hardness of 14 GPa [McColm, 1997]. The experimental value for Si is 10 GPa [CES, 1998]. Most metals would have the compression term as being the more dominant part in the expression. Usually the theoretical hardness calculated from relationship 7 gives hardness values that are higher than the real value. Like most models, relationship 7 is just a representation and is not necessarily exactly the best relationship for all materials or situations [McColm, 1997].

Hardness is a material property that is related to the tensile and shear strength of a material. Specifically, tensile strength (tensile stress) is the load or force applied to a cross sectional area, where hardness is the measurement of a load or force as a function of the area of deformation caused by that force. No direct relation exists between the two properties because tensile stress usually involves forces across large cross sectional areas. On the other hand, hardness involves forces over areas, only a few tens of microns wide. Proportional relations between the two properties can be constructed from experimental research. These relationships, however, are specific to the kind of material and hardness technique used. For example, Brinnell hardness (H_B) and tensile strength (TS (MPa)) can be related for steels and is shown in the following relation:

$$TS(MPa) = 3.45 \bullet H_B \quad (8)$$

The relationship between Brinnell hardness (H_B) and tensile strength (TS (MPa)) for cast irons is:

$$TS(MPa) = 2.307 \bullet H_B - 153.23 \quad (9)$$

[Callister, 1997]. Generally, tensile strength increases with hardness.

Since many different techniques and scales are used for measuring hardness, no standard scale or conversion exists for all hardness measurements. Also, most hardness techniques have both quantitative and qualitative aspects in measuring hardness based on certain procedures and different kinds of materials. Many different tables that compare common hardness values are available for groups of materials where approximate relationships can be used to estimate one hardness scale to another. An example of an approximate relationship between Rockwell C and Vickers was explained earlier in discussing relationship 2. Figure 16 shows an example of different hardness scales.

Figure 16: Conversion chart of different hardness values [Callister, 1997].

3.2 Hardness versus Load and Error with Micro-hardness Techniques

Deciding on a specific hardness technique and scale is dependent on grain size of the structures in the material and the specific applied load needed for the test. Hard materials frequently contain a large number of small grains. More grains within a sample cause more barriers that prevent dislocation movement across grain boundaries. To make accurate measurements, control of the indent to grain size ratio is needed. A small grain size material requires a small indenter to prevent error from grain boundary defects and crack deformation. Thus, a range of instrumentation is necessary to enable various load ranges to control the ratio of the indent to grain size [McColm, 1997]. Since measured hardness values vary with changing loads on the indenter. Figure 17 shows the transition of indentation hardness versus applied load. This figure shows three different areas: area (a.) shows that hardness increases as the load decreases, and area (c.) shows that as load increases hardness becomes constant. In areas (a.) and (b.), micro-hardness techniques are used, like Knoop and Vickers, but in area (c.) Rockwell and Brinnell techniques are most common. Most accurate results are done at higher applied loads, because more deformation area can be measured. The problem with higher applied loads is that they may fracture brittle materials. Thus, it is best to use the maximum applied loads that a material can withstand to measure hardness without fracture.

Figure 17: Plot of hardness versus load for indentation hardness methods [McColm, 1997].

In this research, AlMgB_{14} materials were measured by using the Vickers technique. Most Vickers and Knoop techniques involve optical microscopes that have magnifications that range from 400X to 1000X. Figure 18 shows a plot of hardness versus load for a SiC standard and three different AlMgB_{14} samples. These materials were measured on a Leco-Wilson Tukon Tester with a 500X microscope that used optimal imaging software. The figure shows the same pattern as observed in area (a.) of Figure 16; as the load decreases the measured hardness values will increase. The plots are constructed from average hardness measurements calculated from at least 8 measurements at each load. Sample 83 was a baseline sample with a slight additive of Si, Sample 7 had 30 wt% of TiB_2 alloying additive and Sample 48 had 20 wt% of TiC alloying additive. A baseline sample is AlMgB_{14} that had a small amount of Al_2MgO_4 spinal and had the properties as discussed in Chapter 1. One other important observation is that the measured SiC hardness values did not increase as drastically as the measured hardness values for AlMgB_{14} samples when applied load decreased.

Figure 18: Hardness versus load for a SiC standard and three AlMgB_{14} samples (7, 48, and 83).

Figure 19 shows indentations at various loads for AlMgB₁₄ samples. Table 2 presents load and dimensions of the different indentations in Figure 19. The data in Table 2 are derived from the AlMgB₁₄ samples in whose average measured hardness values are plotted in Figure 18. Figure 19 and Table 2 show that as the hardness decreases the applied load increases and the indentation dimensions increase. Smaller loads cause smaller indentations, and smaller indentations give higher hardness values. Indentations caused by smaller applied loads can give hardness measurements that are misleading. A sufficiently large applied load is needed to give a significant amount of permanent deformation to obtain accurate hardness measurements.

One major problem with smaller indentations is that the accuracy of measuring the indentations decreases because human error increases in measuring the dimensions of the indentations. Thus, to get the most accurate hardness measurements for any material the largest applied load possible should be used. Other sources of error occur in Vickers hardness when the indentation is not square, the square is in a different direction, and/or the cut of the diamond is not a 136° angle. Error occurs when indentations are made on defects. Defects either will prevent deformation to occur or increase the amount of deformation beyond what it should be. This will lead to a misrepresentation of the hardness of that material [McColm, 1997]. Samples with flat surfaces with respect to the indenter will produce the least error.

Table 2: Listing and the Corresponding Data for the Pictures in Figure 19.

Picture in Fig. 19	Load (g)	Hardness Range (Vickers)	Indentation Dimension Range (μm)
a	50	7990-9020	3.21-3.41
b	100	5590-6520	5.33-5.76
c	200	4370-5210	8.44-9.13
d	300	3820-4210	11.5-12.0
e	500	3540-4050	15.1-16.2
f	1000	3000-4000	21.2-24.9

Figure 19: Vickers indentation in AlMgB_{14} at various loads. The cross hairs show the distance of each indentation. Pictures were taken from a microscope at 500X with no etching. See Table 2 for load values of a-f.

Rough or sloped surfaces will cause indentations to change shape or have additional defects.

3.3 A Study of Hardness Variation between Two Hardness Machines

3.3.1 Purpose of the Study

The purpose of this component of the study is to observe the variation between two hardness testers used in this thesis project. This study was performed to determine whether (1) differences in hardness measurements exist between the two machines and, (2) whether such differences, if found, can be correlated to each other.

3.3.2 Analytical Procedure

Q-Q plotting technique was used to find a relationship between the two machines. First, one set of hardness data was measured from one machine. Another set of data was measured from the other machine using the same sample. Next, each data set was sorted from

from least to greatest. Each data point was matched with a fraction called a quantile that was based on the number of data points. The least data point was matched with quantile $Q_1 = \frac{1}{n}$.

The next least data point was matched with $Q_2 = \frac{2}{n}$. This continued until the greatest point matched with quantile $Q_n = \frac{n}{n}$. The data points were plotted as quantile versus hardness.

From the plots, relationships were made with respect to the coefficient of determination (R^2). For accurate relationships R^2 needed to be close to or equal to 1. The closer R^2 was to 1, the more the relationship accurately represented the data set. R^2 is defined in equation 10.

$$R^2 = \frac{\sum_{i=1}^n (y_i - \text{mean})^2 - \sum_{i=1}^n (y_i - x_i)^2}{\sum_{i=1}^n (y_i - \text{mean})^2} \quad (10)$$

Where, mean = average of the data

y_i = individual data point

x_i = relationship point

n = number of data points.

Once the relationships were found for each data set, the relationships were plotted against each other where one relation followed the x-axis and the other relation followed the y-axis. If the plot between the two relations were linear, the data distributions of each machine had similar shapes. If there was variability in the plot, then the shapes of the two distributions were different. An example of this analytical procedure follows.

3.3.3 Example of Analytical Procedure

To show an example of the analytical procedure, some hypothetical data is presented from two different machines in this example. A sample's hardness was measured from two different machines. The first machine gave five hardness values: 1110, 1400, 1240, 1600, and 1530. The second machine gave seven hardness measurements: 2000, 1800, 1850, 1700, 1600, 1450, and 1759. Each data set was sorted in ascending order and quantiles are

matched, as shown in Table 3. Then plots of quantile versus hardness were constructed and shown in Figure 20. The relationship and R^2 for Machine 1's data set was:

$$\text{Quantile} = 0.0016 (X_1) - 1.5348 \quad (11)$$

$$R^2 = 0.9852$$

Where, X_1 was Machine 1's hardness data point

The relationship and R^2 for Machine 2's data set was:

$$\text{Quantile} = 0.0017 (X_2) - 2.3842 \quad (12)$$

$$R^2 = 0.9571$$

Table 3: Sorted Data with Matching Quantile

Machine 1	Quantile		Machine 2	Quantile
1110	0.2		1450	0.14
1240	0.4		1600	0.29
1400	0.6		1700	0.43
1530	0.8		1759	0.57
1600	1		1800	0.71
			1850	0.86
			2000	1.00

Figure 20: Plots of example sample data measured with two different hardness machines.

Figure 21: Correlation between Machine 1 and Machine 2.

Where, X_2 was Machine 2's data point. Figure 21 shows the result of plotting the relation between Machine 1 and Machine 2.

3.3.4 Experimental Procedure

Hardness was measured by placing the sample under an optical aperture in the tester. An area that contained few defects was selected by looking through the microscope or at an image produced by optical imaging software. Next, the Vickers indenter was positioned where it would make an indentation in that area. The hardness tester applies a load, and the indenter was pressed against the sample. Then after about 15 seconds the indenter was removed. The microscope was used to find where the indentation was located. The dimensions of the indentation were measured, and hardness was calculated. Hardness measurements were taken from two different hardness machines. Both machines were Leco-Wilson Tukon Testers. One machine was located in Gilman at Iowa State University and the other was found in Metals Development of Ames Laboratory. The Tukon Tester in Gilman was set at a 20 seconds dwell time, 1 kg load and a 400X magnification. The following relation calculated the Vickers hardness for this machine:

$$DPH = \frac{7.417 \cdot 10^6}{(f.u.)^2} \quad (13)$$

Where f.u. is filar unit and is a measurement in the objective the microscope. DPH is equal to Vickers. The Tukon Tester in Metals Development was set at a 25 second dwell time, 1 kg load and 500X magnification. The indentations were measured by using optimal imaging software, and the software calculated the hardness. Thirty samples were used in this study. Four of them were standards, 19 baseline AlMgB₁₄, 6 AlMgB₁₄ with TiB₂ additive, and 1 AlMgB₁₄ with AlN additive. Each sample had at least 5 hardness values measured from each machine.

3.3.5 Results Between the Two Machines

Figures 22 and 23 show the relationships that were calculated for the various samples between the two machines. Also these figures show an average correlation for these various samples. Figure 24 shows both an overall correlation and an average correlation. The overall correlation followed the example in section 3.3.3 using all the data points of the thirty samples. The average correlation was made from averaging all the slopes and y-intercepts of the various samples' correlations that follow the same procedure in the example in 3.3.3. The data for this study are shown in Table B4 of Appendix B. Here is the calculated average Correlation:

$$H_{MD} = 1.3484 \cdot H_G - 469.94 \quad (14)$$

The Overall Relation:

$$H_{MD} = 1.1596 \cdot H_G - 23.617 \quad (15)$$

3.3.6 Discussion of Experimental Results

The goal of this comparison between these two hardness testing machines was to find out how clearly their data sets correspond to one another. Ideally the two machines would yield a 1:1 ratio, indicating the same hardness values for a given sample, whichever machine was used to perform the measurement. This analysis has shown that this was not the case for these hardness testers. Both Tukon Testers were calibrated within 6 months of the analysis,

Figure 22: Calculated correlations for specific samples and an average correlation between Metals Development Tukon Tester and Gilman Tukon Tester.

Figure 23: Calculated correlations for specific samples and an average correlation between Metals Development Tukon Tester and Gilman Tukon Tester.

but the Gilman Tukon Tester consistently measured lower hardness values compared to the Metals Development machine. Many hardness measurements taken on many standards showed the Metals Development unit to be the more accurate machine. For example, the Metals Development machine measured consistently 800 vickers for a standard provided by ASTM standards that was rated as 753 Vickers. Figure 24 shows that at about 2500 Vickers for Gilman is 2500 Vickers for Metals Development at 3000 Vickers for Gilman it is about 3500 Vickers for Metals Development. One major source of error was that the samples had

wide distributions of hardness. Some samples had such large variance in measurements that relations plotted between the quantile and hardness caused the R^2 values to be between 0.900 and 1.0. This indicates that the relations are relatively good, but there is still some error. One final source of error is that the correlation of each sample was assumed to be a linear relation. In some cases this linear relation was not the best choice for the correlation. The error caused by always choosing the linear relation for finding the correlation would cancel out in calculating the average overall relationships.

Figure 24: Average and Overall Correlations for Metals Development versus Gilman.

CHAPTER 4: PREVIOUS AND PUBLISHED RESEARCH

4.1 Previous Techniques in Producing AlMgB_{14}

The first technique used to prepare AlMgB_{14} was a crystal flux method. This procedure consisted of weighing out Al, Mg and B in the proportions of 14 parts Al, 1 part Mg, and 2 parts B into an alumina crucible. Next the alumina crucible was placed under an inert atmosphere, usually argon. The furnace was heated to a temperature between 1300°C and 1500°C for a few hours, after which it was slowly cooled. The resulting material was treated with hot hydrochloric acid to etch away the excess Al. The desired products were millimeter-sized crystals thought to be AlMgB_{14} . Larger crystals were produced by taking the same mixture and heating it to 900°C for six to seven hours [Matkovich and Economy, 1970]. Figure 25 shows an example of the sizes of the crystals produced. Often in the crystal flux method, $\alpha\text{-AlB}_{12}$ and $\beta\text{-AlB}_{12}$ compounds were byproducts in producing AlMgB_{14} .

Figure 25: SEM photograph of a single crystal of AlMgB_{14} . Axis follows the (001) plane [Higashi et al., 1993].

A second procedure for making AlMgB_{14} materials was mechanical alloying plus a hot uniaxial pressing technique. The material properties shown in Table 1 in Chapter 1 were measured from samples produced by this method. This hot uniaxial pressing technique consisted of weighing out powder loads of 74.69 wt% boron, 13.31 wt% aluminum and 12 wt% magnesium. Some samples were made from chunk material that was milled into powder, while other samples were made by powders bought from different vendors. The powders were transferred into a mechanical alloying apparatus and milled for time intervals that varied with the type of mechanical alloying system used. The two different kinds of mechanical alloying were Spex milling and planetary milling. For Spex milling 3 to 5 gram loads of powder were placed into a stainless steel Spex vial and milled for 12 hours. For planetary milling about 25 to 50 grams of powder were loaded into the steel planetary vial and the milling was for 50 hours to 100 hours.

Once the milling was done, the loose powder was removed from the vial by scraping and chiseling the inner walls of the vials. All the weighing and cleaning was performed under an inert atmosphere. Then, 1 gram quantities were pressed in the hot uniaxial press under temperatures ranging from 1400°C to 1500°C for 60 minutes under pressures ranging from 15,000 to 50,000 psi. The pressing occurred under either an inert or vacuum atmosphere. During the pressing an outgassing or plating effect occurred. The outgassed material was found to be Mg [Harringa, 2001]. Most samples were half-inch diameter disks that were about 2 mm thick as shown in Figure 26. The various processing conditions for each sample made in this research were shown in Appendix C and Appendix D. These appendices include both baseline and alloying additive samples. Appendix E shows the basic characterization of these samples. The half-inch diameter disks were ground and polished using diamond embedded steel grinding plates and 1 micron diamond grinding slurries. These polished surfaces made it possible to measure the properties of the AlMgB_{14} specimens. The mechanical alloying caused refinement of the powder size and a very small amount of alloying was found to occur mechanical alloying, but the AlMgB_{14} crystals did not form until hot pressing at high temperatures was performed.

Figure 26: Three samples produced by uniaxial hot pressing.

4.2 Background Information on Mechanical Alloying

Mechanical alloying is a non-equilibrium process that can produce metastable structures with unique properties. Mechanical alloying is exactly that, a mechanical means to form an alloy. It consists of introducing material into a container with some media, usually steel balls, and applying mechanical energy to agitate the container. The media collide with each other and the material. These collisions transfer sizeable amounts of kinetic energy. Kinetic energy in the system from the numerous collisions causes the material to fracture or deform, exposing new atomic surfaces, and bond with other constituents in the material, forming an alloy. Mechanical alloying can refine the microstructures, homogenize the composition, increase solubilities in solids, create metastable crystalline phases, and produce metallic glasses. Mechanical Alloying was first developed by the International Nickel Company in the 1960's to produce oxide dispersion-strengthened alloys. The different kinds of milling equipment are attrition mills, vibrating ball mills, shake mills (Spex mill), and tumbler ball mills (planetary mill) [Kock, 1989]. For this research only Spex mill and planetary mill were used. In Figure 27, picture (a) shows that a Spex mill moves and shakes in two different directions, while picture (b) shows the planetary mill moves in within a fixed plan. Since the Spex milling (shake milling) technique caused more energy by moving in more than one direction, this system has a higher kinetic energy and faster rate of mechanical alloying than the planetary milling system. The kinetic energy is dependent on the internal

Figure 27: Schematics of mechanical alloying motion. Picture (a) is Spex mill motion and Picture (b) is planetary mill motion.

mechanics of the mill, the physical movement of the milling, and the electrical energy supplied to the mill. In these systems, the maximum kinetic energy transfer occurs when the milling media, the balls, are at their highest velocities and colliding with balls that are not moving or moving in the other directions. The highest kinetic energy system is shaker mills. Shaker mills (Spex mills) can have ten times faster milling rates than tumbler mills (planetary mills). This kinetic energy causes heat through friction, and can cause temperature changes within the system. Specifically, the Spex mill can experience temperature increases 100 to 350 Kelvin above ambient [Kock, 1989].

4.3 Crystallography of AlMgB_{14}

The AlMgB_{14} structure is based on four B_{12} icosahedral units positioned within an orthorhombic unit cell containing 64 atoms [Collie, 1981]. The unique electronic, optical, and mechanical properties of this material are thought to result from complex interactions within each icosahedron (intrahedral bonding) combined with interactions between the icosahedra (intericosahedral bonding). The icosahedra are arranged in distorted, close-packed layers, with atoms between each icosahedra, which are shown in Figure 28 [Matkovich and Economy, 1970]. A group in Japan, headed by Higashi and Ito conducted an extensive crystallographic study on the 1:1:14 compound and established the lattice parameters and atom positions but performed no property measurements. Crystallographic studies indicate that the metal sites are not fully occupied in the lattice so that the true chemical formula may

Figure 28: An Icosahedral B_{12} network parallel to the (001) plane of the $AlMgB_{14}$ structure [Higashi et al., 1993].

be closer to $Al_{0.75}Mg_{0.78}B_{14}$ [Higashi et al., 1993]. The lattice parameters for this crystal structure are $a=5.8480 \text{ \AA}$, $b=8.1120 \text{ \AA}$, and $c=10.3120 \text{ \AA}$ [International Centre For Diffraction Data, Card # 39-0459, 1997]. Table A1 in Appendix A show the d-spacing, diffraction angle using a Cu-K α radiation, intensity, and the corresponding lattice plane.

4.4 Most Recent Research on $AlMgB_{14}$

The most recent research on $AlMgB_{14}$ was performed at Iowa State University (ISU) [Cook, et al., 2000]. A significant portion of the project was devoted to identification and optimization of a suitable method for preparing an $AlMgB_{14}$ alloy without any additives, and consolidation of the powder into a dense compact by hot uniaxial pressing. Mechanical alloying (MA) was selected as the initial route to preparation of dense compacts because of its ability to generate fine, sinterable powders. As the particle size is reduced, the diffusion distances become smaller, thereby enhancing sintering. An additional benefit of mechanical alloying is the high surface-to-volume ratio, which promotes chemical reactivity and alloy formation. Prior research with this technique has demonstrated that reasonably good control of oxygen impurities can be obtained by restricting handling of the powders to a glove box environment with less than 1 PPM oxygen [Cook, et al., 1992].

A SEM backscattered electron image of a typical baseline sample consolidated by hot pressing from Cook's ISU research group is shown in Figure 29a. At this magnification, it is clear that the microstructure is highly heterogeneous, with regions of widely varying phase contrast. An EDS spectrum was obtained from both the light and dark regions; the dark areas were found to correspond to AlMgB_{14} while the lighter contrast regions contain both AlMgB_{14} and Fe. A higher magnification BSE image of one of the lighter regions is shown in Figure 29b. The bright areas, identified as points "B" and "C" in the photo, contain high concentrations of Fe, in addition to the baseline material. The composition at point "A" appears closer to that of the nominal alloy. What is remarkable about the microstructure is the fine distribution of phases at a sub-micron level. A high magnification image shows that compositional contrast exists down to a scale of 100 nm. This material clearly contains large-scale inclusions, on the order of 10 microns; however, the largest volume fraction is composed of a nanoscale composite.

Other recent research has also studied the static reactivity of AlMgB_{14} with iron, steel and titanium. The study consisted of several sets of diffusion "couples" between the AlMgB_{14} and 304L stainless steel, pure iron, and titanium in order to examine the effects of time, temperature, and applied pressure on reactivity. Two configurations were examined.

Figure 29: a) Back-scattered electron SEM image of mechanically alloyed, hot pressed AlMgB_{14} pressing. b) High-magnification BSE SEM image of baseline AlMgB_{14} material [Cook, et al., 2000].

The first configuration was a piece of dense AlMgB_{14} sandwiched between nominally 1 mm thick iron and titanium disks, the other configuration was a AlMgB_{14} disk positioned against a 6.35 mm diameter steel rod segment. The AlMgB_{14} surfaces were prepared by grinding against a series of progressively finer diamond polishing wheels and rinsing with hexane between steps. The iron and titanium surfaces were also polished and rinsed prior to assembly of the sandwich. The components were positioned inside a graphite die that was placed in a high temperature graphite furnace for testing. All tests were conducted under vacuum conditions (10^{-6} Torr) and a light load was applied to the die ($\sim 1 - 2$ MPa) in order to hold the components in intimate contact. The temperature of the furnace was ramped at $10^\circ\text{C}/\text{min.}$ to a soak point of 1000°C to 1300°C and held for two hours. One of the diffusion couples, prepared at a temperature of 1200°C for 2 hours, was sectioned with a low speed diamond saw, mounted in diallylphthalate resin along with Al and Mg standards, and polished with 0.25 micron diamond paste. A SEM backscattered electron image of a typical AlMgB_{14} -Fe interface is shown in Figure 30a. The bright region on the right side corresponds to the iron while the darker region on the left corresponds to the boride. A large number of bright spots are observed on the boride side and EDS analysis indicates that these spots are predominantly iron, presumably wear debris from the mechanical alloying process. These spots extend throughout the entire boride specimen. The presence of the irregular interface suggests that some diffusion between the components occurred. In contrast, Figure 30b shows the corresponding AlMgB_{14} -Ti interface in which complete de-bonding occurred with formation of a $10\text{ }\mu\text{m}$ gap between the materials. In all the samples there was no indication of a reaction between the boride and titanium [Cook, et al., 2000]. A series of qualitative “pull off” tests were also conducted between pieces of the boride material and 6.35 mm diameter segments of 304L stainless steel rod. A similar combination of temperature and pressure were employed with the objective being to provide an indication of the conditions at which significant reactivity between the components occurs. The couples were subjected to temperatures ranging from 1000°C to 1300°C for one hour. The only evidence of a reaction in these tests was indicated by the 1300°C specimen, in which a slight amount of force was necessary to separate the pieces. Some darkening of the specimen and

Figure 30: a.) SEM Image of Iron-AlMgB₁₄ Interface After a 2 Hour Heat Treatment at 1200°C. The Bright Region on the Right-Hand Side Corresponds to the Iron. (BSE mode).
 b.) SEM Image of Titanium-AlMgB₁₄ Interface After a 2 Hour Heat Treatment at 1200°C. The Bright Region on the Left-Hand Side Corresponds to the Titanium. (BSE mode).

iron occurred during the thermal treatment, which may be due to carbonization from the furnace components [Cook, et al., 2000].

4.5 Origins of AlMgB₁₄

Study of the ternary AlMgB₁₄ evolved from investigations of aluminum and magnesium borides. Presently a significant amount of research has been performed on the processing and properties of α -AlB₁₂ and β -AlB₁₂, but comparatively little has been done with magnesium borides. In Appendix A, Figures A1, A2, and A3 show phase diagrams of Al-B, B-Mg, and Al-Mg. The discovery of AlMgB₁₄ was first reported by a Russian group, led by L. Ya Markovskii. In the 1950's, Markovskii performed many experiments to characterized magnesium borides, and discovered that MgB₁₂ could be formed near 1200°C. He also claimed that the material dissociated at 2000°C and has a high degree of chemical and physical stability [Markovskii, et al., 1954]. Since only this research cites the existence of MgB₁₂ and no other sources were found to support his claim, MgB₁₂ is not shown in the ASM phase diagram of Figure A2 of Appendix A.

Knowing that both aluminum and magnesium can form B₁₂ compounds, Markovskii and fellow Russian researchers reported finding a double boride [Vekshina, et al., 1968].

They identified the material as AlMgB_{12} , a compound that formed at 1000°C and was insoluble in hydrochloric acid. In 1970, V. I. Matkovich and J. Economy, members of a research team at Carborundum Company, published a crystallography study of AlMgB_{14} [Matkovich and Economy, 1970]. The Matkovich and Economy group determined the crystal structure of AlMgB_{14} , and the cell constants were nearly identical to those found by Markovskii's research. Table 4 shows the lattice parameters found by the two research studies. It appears likely that the Russian team's report of AlMgB_{12} was actually the AlMgB_{14} compound.

Table 4: Shows the lattice parameters of Markovskii's research [Vekshina, et al., 1968] and Matkovich and Economy [Matkovich and Economy, 1970]

Lattice Parameter	Markovskii (AlMgB_{12})	Matkovich and Economy (AlMgB_{14})
A	5.86 Å	5.848 Å
B	10.38 Å	10.313 Å
C	8.17 Å	8.115 Å
Space Group	Jmma	Imam

4.6 Past Evaluation of Electronic Properties of AlMgB_{14}

Recent advances in computational band structure methods have enabled scientists to probe the electronic structure of complex materials considered intractable only a few years ago. At the time of the initial x-ray structure refinement of the baseline ternary AlMgB_{14} compound in the 1970's, it was impossible to evaluate the band structure of a material containing 64 atoms per unit cell. Today, using modern computers, such calculations are now feasible, and preliminary theoretical studies of the AlMgB_{14} compound by Ames Laboratory scientists yielded intriguing preliminary results.

First principles, full potential, self-consistent band structure calculations performed by Harmon et al. at Iowa State University, determined a Density of States (DoS) for the full (64 atoms) unit cell structure showing that the Fermi level lies in states above a band gap of about 2 eV. By comparison, cubic boron nitride has a band gap of 6 eV. The Fermi level corresponds to the upper-most occupied energy state in the ground state configuration and roughly indicates the highest occupied energy level. The DoS refers to the number of

available energy states at an energy, E , and is related to the probability to occupancy by the relation in equation 16 [Jiles, 1994].

$$DoS = \frac{N(E)}{2 * f(E)} \quad (16)$$

Where, E = Fermi Energy Level

$N(E)$ = Number of Electrons on that Energy Level

$f(E)$ = Probability of Occupancy or Fermi Function

If the DoS calculations take into account the observed 25% vacancies on the Al and Mg sites, the Fermi level then falls below the band gap, within a broad set of bands having predominately boron character, which lowers the total energy per atom of the vacancy-rich structure. There is one conduction hole per unit cell and, thus, the ordered structure should be metallic. With highly disordered vacancies, the scattering of electrons can be very high, and some of the electronic states near the top of the valence bands could become localized. Thus, one would expect the electrical conductivity to depend on the sample preparation methods, since processing parameters, such as cooling rate, will determine the degree of disorder or vacancy concentration. Also, doping the sample with, for example, Si would add electrons to the valence band and fill the valence band states. Consistent with typical ceramic behavior, it is expected that when the states are completely filled and the Fermi level lies in the band gap, the material will have the maximum hardness, as shown in the simplified schematic density of states diagram of Figure 31 (Private Communication With B. Cook and B. Harmon). Thus vacancies in this material may play a vital role in determining the electronic structure where in doping can be used to affect the hardness, resistivity, and other important properties. The ability to vary hardness by adjusting the lattice occupancy is an entirely new and exciting concept. Clearly, there is a great deal of complexity associated with these materials and a great deal of basic research is needed to explore the powerful influences of the vacancies and of the doping on atomistic design of this new family of ultra-hard materials.

Although no direct relationship has been determined between electrical properties and hardness, the electrical properties can be useful in learning important information concerning this material. In the past, AlMgB₁₄ materials produced by the crystal flux were small crystals as shown in Figure 25. These small crystal sizes make exact conductivity measurements

Figure 31: Idealized density of states representation of AlMgB_{14} , illustrating the effect of metal site occupancy on the relative position of the Fermi level (vertical lines). Note that doping additives are required to shift E_F into the gap region [Private Communication with B. Cook and B. Harmon].

difficult. Only estimates of the conductivity could be determined using the two-point probe method. The major error was that the contact areas in the two point probe method were small. The smaller the areas the more influence the edge effects will have in introducing error to the conductivity values. Another more reliable method was to analyze the thermoelectric properties of this material parameter [Werheit et al, 1993]. Thermoelectric materials have the property of converting heat into electrical power. A typical measurement of thermoelectric properties is the thermoelectric power (Seebeck coefficient). Other related thermoelectric properties are electrical resistivity and thermal conductivity. The thermoelectric power is the difference of voltage divided by the difference in temperature, which is shown in equation 17.

$$S = \frac{dV}{dT} \quad (17)$$

Where,

S= Seebeck Coefficient (Thermoelectric Power)

dV= Voltage Difference

dT= Temperature Change

The Seebeck coefficient is a proportionality constant, and the Seebeck effect is the linear fit of the Seebeck coefficient versus temperature. The relationship between Seebeck coefficient, resistivity, and thermal conductivity is shown in equation 18 [Wood, 1988].

$$Z = \frac{S^2}{\rho * \Lambda} \quad (18)$$

Where, Z = Figure of Merit

ρ = Resistivity

Λ = Thermal Conductivity

The thermoelectric power represents the number of energy carriers over the temperature gradient. Across that temperature gradient is a concentration gradient of energy carriers, where the least part of the temperature gradient has the smallest concentration of energy carriers [Jiles, 1994]. Thus, a material under a temperature difference will have greater numbers of charge carriers at the hot end and these can diffuse to the cold end, where the material has lower energy. Seebeck measurements can be used to determine whether the material is a p-type or n-type semiconductor. If the material is p-type, the vacancies diffuse to the cold end and if the material is n-type, the electrons move to the cold end [Ioffe, 1957]. Figure 32 shows a plot of some thermoelectric properties versus kind of a material.

Figure 32: Plot of Seebeck and Electrical Conductivity (which is the inverse of resistivity) versus Kind of Material [Ioffe, 1957].

Figure 32 shows metals having the lowest Seebeck coefficients and the highest conductivities, where insulators are just the opposite. AlMgB_{14} is considered a semiconductor.

In 1979, I. A. Bairamashvili and other Russian researchers were first to report on the electrical properties of AlMgB_{14} . They prepared crystals by the flux growth method in a crucible heated to 1800°C , then cooled the material slowly. The Seebeck coefficient was measured over temperature ranges from 300°C to 1400°C . Figure 33 shows a plot for an AlMgB_{14} sample from Bairamashvili, et al. They observed that the electrical conductivity and the thermoelectric power increase over a large temperature range and proposed that movement of the energy carriers occurred. Their research concluded that AlMgB_{14} has only one sub-band of localized states, which forms the edge of the valence band [Bairamashvili, et al., 1979]. In comparison, Higashi and Werheit claimed a room temperature resistivity of $50 \Omega\cdot\text{m}$ and a band gap of 1.51 eV. Higashi attempted to measure the Seebeck coefficient, but the small crystal size and irregular shapes prevented accurate measurement of this transport parameter [Werheit et al, 1993].

Figure 33: Plot of Seebeck Effect Versus Temperature. These data came from I. A. Bairamashvili and L. I. Kekelidze research [Bairamashvili and Kekelidze, 1979].

4.7 Previous Research on Effect of Additives to AlMgB₁₄

In addition to studying the baseline materials produced by hot uniaxial pressing techniques, the ISU group also investigated several AlMgB₁₄ alloys that contain additions of either elemental silicon, previously found to increase hardness, or with compounds such as TiB₂, AlN, and BN. Samples were prepared in the same manner as the stoichiometric “baseline” materials except that a few percent of the additive were added to the powder charge. Microhardness values of the Si-doped samples were consistently higher than those of the baseline material by 10 to 20 percent, typically ranging between 30 and 38 GPa. The reason for the increased hardness accompanying silicon addition is uncertain at present. It is assumed that the Si atoms substitute for Al in the orthorhombic unit cell, but the similarity in atomic radius and electronegativity between Si and Al would suggest similar bonding characteristics [Cook, et al., 2000]. If the sites corresponding to the Al atoms were smaller than the Mg sites, it is possible that the slightly smaller Si atoms might give rise to a higher occupancy than the 74.8% reported by Higashi and Ito [Higashi, 1983]. Consequently, the overall inter-icosahedral bonding might be stronger, leading to a more rigid unit cell. An example of the beneficial role of chemical additives to the baseline compound was demonstrated by additions of TiB₂. Baseline samples were prepared as described and then alloyed with TiB₂. The microhardness of the resultant hot pressed compact was found to range from 40 GPa to 46 GPa, depending on the position of the indenter. A two-phase microstructure was evident, with a high density of second phase distributed uniformly throughout the material, giving an increase to the density [Cook, et al., 2000].

Most materials exhibiting extreme hardness do so because of a combination of high symmetry in their unit cell coupled with strong covalent bonding. While one can find numerous examples of hard materials exhibiting both ionic (Al₂O₃, ZrO₂, and BeO) and metallic (TiB₂, VC, TiC, and TiN) bonding, none of these systems reach the “superabrasive” category, a term reserved for materials possessing a hardness of 32 GPa or higher. The AlMgB₁₄ system appears unique in that while the hardness of doped or composite specimens rivals that of cubic boron nitride, the unit cell is complex and is of lower symmetry than the conventional cubic systems.

Additives not only change the hardness, but also electrical properties. Bairamashvili, et al., research has shown that adding nickel will change electrical properties in AlMgB_{14} . Figure 34 shows two Seebeck Effect versus temperature plots of a baseline sample and sample doped with nickel. The AlMgB_{14} baseline sample had a higher Seebeck effect than the nickel doped AlMgB_{14} sample. Adding the nickel made the AlMgB_{14} material more conductive, which reduced the Seebeck effect. Other research has shown that using Fe as a dopant causes a hopping conduction effect which also lowers the Seebeck effect and increases the conductivity [Kazanin, 1989].

Figure 34: Plot of Seebeck Effect Versus Temperature. This data came from I. A. Bairamashvili and L. I. Kekelidze research [Bairamashvili and Kekelidze, 1979].

CHAPTER 5: THERMAL CHARACTERIZATION

5.1 Importance of Thermal Characterization

In designing new products, the engineer must consider all the interactions that cause heat and know how to assure that the material will respond adequately to these interactions. For example, automobile companies have to build vehicles to withstand ambient temperatures ranging from -50°F (-58°C) to $+125^{\circ}\text{F}$ (257°C). Another example is a saw blade; friction forces interact with the blade causing heat energy that can change the properties of the blade. Thus, knowing the thermal characteristics of a material in different applications, techniques, and designs is fundamental to making successful products. A thermal property is a material's response to an amount of heat energy. Physical and chemical changes can occur when heat energy is increased or decreased. Typical responses to the heat energy include: transformation from one crystal structure to another, from solid to liquid, liquid to vapor, solid to vapor, crystallization from an amorphous state, change of magnetization, and/or change in material.

Thermal analysis and characterization includes many techniques, but all involve the use of temperature measurements. However, no overall standard exists on how the temperature is applied. For example, depending on the method, one may measure: amount of energy input to maintain a temperature, amount of temperature difference for a given energy, and/or the change in properties as a function of temperature. The only "constant" is that some feature changes as a function of temperature. The basic properties that are standard in measurements are heat capacity, thermal expansion, enthalpy, and thermal conductivity. Other measurements often examine how hardness, density, crystal structure, resistivity, and many other properties change as temperature changes.

Very little research has been done on the characterization of the thermal properties of AlMgB_{14} materials. Some of the early baseline samples in this research produced by the hot uniaxial method described in Chapter 4 section 4.1 were broken up and mounted for metallography analysis. The mounting process consisted of placing bakelite mounting material and a piece of the sample in a die. This die was put into a heated hydraulic press at a temperature of 150°C and pressed at 1000 psi. Then the system was cooled, and the mounted sample was removed. It was found that the mounted samples decreased in hardness

they possessed before the mounting and had more cracks. It was not known at the time whether the bakelite, the pressure, temperature or some combination of these factors caused the loss of hardness. It was felt that studying temperature effects would give the most information about the cause of the loss of hardness during this metallographic preparation process. The techniques used to analyze the thermal properties were different heat treatments, thermomechanical analysis, differential thermal analysis, and x-ray diffraction at various temperatures.

5.2 Heat Treatment Experiments

A heat treatment is the process of heating or cooling a material to a certain temperature in a specific environment, keeping that temperature for a certain amount time, and then returning the material back to normal room temperature. Three different heat treatments were conducted: sample 28, 73 and 78. All the samples were AlMgB₁₄ baseline samples. Each sample was heat treated individually. Both sample 28 and 78 were made from powders that had been mechanically alloyed by Spex milling. Sample 73 powder was Terbula mixed, but not milled. All the processing conditions for these samples are shown in Appendix C, and some of the characterization properties are shown in Appendix E. Table 5 shows the temperature of each heat treatment, the amount of time of heat treatment, the cooling rate, and the hardness before and after each experiment. Table 5 shows that all three samples had hardness values higher than the hardness values after the heat treatment. It also shows that the samples that had the longest and highest temperature heat treatments lost the greatest amount of hardness.

Table 5: Shows Heat Treatment Parameters.

Sample ID #	Heat Treatment Temperature (°C)	Heat Treatment Time (hr)	Cooling Rate (°C/min)	Average Hardness Before (Vickers)	Average Hardness After (Vickers)
28	1200	3	20	3218.4	2893
73	1450	6	10	837.5*	381*
78	1450	6	10	2718	1869

* Sample 73 was mixed, but not milled. The effect of this processing difference on hardness and composition is discussed on p. 7.

All the heat treatments were done in a furnace under a flowing argon atmosphere. All the samples had similar results, but Samples 28 and 78 showed the same kind of patterns in SEM and XRD analysis. During the heat treatment the samples were placed in a alumina crucible. The inside of the alumina crucible was black after each of the heat treatment. Earlier it was stated that when making samples with the hot uniaxial pressing method, large amounts of outgassing occurred and plating of a material on the surfaces of the furnace occurred. Joel Harringa of the ISU research group analyzed this material and found it to be Mg. During the heat treatment, Mg metal must have evaporated from the sample and coated the inside of the alumina crucible. The density of Sample 28 was not measured before the heat treatment, but afterwards it had a density of 2.86 g/cm^3 . The density of Sample 78 before the heat treatment was 3.076 g/cm^3 and after heat treatment the density was 2.890 g/cm^3 . Sample 78 was made with a less pure boron powder and thus had slightly more impurities, giving it a higher density.

Figure 35 shows an SEM analysis of the microstructure of Sample 28 before the heat treatment. Figure 35 (a.) shows an SEM micrograph at 1000X. Figure 35 (b.) and (c.) show SEM micrographs at 10000X. Figure 35 (d.) shows the energy dispersive x-ray spectroscopy (EDS) scan taken at the cross in picture (b.). Figure 35 (e.) shows the EDS scan taken at the cross in (d.). Figure 35 shows that sample 28 had the normal AlMgB_{14} material characteristics. The EDS scan in (d.) shows that the dark gray phase has an EDS scan consistent with a AlMgB_{14} composition, and the EDS scan in (e.) shows that the material has Fe, Al, Mg, and O. This area was assumed to have both iron oxide and Al_2MgO_4 spinel. The iron impurities presumably came from the steel vial used to mechanically alloy the powders for sample 28. Figure 36 shows a SEM micrograph after the heat treatment of sample 28. It appears that more of the light gray and white phases formed. This would suggest more iron oxide and Al_2MgO_4 formed. The amount of AlMgB_{14} phase was less compared to the SEM micrograph in picture (a.) of Figure 35. Also comparing the two micrographs, not only was there more white or light gray phase material but these particles were larger. EDS analysis of the white and light gray particles in Figure 36 had the same EDS scan as shown in picture (e.) in Figure 35. It was quite difficult to differentiate between the iron oxide and the Al_2MgO_4 spinel. Comparison of Figures 35 and 36 leads

Figure 35: SEM and EDS pictures of Sample 28 in backscattered mode before heat treatment (a.)-SEM micrograph at 1000X. (b.)-SEM micrograph at 10000X shows location of EDS shown in picture (d.). (c.)-SEM micrograph at 10000X shows location of EDS shown in picture (e.)

to the conclusion that the heat treatment caused the iron oxide and Al_2MgO_4 spinel phases to precipitate and grow. Possible reasons why these phases grew during this heat treatment were that oxygen impurities from the flowing argon gas and residual oxygen present in the B, Al, and Mg as impurities reacted with the Al and Mg materials causing Al_2MgO_4 spinel to form. The flowing argon was an ordinary grade and not ultra-pure. It's unclear why more iron oxide would appear, since the amount of iron is unlikely to change during the heat treatment.

Figure 36: Backscattered SEM micrograph of Sample 28 after the heat treatment.

Since EDS alone cannot definitively determine the phases present in a specimen, x-ray diffraction (XRD) spectroscopy was performed before and after the 1450° heat treatment of Sample 28. Figure 37 shows XRD scans before and after the heat treatment of Sample 28. The XRD scans were continuous scans, taken with Cu-K α x-ray radiation tube at 45 kV potential. Also included in Figure 37 are the diffraction patterns for AlMgB₁₄, Al₂MgO₄ spinel, and FeB taken from the Joint Council on Powder Diffraction Spectra (JCPDS) reference file. Appendix A Table A5 shows the x-ray diffraction peaks for FeB. XRD shows that Sample 28, before heat treatment, not only had Al₂MgO₄ spinel and iron oxide, but it also had FeB. After the heat treatment, the XRD scan shows that the AlMgB₁₄ peaks lost intensity, and the impurities, Al₂MgO₄ spinel, iron oxide, and FeB, peak intensities increased. This helps explain why more Fe compounds appear in Figure 36. During the heat treatment, the iron oxide loses some of its oxide and reacts with the boron material. Since FeB is a binary compound and more boron exist in the scanned material, more FeB phases would appear in comparison to Fe₃O₄ phases.

Sample 73 was made from a powder batch that was turbula mixed for thirty minutes. These processing conditions gave rise to low hardness values suggest that the material was mixed but did not react to form AlMgB₁₄. The extent of out gassing was large when this sample was hot uniaxial pressed. Since the sample 73 was only mixed and not milled, it did not have any iron impurities. Sample 73 was heat treated in a flowing argon atmosphere,

Figure 37: XRD scans before and after heat treatment of Sample 28, and includes diffraction patterns of FeB, Al₂MgO₄, and AlMgB₁₄. Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997]

and the heating and cooling rates were rapid. Sparks were observed emanating from the furnace surface when the furnace was opened. Table 4 shows that this sample's hardness was much lower than baseline AlMgB₁₄ materials in Table 1 of Chapter 1. It was observed through an optical microscope that Sample 73 had extensive porosity, and it was difficult to

find areas to make quality hardness measurements. The density of the sample before the heat treatment it was 2.47 g/cm^3 and after the heat treatment was 1.92 g/cm^3 . There was heavy outgassing of Mg during pressing of the sample, and it seems likely that more Mg outgassing occurred during the heat treatment. This Mg loss probably caused the density to decrease. Mg oxidation could also account for the sparking that occurred on the furnace walls. Figure 38 (a.) shows Sample 73 before heat treatment and Figure 38 (b.) shows Sample 73 after the heat treatment.

Figure 39 shows the XRD scans before and after the heat treatment of Sample 73. The EDS measurements taken before and after showed that the white areas consisted of Al, Mg, and O, and these were assumed to be spinel structures. The XRD scan shown in Figure 39 agrees with that assumption. EDS showed the dark areas were Al, Mg, and B. The XRD shows that AlMgB_{14} was in the sample before the heat treatment, but after the heat treatment AlMgB_{14} peaks were absent. This suggests conversion of the AlMgB_{14} phase into spinel during heat treatment.

a. Before Heat Treatment

b. After Heat Treatment

Figure 38: SEM backscattered electron micrographs of Sample 73.

Figure 39: Shows measured XRD scans before and after heat treatment of Sample 73, and includes diffraction patterns of Al_2MgO_4 , and AlMgB_{14} . Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997].

5.3 Thermal Expansion Analysis

Thermal Mechanical Analysis (TMA) provides measurements on many parameters including fracture toughness, yield strength, elastic modulus, and ultimate strength. Most important parameter for this research was that it measures how the shape of the sample changes as a function of temperature. The TMA can provide characterization on almost any material: ceramics, metals, polymers, and composites. Transformations such as shrinking and expansion can be characterized by TMA. A device called the LVDT measures the dimension change as the sample temperature changes. Usually the material expands at a constant rate until it hits a transformation temperature. At the transformation temperature the material will increase its expansion rate, decrease its expansion rate, or contract. The TMA software plots the probe distance as a function of temperature. Using relationship 19, the thermal expansion can be calculated.

$$\alpha = \frac{\Delta l / l_0}{\Delta T} = \frac{\Delta V / V_0}{\Delta T} \quad (19)$$

Where, α = Thermal expansion coefficient

Δl = The change in length of the sample

ΔV = The change of volume

l_0 = The initial length of the sample

V_0 = The initial volume

ΔT = The change in temperature of the sample [Callister, 1997].

The thermal expansion coefficient can be measured by dividing the slope of the line on the graph, which is $\Delta l / \Delta T$, by the initial length. This method is simply a variation of the equation above. Possible sources of error include jarring or vibration of the TMA apparatus, incorrect calibration of the apparatus, and/or other malfunction.

The TMA used was a Perkin Elmer 7; Figure 40 shows a schematic of a TMA apparatus. The sample rod provides a constant pressure to the sample as the sample is heated. The position of the sample rod changes as the sample expands. The LVDT measures the movement of the sample rod and compares this to the reference rod. The data are sent to a data acquisition device [Akinc, 2000]. The maximum temperature that this device reliably

Figure 40: Shows a schematic of a TMA [Akinc, 2000].

attained was 950°C and the optimal heating rate was 10°C/min. The gas flowing in the furnace was helium. The thermal expansion profile of the sample stage was measured before making the sample measurements. The sample stage dimension changed slightly upon heating the furnace. For this particular TMA, the sample stage was a quartz tube. The TMA plot for the quartz tube is shown in Figure 41. The plot in Figure 41 shows that instead of pushing the sample rod up as the temperature rose, the quartz tube contracts until about 760°C, then the quartz stage expands from 760° to 950°, pushing the sample rod up. The quartz stage pulled away from the sample rod with an average thermal expansion coefficient of $-1.150 \times 10^{-2} \text{ } ^\circ\text{C}^{-1}$ over a temperature range of 50°C to about 760°C. The average thermal expansion coefficient of the quartz tube as it pushed up on the rod, over a temperature range of 765°C to 950°C, was $2.473 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$. The quartz profile was subtracted from each sample's TMA profile.

Figure 41: Shows a TMA plot for the quartz tube stage at heating rate of 10°C/min.

Six baseline samples were analyzed using TMA. Each of these samples were made by the hot uniaxial pressing technique. The samples were deliberately broken up because 1/2 inch diameter disks were too large to fit into the TMA chamber. Figure 42 shows TMA profiles for each of these baseline samples. Two scans was done on two pieces from sample 24. The processing parameters for these samples are shown in Appendix C, and some of the characterization data are shown in Appendix E. Each TMA plot shown in Figure 42 is shown separately in Appendix F without the initial probe distance subtracted out of them. All the samples were heated at a rate of 10°C/min under helium. The curves in Figure 42 were obtained by subtracting the initial probe distance from each profile. Figure 42 shows that the various AlMgB_{14} baseline samples have three common regions, which are numbered 1, 2, and 3. In region 1, the samples expand at a nearly constant rate from approximately 50°C to 400°C. At about 400°C the samples' expansion slopes changed. In region 2, some samples increased in expansion at a higher rate, while others first had some contraction and then expanded again. By region 3, which begins about 700°C, most of the samples expansion rates became nearly constant again. Samples 2 and 5 did not follow the same

Figure 42: TMA plot of for various AlMgB₁₄ Samples where the initial probe was subtracted from each plot.

behavior as the other samples. Both samples had their first change in expansion rate appear in region 3 and not in region 2. The changes in slope of these TMA plots suggests that a reaction is occurring. From what was previously known, the kinds of reactions that were occurring during the heating include the transformation of AlMgB₁₄ with Fe impurities to Al₂MgO₄ spinel and FeB compounds. None of same sample followed same exact expansion path and the two scans on sample 24 did not follow the same paths. The reason for the variation in path is that each sample had different thicknesses and the TMA was very sensitive to vibrations within the lab. Thus, a TMA plot from a run during when a furnace was on in the room would be slightly different from a TMA plot from a run when the furnace was off. Table 6 shows the thermal expansion coefficient over each region and the overall thermal expansion coefficient for each sample. The thermal expansion coefficients were calculated from the TMA plots in Appendix F and not from Figure 42. The reason was that the initial probe distance had to be used to calculate accurate thermal expansion coefficients. Region 1 on average had the lowest thermal expansion coefficients and region 3 had the

Table 6: Shows the thermal expansion coefficient of each region and overall coefficient for the samples in Figure 43.

Sample ID #	Region 1 (°C ⁻¹)	Region 2 (°C ⁻¹)	Region 3 (°C ⁻¹)	Overall (°C ⁻¹)
1	7.13*10 ⁻⁶	1.58*10 ⁻⁵	1.36*10 ⁻⁵	1.19*10 ⁻⁵
2	4.95*10 ⁻⁶	6.49*10 ⁻⁶	1.13*10 ⁻⁵	7.00*10 ⁻⁶
5	5.92*10 ⁻⁶	5.84*10 ⁻⁶	4.29*10 ⁻⁶	5.52*10 ⁻⁶
24 – 1 st Scan	6.13*10 ⁻⁶	6.01*10 ⁻⁶	1.11*10 ⁻⁵	7.26*10 ⁻⁶
24 – 2 nd Scan	6.77*10 ⁻⁶	9.83*10 ⁻⁶	1.5*10 ⁻⁵	1.01*10 ⁻⁵
26	5.91*10 ⁻⁶	3.66*10 ⁻⁶	1.06*10 ⁻⁵	6.48*10 ⁻⁶
70	5.68*10 ⁻⁶	1.26*10 ⁻⁵	1.02*10 ⁻⁵	9.28*10 ⁻⁶
Average	6.070*10 ⁻⁶	8.604*10 ⁻⁶	1.087*10 ⁻⁵	8.220*10 ⁻⁶

highest expansion coefficients. The average overall thermal expansion coefficient was 8.22*10⁻⁶ °C⁻¹. A black coating was observed on the quartz tube stage after each test. This coating came from the out gassing of samples during heating.

5.4 Differential Thermal Analysis

Differential thermal analysis (DTA) is a technique that measures the difference in temperature between an inert reference material and the sample being examined as a function of changing temperature [Dodd, 1987]. DTA data can be used to calculate enthalpy and specific heat values. The endothermic or exothermic behavior of a reaction can be measured by DTA. Figure 43 shows an example of an idealized DTA plot. An endothermic reaction occurs when the sample's temperature falls behind that of the reference while both the samples are being heated. An exothermic reaction can be identified when the temperature of the sample is greater than the reference sample. The change in enthalpy can be calculated from these DTA plots as shown in relationship 20. Enthalpy is the heat content of a material.

$$\pm \Delta H = \frac{A}{k * m} \quad (20)$$

Where, A = Area of minimum or maximum peak in DTA plot

k = Calibration constant

m = Mass of the sample

[Dodd, 1987].

Figure 43: An idealised DTA curve for an endothermic reaction [Akinc, 2000].

The specific heat can be calculated from the heating rate and the rate of change of enthalpy between the onset and ending temperature of each DTA peak. Relationship 21 shows how to calculate the specific heat of the material.

$$\Delta C_p = \frac{d}{\text{heating_rate} * m} \quad (21)$$

Where, d = Rate of change of enthalpy between the onset and ending temperature
 m = Mass of the sample

[Dodd, 1987].

DTA requires both the reference and sample to be slowly heated. Sample temperature will change when a reaction or transformation, such as change in crystal structure occurs. Ideally a minimum or maximum peak will be observed. Both the sample and reference are continually heated at a constant rate and after an “enthalpy event”, the sample eventually returns to the temperature of the reference [Dodd, 1987]. DTA has advantages in that DTA can handle both small and large samples, can go up to very high temperature, is very sensitive, and can directly measure enthalpy changes. Some sources of error are usually from

miscalibration of the DTA and the reference as well as vibrational effects. Figure 44 shows a schematic of the DTA device.

In this research, the DTA system was a Perkin Elmer DTA that provided data from room temperature to 1500°C. Only sample 24 was examined using DTA. The processing parameters for this sample is shown in Appendix C and basic characterization is shown in Appendix E. The sample was heated at a rate of 10°C/min from 30°C to 1475°C in an argon atmosphere. The mass of the sample was 18.450 mg. Figure 45 shows the DTA profile for Sample 24. The DTA profile shows that no significant endothermic or exothermic reactions occurred until 1045°C and this first reaction was small. Although the TMA analysis showed thermal expansion coefficients changes beginning at 400°C, no corresponding events are seen in this DTA plot at 400°C in AlMgB₁₄. The DTA shows that by 1045°C endothermic

Figure 44: Shows schematic of DTA [Akinc, 2000].

reactions begin and by 1316°C the material changes at a drastic rate. More research will have to be conducted with the DTA. Most of the peaks that occurred were endothermic reactions. A total of 4 peaks were observed. Table 7 shows the area of each peak, the change in enthalpy, the change of specific heat at that peak, the onset and ending temperatures. The DTA profile and data show that at temperatures higher than 1000°C AlMgB₁₄ materials are having some thermal induced reactions.

Figure 45: DTA profile for Sample 24. The profile was done under an argon atmosphere and a heating rate of 10°C/min.

Table 7: DTA data for Sample 24 for different endothermic peaks.

Peak #	Area (mJ)	ΔH (J)	ΔC_p (J/(g·°C))	Onset Temperature (°C)	Ending Temperature (°C)
1	11375.3	11.34	2.91	1045.3	1257
2	26939.7	26.86	18.14	1267.5	1348
3	2402.4	2.40	3.61	1349.9	1386
4	20882.1	20.83	14.34	1371.7	1450.6

5.5 X-ray Diffraction at Increasing Temperatures

An Iowa State research group led by Matt Kramer and Bill McCallum have constructed a low thermal gradient furnace x-ray diffractometer at the Advanced Photon Source (APS) Argonne National Laboratory. The design utilizes Debye-Scherrer geometry to apply high temperature x-ray powder diffraction at energies from 35 to 100 keV. The furnace has a maximum temperature of 1527°C. This x-ray diffractometer has capabilities for samples rotation, powder averaging that does not effect the thermal stability and

atmosphere. All the specifications, schematics and errors that correspond to this equipment can be found in reference by L. Margulies, M. J. Kramer and R.W. McCallum.

Two baseline samples were prepared for this analysis. The two samples were ground into micron-sized powder. The two samples were Sample 24 and Sample 84. The powders of these samples were vacuum sealed in 1 mm quartz tubes that have 2 mm thick walls. The two tubes were prepared for each sample, and the samples were sealed at Iowa State University. The quartz tubes were very fragile, and this caused subsequent problems. One tube from each sample broke during placement of the samples in the diffractometer. Both samples were heated in 50°C steps from 50°C to 1100°C. The temperature of each sample was allowed to equilibrate before a diffraction pattern was recorded at that temperature. An x-ray beam was directed through each sample at each temperature, making an exposure on an image plate at each temperature. The exposures were converted into intensity versus diffraction patterns. These image plates are shown in Appendix G. The diffraction patterns had to be converted to d-spacing by application of Bragg's law in order to compare these patterns with those obtained at Iowa State University. Relationship 22 is Bragg's law.

$$n\lambda = 2 * d * \sin(\theta) \quad (22)$$

Where, λ = Wavelength of the X-ray,

θ = Bragg's Angle = half of the diffraction angle

n = is the order of the diffracted beam and is numerically equal to the path difference for successive planes

d = d-spacing.

The wavelength for Cu-K α = 1.5406 Å had to be used to change reference diffraction patterns into intensity versus d-spacing plots. A calibration plot was made with a Si standard to find the wavelength of the x-ray beam used at Advanced Photon Source Argonne National Laboratories. This calibration is shown in Figure 46. An XRD exposure was done on this Si standard giving XRD pattern. A plot of the d-spacing of Si as a function of $(\sin(\text{diffraction angle}))^{-1}$ was constructed and it's shown in Figure 46. The diffraction angles were measured from the peaks that appeared in the Si XRD pattern. The slope of this plot is the wavelength of the x-ray beam at Advanced Photon Source (APS) Argonne National Laboratories. The wavelength of the APS Argonne National Laboratories x-ray beam was 0.31028 Å. This

Figure 46: Shows calibration plot to find the wavelength for the x-ray beam at Argonne National Laboratories. Calculated by Matt Kramer

wavelength was used to change the XRD patterns from APS Argonne National Laboratories into intensity versus d-spacing plots.

Figures 47 and 48 show the diffraction plots as a function of temperature. Also included in each figure are reference diffraction patterns. Both figures show that the diffraction patterns changed as the materials increased in temperature. Specifically both figures show that between the d-Spacing 1.75 Å and 2.3 Å, various diffraction peaks changed intensity. These diffraction peaks increased in intensity and/or disappeared. Also the figures show that each sample had AlMgB_{14} and Al_2MgO_4 spinel peaks throughout each heating transition.

Figure 47 shows Sample 24 x-ray diffraction patterns. Sample 24 is the only sample that was measured by TMA, DTA and x-ray diffraction at various temperatures. Figure 47 shows that sample 24 had iron impurities, and FeB formed in the processing prior to this x-ray analysis. Sample 24 had only significant interaction that occur between FeB, Al_2MgO_4 spinel, and Fe_3O_4 , which is shown in the square region in the figure. The diffraction patterns in Figure 47 showed that the AlMgB_{14} peaks did not change, but the other phase peaks did.

Sample 24's diffraction patterns are consistent with the TMA analysis, because the diffraction peaks began to change at 400°C, and then the peaks stop changing by 900°C. This is shown in the square region. This is similar to the three temperature regions in the TMA analysis, but in the TMA the third region began at about 700°C.

Figure 48 shows the diffraction patterns for Sample 84. In this figure, furnace lines had to be removed, because the intensity of these lines made the specimen lines difficult observe. Some portion of the x-ray beam struck the furnace walls due to a slight misalignment of the specimen, and this introduces "furnace lines" into the diffraction pattern. Figure 48, shows that changes in diffraction peaks did occur, but those changes happen to peaks that were not identified. Those peaks are shown in the ellipses in Figure 48. Some of those diffraction peaks disappeared by 400°C, and then by 900°C the diffraction patterns then show a constant pattern. Like the diffraction patterns shown in Figure 47, the diffraction patterns in Figure 48 follow the same pattern as the three region zones shown in the TMA analysis.

Figure 47: X-ray diffraction patterns at various temperatures for sample 24. The square shows changing intensity peaks as temperature increases. Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997].

Figure 48: X-ray diffraction patterns at various temperatures for sample 84. The ellipses show changing intensity of unidentified peaks as temperature increases. Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997].

CHAPTER 6: FURTHER CHARACTERIZATION

6.1 Four Point Probe Analysis of Baseline Samples

This chapter presents results from compositional analysis and electrical characterization that were done on baseline AlMgB₁₄ materials. A standard test to measure resistivity for material surfaces and thin film materials is the 4-point probe method. The 4-point probe technique (shown in Figure 49) consists of four equally spaced electrodes touching the linear surface of the sample. The four electrodes are supported by springs to prevent sample damage and to apply constant pressure [Constant, 2001]. The electrodes are made from either tungsten carbide or osmium. The 4-point probe used for this research used tungsten carbide tips. Usually, osmium tips are more expensive [Dai, 1997]. A current is applied through the outer electrodes and the resulting voltage drop is measured at the inner electrodes [Constant, 2001]. The assumptions that apply to the 4-point probe technique include the following: the semiconductor resistivity is uniform, the surface is flat, has a high recombination rate so that any minority carriers injected from the electrodes recombine close to the electrodes, the four probe contacts lie in a straight line, and the contact radii are small compared to the probe spacings [Constant, 2001]. A known current is applied, and the resulting voltage is measured. Resistance is obtained by applying Ohm's law, which is shown in equation 23:

$$R = \frac{V}{I} \quad (23)$$

Where, R = Resistance

V = Voltage

I = Current

The general relationship between resistance and resistivity for a bulk length of material is shown in equation 24:

$$R = \frac{\rho l}{A} \quad (24)$$

Where, l = Length through which current flows

A = Cross sectional area through which current flows

ρ = Resistivity

Figure 49: Schematic of the 4-Point Probe [Constant, 2001].

Relationship 24 must be adjusted to correct for errors associated with the AlMgB_{14} thickness and probe spacing having similar dimensions. A correction factor that specifically relates the geometry of the probe spacing, thickness of the sample, and the measured resistance is used.

The resistivity was obtained from equation 25:

$$\rho = 2\pi sRF \quad (25)$$

Where,
 F = Correction factor
 R = Resistance
 s = Probe spacing
 ρ = Resistivity [Runyan, 1975].

The correction factor, F , is dependent on both the probe spacing and the thickness of the samples, and this relationship is shown in equation 26.

$$F = \frac{t}{2s} \left[\ln \frac{\sinh\left(\frac{t}{s}\right)}{\sinh\left(\frac{t}{2s}\right)} \right]^{-1} \quad (26)$$

Where,
 t = Sample thickness
 s = Probe spacing [Runyan, 1975].

The conductivity can be calculated by taking the reciprocal of resistivity.

The procedure consisted of loading the sample into the fixture and attaching the cables to the 4 probes as outlined in Figure 49. A Keithley 237 Source-Measure unit was

used as the current source and a Keithley 614 Electrometer was used to measure the voltage. The Keithley 614 was zeroed when 0 current was applied. Next a current was applied, and the voltage was recorded. Then a different current was applied, and the voltage was recorded. A standard from the National Bureau of Standards was measured to determine the accuracy of this 4-point probe apparatus. This sample was isotropic graphite 12.7 mm in diameter and 1.11 mm thick. At room temperature the graphite sample was supposed to have a resistivity of $14.5 \times 10^{-6} \Omega\text{-m}$. The density of the graphite was 1730 kg/m^3 [Hust, 1984]. Table 8 shows the graphite specimen's applied current, measured voltage, resistance, the resistivity, and percent error based on the value given by the National Bureau of Standards. The correction factor (F) for this standard was calculated to be 0.464, and the spacing between the electrodes was 0.001588 m. The average resistivity was $1.609 \times 10^{-5} \Omega\text{-m}$, and the average percent error was 10.96 %. One possible source of error that may exist with these 4-point probe measurements was that their probe spacing roughly equals the thickness of the sample. The correction factor is most accurate when the probe spacing is much greater than the sample thickness or when the probe spacing is much smaller than the sample thickness.

Eight AlMgB_{14} baseline samples were measured by this method. Table 9 shows the thickness of the sample, the correction factor (F), the average resistance, and average resistivity for these eight samples. Table 9 shows values for resistivity range from as low as $8.11 \times 10^{-5} \Omega\text{-m}$ to as high as $28 \Omega\text{-m}$. The resistivities varied widely because sample 83 had hardly any iron impurities, while sample 35 contained large amounts of iron. This can be seen in their SEM micrographs, shown in Appendix H. Of the samples shown in Table 9, only samples 9, 35, 36, 80 and 83 were examined by SEM analysis.

Table 8: 4-Point Probe analysis of NIST Isotropic Graphite Standard.

Trial #	Applied Current (mA)	Voltage (mV)	Resistance (Ω)	Resistivity ($\Omega\text{-m}$)	Percent Error (%)
1	1	0.0032	0.0032	1.481E-05	2.14
2	5	0.018	0.0036	1.666E-05	14.91
3	10	0.036	0.0036	1.666E-05	14.91
4	50	0.175	0.0035	1.620E-05	11.72
5	100	0.348	0.00348	1.611E-05	11.08

Table 9: Shows the 4-Point Probe results for the AlMgB₁₄ baseline samples.

Sample ID #	Thickness (mm)	F	Average Resistance (Ω)	Average Resistivity ($\Omega\cdot\text{m}$)
9	2.17	0.751	414.72	3.104
15	2.30	0.775	115.95	0.895
16	1.90	0.694	7.827	5.414×10^{-2}
35	1.69	0.642	0.0127	8.11×10^{-5}
36	1.53	0.599	0.141	8.400×10^{-4}
72	1.93	0.701	0.428	2.99×10^{-3}
80	1.85	0.682	0.0367	2.496×10^{-4}
83	2.76	0.843	3248.82	27.30

6.2 van der Pauw Resistivity and Hall Effect

Another method used to find the resistivity of AlMgB₁₄ materials was to use the van der Pauw method. One can also find information on Hall coefficients, mobilities, and the number of charge carries and holes in each sample with this method. Assumptions had to be made to find this information, these were: the contacts were at the circumference of the sample, the contacts were sufficiently small, the sample was homogeneous in thickness, and the surface of the sample did not have any isolated holes [van der Pauw, 1958]. The apparatus consisted of a Walker Scientific T2 electromagnet, a sample holder, Keithley 237 Source-Measure unit as the current source, a Keithley 614 Electrometer to measure the voltage, and a computer to calculate and record the data. The sample was placed into the sample holder, and four electrodes were screwed into the edges of the sample. Figure 50 shows a schematic of a typical sample and the location of the contacts of the electrodes. The resistivity was first measured without a magnetic field. A current entered the specimen through electrode A and leaves through electrode B, which gives a resistance ($R_{AB,CD}$) while electrodes C and D gave a potential difference per unit current. Thus the resistances can be defined as ($R_{BC,DA}$) and ($R_{BD,AC}$) and can be related to the thickness and the resistivity by relationship 27.

$$\exp\left(-R_{AB,CD} \frac{\pi d}{\rho}\right) + \exp\left(-R_{BC,DA} \frac{\pi d}{\rho}\right) = 1 \quad (27)$$

Where, d = Thickness of the sample

Figure 50: Shows a schematic of the contact points for a sample in the van der Pauw method.

ρ = Resistivity.

A simple relationship can be derived from relationship 27 that gives the resistivity of the sample. From relationship 27 equation 28 can be derived.

$$\rho = \frac{\pi d}{\ln(2)} \left(\frac{R_{AB,CD} + R_{BC,DA}}{2} \right) f \frac{R_{AB,CD}}{R_{BC,DA}} \quad (28)$$

Where,

$$f \approx 1 - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right)^2 \frac{\ln 2}{2} - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right)^4 \left(\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^2}{12} \right)$$

[van der Pauw, 1958].

A magnetic field and current were applied, and a Hall probe was set next to the sample. Two potentials were calculated by relationships 29 and 30.

$$V_A = V_{CADB}^{(+B)} - V_{ACDB}^{(+B)} + V_{ACDB}^{(-B)} - V_{CADB}^{(-B)} \quad (29)$$

$$V_B = V_{DBAC}^{(+B)} - V_{BDAC}^{(+B)} + V_{BDAC}^{(-B)} - V_{DBAC}^{(-B)} \quad (30)$$

Where, $V_{i,j,k,l}^{(\pm B)}$ = the potential between the contacts labeled by the last two digits in the subscript (k-l), and the current is applied between the contacts labeled by the first two digits of the subscript (i-j), either in a positive, or negative magnetic field.

These potentials were used to get two different Hall coefficients, and an average Hall coefficient was calculated as shown in the following steps.

$$\begin{aligned}
 R_A &= \frac{(2.5 \times 10^7)d}{BI} * V_A \\
 R_B &= \frac{(2.5 \times 10^7)d}{BI} * V_B \\
 R_H &= \frac{R_A + R_B}{2}
 \end{aligned} \tag{31}$$

Where, d = Thickness of the sample

B = Magnetic Field

I = Current

The Hall coefficient was used to calculate the mobility and carrier concentration as shown in relationships 32 and 33.

$$\mu_H = \frac{|R_H|}{\rho} \tag{32}$$

Where, μ_H = mobility of n or p type charge carriers

$$n(p) = \frac{6.25 \times 10^{18}}{R_H} \tag{33}$$

Where, $n(p)$ = number of carriers per area, where the carrier are either charge carriers or hole carriers [Ndlela, 1989].

The standard from the National Bureau of Standards was measured, and its results were shown in Table 10. Seven measurements were made with a current of 50 mA.

Table 10: Resistivity results to the Isotropic Standard from the National Bureau of Standards using van der Pauw measurements.

Trial #	Resistivity (Ω -m)	Percent Error (%)
1	1.463×10^{-5}	0.90
2	1.465×10^{-5}	1.00
3	1.463×10^{-5}	0.90
4	1.461×10^{-5}	0.75
5	1.463×10^{-5}	0.92
6	1.462×10^{-5}	0.83
7	1.466×10^{-5}	1.06

The average resistivity of the standard measured by the van der Pauw technique was $1.463 \times 10^{-5} \Omega\text{-m}$, which gave an average percent error to the actual value at 0.89%. Compared to the 4-point probe technique, the van der Pauw method had greater accuracy in reproducing for the expected values for the NIST graphite standard. The major advantage to the van der Pauw method is that the sample can be of almost any shape just as long as the surfaces are flat. The major disadvantage to this method is that the thicker the sample, the less accurate the results. Specifically for the equipment used in this research, materials that have high resistance did not yield accurate and reliable measurements.

All of the samples that were examined in the 4-point probe method were examined by the van der Pauw method, but samples of high resistance did not yield reliable results. The baseline samples that gave reliable results were 35, 72, and 80. Table 11 shows their van der Pauw and Hall effect measurements. The error between the 4-point probe and the van der Pauw resistivity measurement are also included in Table 11. The average percent error between the 4-point probe technique and van der Pauw was 18.7% error for the three samples. The data show that n-type extrinsic doping was occurring in these materials, because intrinsic materials usually have $n(p)$ concentrations around 10^{10}cm^{-3} [Hummel, 1985]. A negative value for the Hall coefficient indicates that these baseline specimens were n-type. The data show that the mobilities were low. Possible reasons for the low mobilities are that the material was intermetallic, polycrystalline, had "hopping conducting" phases and had that different type of phases and impurities.

Table 11: Results for AlMgB_{14} baseline samples using van der Pauw method

Sample ID #	Average Resistivity ($\Omega\text{-m}$)	Percent Difference in Resistivity Between 4-Point Probe/van der Pauw (%)	Hall Coefficient (cm^3/C)	$n(p)$ (cm^{-3})	Hall Mobility (μ_H) ($\text{cm}^2/(\text{V-s})$)
35	7.1345×10^{-5}	12.02	-0.001194	5.872E+21	0.1676
72	2.0653×10^{-3}	31.0	-0.0065625	3.792E+20	0.08125
80	2.164×10^{-4}	13.18	-0.00095	2.044E+21	0.15025

6.3 Seebeck Effect for Baseline Samples

As described in section 4.6, previous research showed that single crystal AlMgB_{14} samples had a positive slope for Seebeck effect. A positive slope for Seebeck effect shows that the material displays p-type conduction, while a negative slope would show n-type behavior. Two different baseline samples were measured, samples 1 and 16. The samples were setup in a 2-point probe system that had an induction furnace coil around it. This apparatus was set up in a vacuum system. The samples were heated up at a rate of $10^\circ\text{C}/\text{min}$. Current was applied and change in voltage per change in temperature was measured. Each sample's plot is shown in Figure 51. Both plots show the baseline material to have p-type behavior, but one interesting feature was that Sample 1 went from n-type to p-type at about 120° . Earlier in the van der Pauw analysis, the baseline materials were shown to be n-type. This seems to contradict the Seebeck results and indicate that mixed conductivity (electrons and holes) exists. This data and previous data show that the AlMgB_{14} material may have

Figure 51: Seebeck plots for samples 1 and 16.

both p and n type characteristics at the same time. Comparison of these results with those from previous research shows that, the samples produced in this research had much smaller Seebeck values than the values in the past. The presence of iron and Al_2MgO_4 spinel impurities presumably result in lower Seebeck values in specimen 1 and 16.

6.4 Finding the Volume Fractions of Other Phases in AlMgB_{14} Baseline Materials

This particular part of the research is concerned with the amount and composition of phases. In 1848, A. Delesse designed the first quantitative method for microscopic analysis. He proved mathematically that the areas of the phases seen in a planar cross section within an aggregate mineral specimen are directly proportional to the volumes of those phases within the rock [Rhines, 1968]. Quantitative microscopy allows one to utilize a microscope image to characterize properties of that material. By providing knowledge of internal structure, quantitative microscopy can provide relationships between the constitution, physical properties, and behavior characteristics in materials. Measurements made with quantitative microscopy are often statistical in nature and are based on the assumption that the section under investigation is representative of the material as a whole. Characterization by this method cannot be made for such a limited section without this basic assumption. SEM pictures were recorded, scanned into a computer, and analyzed with imaging software to calculate the volume percent of AlMgB_{14} and other compounds within each sample.

The imaging software used was "NIH Image", and for best analysis the SEM pictures were converted into Tiff (TIF) format files. Each image was opened by the software and was calibrated to scale. The calibration procedure consisted of taking the scale marker and finding the number of pixels that represent a certain length that right magnification. After the calibration procedure, an area was selected and its total area was measured. Then the image was adjusted so that the phases being examined would be measured as the dark phase and the background shown as white. The threshold was activated which converted the image to black and white. The previous area was selected again, and the area was measured, giving the area of the black regions. Taking the second measurement and dividing by the first measurement gives the fraction of area of the examined phase. By Delasse's proof, one can

assume that the area % of a phase corresponds to volume % of that phase in the bulk material. This procedure is shown in Figure 52.

All the SEM micrographs were at a magnification of 1000X and were in backscattered electron mode. A total of 22 SEM pictures were examined, and each picture's analyzed data are shown in Appendix E, Table 6E. Table 12 shows the samples that were analyzed, the number of pictures for each sample, the average percent volume of AlMgB_{14} , and the average percent volume of other phases. It was assumed that the other phases consisted of Al_2MgO_4 spinel, FeB , and Fe_3O_4 , as described in Chapter 1. The table shows that samples vary drastically in the amount of other phases from 4% to 31%. Having such a variance in the content of each sample may account for the differences seen in hardness, density, thermal, and electrical properties in these specimens.

Figure 52: Quick procedure in measuring area of certain phases and setting up for future area calculations.

Table 12: Shows the results of phase analysis of each sample.

Sample ID #	Number of Pictures	Average Volume Percent AlMgB_{14}	Average Volume Percent Other Phase
8	4	75.2	24.77
12	2	69.3	30.73
24	2	82.9	17.08
27	1	72.5	27.46
28	1	96.2	3.83
36	1	72.9	27.08
78	3	87.4	12.56
80	2	69.4	30.62
83	6	94.4	5.58

CHAPTER 7: THE EFFECTS OF ADDITIVES

7.1 Procedures for Producing Additive Samples

Most products used in society are made from combinations of elements, compounds, composites, mixtures and blends. The purpose of forming these combinations of materials is to produce a material that gives the best properties for certain applications. It was shown in previous sections that AlMgB_{14} was influenced greatly by certain additives. The ISU research showed that AlMgB_{14} could have hardness increased by adding TiB_2 . Adding Ni to AlMgB_{14} , will increase its conductivity.

Different materials can be added to AlMgB_{14} to attain more desirable properties for different applications. This research considered four different alloying additives to AlMgB_{14} . After a preliminary study of hardness and density resulting from four alloying additives to AlMgB_{14} , two of these additives were selected for further investigations. The four alloying additive materials used in the initial study were titanium diboride (TiB_2), titanium carbide (TiC), aluminum nitride (AlN) and hexagonal boron nitride (h-BN). TiB_2 and TiC were chosen as alloying additives, because their high hardness and refractory properties that could enhance AlMgB_{14} . In addition, it was thought that Ti might diffuse into the AlMgB_{14} structure and change the Fermi level in the electronic band structure, possibly resulting in greater hardness. AlN was chosen because it is a material often used to clean impurities and react with oxygen. Hexagonal boron nitride was chosen because Spex mill processing might form amorphous phase, which would increase the hardness of the AlMgB_{14} materials.

Two different methods were used in producing these alloying additive samples. All these additive samples were made by hot uniaxial pressing techniques. The powder used in making these samples were contaminated by Spex milling. All the powders were kept in a glove box to minimize reaction with O_2 and/or H_2O vapor, and all the following procedures were done in inert atmosphere until completion of hot pressing. The first step was the same for both methods, producing standard baseline AlMgB_{14} powder. The powder loads for a standard baseline sample consisted of 74.69 wt% boron, 13.31 wt% aluminum and 12 wt% magnesium. These materials were placed in the mechanical alloying vial in an inert atmosphere in the glove box. Then the mechanical alloying vial was milled for 12 hours and

brought back into the glove box. After the milling, all the contents were cleaned out of the vial. The contents were separated as “loose” and “chunk” material. The first procedure (Procedure 1), developed by Joel Harringa at Iowa State, consisted of taking a load of milled B, Al, and Mg powder of the aforementioned proportions and putting it into a Spex vial; the chunk material was set aside. An amount of additive material was put into the Spex vial. The Spex vial would be milled for 30 minutes. All the material was cleaned out of the Spex vial and separated into two groups, loose and chunk material. A 1 gram load was put into the hot uniaxial press.

The second procedure (Procedure 2) consisted of taking a load of both loose and chunk B, Al, and Mg powder of the baseline proportions and putting it into a Spex vial. An amount of additive material was put into the Spex vial. The Spex vial was milled for about 4 hours. All the material was cleaned out of the Spex vial and separated as loose and chunk material. A 1 gram of loose powder was put into the hot uniaxial press. All the processing parameters for each of the additive samples are shown in Appendix D, and the basic characterization properties are shown in Appendix E.

7.2 Comparison of Hardness and Density between Baseline and Additive AlMgB₁₄ Materials

The amount of investigation into AlMgB₁₄ materials with alloying additives was dependent on hardness and density measurements. Microhardness was measured by a Vickers Tukon Tester in the ISU Metals Development Building, and density was measured by Archimedes' method.

At least two samples were made with each specific type of additive. A total of 30 AlMgB₁₄ with alloying additive samples were analyzed: 20 TiB₂, 5 TiC, 2 AlN, and 3 h-BN samples. Additive amounts ranged from 10wt% to 40wt%. Tables D2 – D4 in Appendix D show the specific processing parameters for the different samples used. Table 13 shows the type of alloying additive, the maximum and minimum hardness measured, and the average density measured for each sample that had alloying additives. Figure 53 shows a bar graph of the average hardness measured as a function of alloying additive, and the figure also shows a

line graph of the average density measured as a function of alloying additive. Average hardness and density for baseline composition AlMgB_{14} without additives is also shown in Figure 53 for comparison. Table 13 and Figure 53 show that materials made with TiB_2 alloying additives gave the highest hardness measurements. AlMgB_{14} materials that had TiC additives didn't change the hardness compared to the AlMgB_{14} baseline materials. All the AlMgB_{14} materials that contained either TiC or TiB_2 had an increase in density. AlMgB_{14} materials that contained either AlN or h-BN decreased hardness of AlMgB_{14}

Table 13: Shows maximum and minimum hardness and average density measured for various AlMgB_{14} materials with alloying additives.

Alloying Additive	Minimum Hardness (Vickers)	Maximum Hardness (Vickers)	Average Density (g/cm^3)
TiB_2	2435	4831	3.142
TiC	2191	3513	3.522
AlN	1746	2413	2.776
h-BN	452	1066	2.421

Figure 53: Average hardness as a function of alloying additive (bar graph) and average density as a function of alloying additive (line graph).

materials. AlMgB₁₄ materials that contained h-BN did not sinter well, which produced samples that had high porosity. From these results, it was decided to investigate further in to AlMgB₁₄ materials that contained TiC or TiB₂.

7.3 The Effects Caused by TiB₂ Additives

To observe how TiB₂ effects AlMgB₁₄, samples with different amounts of TiB₂ were made. A total of 20 samples with TiB₂ alloying additives were made: 3 at 10 wt%, 2 at 20 wt%, and 15 at 30 wt%. The decision to make a greater number of samples at 30 wt% of TiB₂ was motivated by earlier research at ISU that found that these samples gave hardness values exceeding 40 GPa. The samples made with lower weight percentages gave maximum hardness measurements between 30 and 38 GPa. Table 14 shows the maximum hardness, minimum hardness, and the average density values measured for each TiB₂ additive weight percentage. Table 14 shows that as the weight percentage of TiB₂ increases in AlMgB₁₄ materials, both the maximum hardness and the density increase. Table 1 in Chapter 1 listed the density of TiB₂ as 4.50 g/cm³. Figure 54 shows the plot of average hardness measured versus TiB₂ weight percentage. The beginning point of the plot in Figure 54 was the average hardness of AlMgB₁₄ baseline material, and the ending point was the average density for 100% TiB₂ bulk material from Table 1 in Chapter 1. Figure 54 shows that the average hardness of the 20 wt% TiB₂ samples was much greater than the 10% and 30% samples. This phenomenon occurred because the variance was larger since more 30 wt% samples were characterized, giving a much higher distribution of hardness measurements. The difference between the maximum and minimum values in Table 14 showed that 30 wt% samples had a larger range of hardness then the 20 wt% samples.

Table 14: Shows maximum and minimum hardness and average density measured for various AlMgB₁₄ materials with different amounts of TiB₂ alloying additives.

Amount of TiB ₂ (wt%)	Minimum Hardness (Vickers)	Maximum Hardness (Vickers)	Average Density (g/cm ³)
10	2503	3129	3.044
20	3275	3986	3.094
30	2776	4831	3.162

Figure 54: Shows a plot of average hardness measurements for different weight percentages of TiB₂

Figure 54 also shows that the hardness properties of AlMgB₁₄ materials with TiB₂ do not appear to follow the rule of mixtures principle. Both Figure 54 and Table 14 show that the hardness values of AlMgB₁₄ with TiB₂ additives were greater than the hardness values found for 100 wt% TiB₂.

Analysis of these specimens was made by SEM, EDS and XRD. Figure 55 shows SEM micrographs of standard baseline, micrograph (a.); sample with 10 wt% of TiB₂, micrograph (b.); and a sample with 30 wt% TiB₂ micrograph (c). The white phases that appear in micrograph (a.) were characterized in Chapter 1 as Al₂MgO₄-spinel. Micrographs (b.) and (c.) have arrows labeled 1 that show TiB₂ chunks, because EDS showed those phases only had Ti in them. These TiB₂ chunks appeared very bright in the backscattered mode than all the other phases due to the relatively high atomic number of Ti. EDS showed in micrographs (b.) and (c.) that the dark grey and black areas contained Al, Mg, and B, which was assumed to be AlMgB₁₄. In the other white phases, Fe, Al, Mg, and O appeared, which would be consistent with the presence of both iron oxide, iron boron and Al₂MgO₄ spinel in

Figure 55: SEM pictures of AlMgB₁₄ in backscattered electron mode at 1000X. Micrograph (a.) is a standard baseline (Sample 83), micrograph (b.) has 10 wt% of TiB₂ (Sample 41), and micrograph (c.) has 30 wt% of TiB₂ (Sample 7).

the samples. The phases other than TiB₂ chunks in micrographs (b.) and (c.) had the same features as the phases in micrograph (a.), which was standard baseline material. The SEM micrographs showed that larger TiB₂ phases appeared in the SEM micrographs as the wt% of TiB₂ increases. The XRD plots in Figure 56 on page 95 appear to indicate that AlMgB₁₄ samples with TiB₂ additives contained some AlMgB₁₄, TiB₂, Al₂MgO₄ spinel, FeB, and Fe₃O₄ phases, although the complexity if the XRD attains and the superposition of several key peaks makes definitive interpretation difficult. Figure 56 shows that as the composition of TiB₂ increases, the other phases' peaks appear to diminish in intensity. The TiB₂ peaks' intensity did not change much. The reason that the TiB₂ intensity peaks were more visible then the AlMgB₁₄ peaks was the amount of B. The higher amount B in a compound the lower the scattering and the intensity of reflected x-rays beams.

TiB₂ alloying additives also had a major effect on the electrical properties. Table 1 in Chapter 1 showed that pure TiB₂ has resistivity ranging between $1 \cdot 10^{-7}$ to $2 \cdot 10^{-7} \Omega\text{-m}$. Nine AlMgB₁₄ samples with TiB₂ alloying additive were analyzed using the 4-point probe and van der Pauw techniques described in Chapter 6. Table 15 shows the 4-point probe results and Table 16 shows the van der Pauw results. Table 15 presents the amount of TiB₂ alloying additive, thickness, correction factor (F), and average resistivity found for the nine samples

using 4-point probe. The overall average resistivity for samples with 10 wt% of TiB_2 was $3.60 \times 10^{-3} \Omega\text{-m}$, for samples with 20 wt% of TiB_2 was $2.79 \times 10^{-4} \Omega\text{-m}$, and for samples with 30 wt% of TiB_2 was $7.92 \times 10^{-5} \Omega\text{-m}$. A plot of these overall average resistivities versus composition is shown in Figure 57. The overall averages for 4-point probe and the values shown in Table 15 suggest that the greater the wt% of TiB_2 added to AlMgB_{14} , the lower the resistivity. This seems reasonable since TiB_2 has resistivity values close to $10^{-7} \Omega\text{-m}$. Table 16 shows the van der Pauw results for the same samples and the percent difference between the two different techniques. The average percent difference between the two techniques was 25.1% for these samples. These overall averages and the values shown in Table 16 indicates that adding TiB_2 to AlMgB_{14} the lowers the resistivity. Compared to the baseline results presented in Chapter 6, samples with TiB_2 have lower resistivities than samples of baseline composition. The data show that both n-type and p-type extrinsic doping was occurring in these samples, because the Hall coefficient values were negative for samples with 10 wt% and 20 wt% of TiB_2 , and the Hall coefficient was both positive and negative for 30 wt% of TiB_2 . Doping with resulted in primarily n-type conductivity, but like the baseline results presented in Chapter 6 they showed both n-type and p-type characteristics. A large amount of variation occurred in the mobility data. A major reason for the variation is that all

Table 15: Shows 4-point probe results for TiB_2 alloying additive samples.

Sample ID #	Amount of TiB_2 (wt%)	Thickness (mm)	F	Average Resistivity ($\Omega\text{-m}$)
7	30	1.4	0.560	4.86×10^{-5}
38	20	1.3	0.529	3.37×10^{-4}
39	20	1.78	0.665	2.22×10^{-4}
40	10	1.99	0.714	1.60×10^{-3}
41	10	2.3	0.774	5.59×10^{-3}
42	30	1.95	0.705	4.62×10^{-5}
43	30	1.77	0.663	1.80×10^{-5}
64	30	1.87	0.687	1.97×10^{-4}
65	30	1.84	0.680	8.55×10^{-5}

Figure 56: Measured X-ray diffraction patterns for AlMgB₁₄ materials with various alloying additive compositions of TiB₂. Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997]

Table 16: Shows van der Pauw results for TiB₂ alloying additive samples.

Sample ID#	Amount of TiB ₂ (wt%)	Average Resistivity (Ω -m)	Percent Difference (%)	Hall Coefficient (cm^3/C)	n(p) (cm^{-3})	Hall Mobility ($\text{cm}^2/\text{V-s}$)
7	30	3.68×10^{-5}	24.4	4.87×10^{-3}	$9.98\text{E}+20$	1.704
38	20	1.61×10^{-4}	52.2	-2.98×10^{-4}	$9.96\text{E}+20$	0.395
39	20	1.59×10^{-4}	28.7	-4.25×10^{-4}	$9.64\text{E}+20$	0.411
40	10	1.94×10^{-3}	21.4	-2.31×10^{-3}	$1.22\text{E}+21$	0.044
41	10	4.33×10^{-3}	22.5	-0.135	$8.50\text{E}+19$	0.382
42	30	3.64×10^{-5}	21.2	5.44×10^{-4}	$1.37\text{E}+21$	1.280
43	30	1.52×10^{-5}	15.4	2.70×10^{-4}	$1.65\text{E}+21$	2.532
64	30	1.35×10^{-4}	31.4	3.49×10^{-3}	$8.78\text{E}+20$	0.529
65	30	7.84×10^{-5}	8.3	-3.05×10^{-3}	$1.24\text{E}+21$	0.652

Figure 57: Plot of average resistivities versus composition of TiB₂ alloying additive. The y-axis is a log scale and the x-axis is a linear scale.

the samples contain different amounts of various phases. XRD showed that each sample appeared to contain AlMgB₁₄, TiB₂, Al₂MgO₄-spinel, FeB, and Fe₃O₄ phases.

Samples 6 and 67 were both analyzed using TMA; each sample contained 30 wt% TiB₂. Sample 67 had x-ray diffraction performed over the temperature range from room temperature to 1100°C. The TMA analysis used the procedure described in Chapter 5, section 5.3. Three TMA runs were conducted, one on sample 6 and two on sample 67. The heating rate was 10°C/min for a heating range from 50°C to 950°C in flowing helium gas.

Figure 58 shows the TMA plots for these samples, where the initial probe position was subtracted to get all TMA plots on the same graph. Appendix F, Figures F4, F9, and F10 show the individual TMA plots and from these plots the thermal expansion coefficients. Figure 58 shows that Sample 6 had an observable change in the thermal expansion coefficient in the location where Arrow A points, which was about 500°C. This point separates Sample 6's TMA plot into two regions, Region 1A and Region 2A. In Region 2A, Sample 6 had an increase in the expansion coefficient. Sample 6 shows only one slight reaction occurring, which was different than the baseline TMA runs in Chapter 5. The data for Sample 6 seems to indicate that the TiB_2 stabilized the AlMgB_{14} materials. The two TMA runs of Sample 67 showed sharply different behavior. The TMA plots for Sample 67 show that four observable changes occurred giving 4 different regions: Region 1B, Region 2B, Region 3B, and Region 4B. Region 1B started at 50°C and ends at about 350°C. Then the expansion coefficient increased in Region 2B for one TMA run, but the other TMA run showed that the thermal expansion coefficient does not change until the end of Region 2B. Region 2B ends at roughly 630°C where the material began to contract giving a negative expansion coefficient in Region 3B. At roughly 700°C, Sample 67 began to expand again where Region 3B ended and Region 4B began. Sample 67 suggests that the TiB_2 decreased the stabilization of AlMgB_{14} materials as temperature increases in comparison to the AlMgB_{14} baseline samples in Chapter 5. These dissimilar behaviors in the temperature variation of the thermal expansion for samples 6 and 67 is probably attributable to variations in the vol% of the several kinds of phases that appeared in the microstructures observed in the SEM pictures in Figure 55. Table 17 shows the temperature ranges for each region, the thermal expansion for each range in each region, and the overall thermal expansion of each sample. The average thermal expansion coefficient for the three runs from 50°C to 950°C was $7.13 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. The average thermal expansion coefficient for the same temperature range for AlMgB_{14} baseline materials presented in Chapter 5 was $8.22 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. The materials with the TiB_2 additive had a slightly smaller overall thermal expansion coefficient for the 50° to 900° than the baseline samples.

Figure 58: TMA plots of AlMgB_{14} materials with 30 wt % of TiB_2 alloying additive where the initial probe was subtracted from each plot. Arrow A indicates where Sample 6 has a change in thermal expansion coefficient and splits Sample 6 TMA into Region 1A and Region 2A. For Sample 67 four regions within its two TMA runs are marked.

Table 17: TMA results for AlMgB_{14} materials with 30 wt% TiB_2 . Results from Figure 58.

Sample ID #	Region	Temperature Range (°C)	Thermal Expansion Over Region (°C ⁻¹)	Overall Thermal Expansion (°C ⁻¹)
6	1A	50-500	6.73×10^{-6}	8.44×10^{-6}
	2A	500-900	10.3×10^{-6}	
67-1 st Run	1B	50-350	7.30×10^{-6}	5.703×10^{-6}
	2B	350-630	7.98×10^{-6}	
	3B	630-706	-16.04×10^{-6}	
	4B	706-950	7.97×10^{-6}	
67-2 nd Run	1B	50-350	8.67×10^{-6}	7.24×10^{-6}
	2B	350-630	12.97×10^{-6}	
	3B	630-706	-10.52×10^{-6}	
	4B	706-950	4.390×10^{-6}	

X-ray analysis at various temperatures was done at the Advanced Photon Source (APS) at Argonne National Laboratory. Figure 59 shows the diffraction plots taken at 12 different temperatures for Sample 67. The procedures found in section 5.5 of Chapter 5 were used for this x-ray analysis. Also included in this figure are reference diffraction patterns. All the XRD data were plotted as intensity versus d-spacing. Sample 67 diffraction plots show that the TiB_2 peaks were the most intense and did not change as the temperature increased. Also the plots show that Sample 67 had all the impurity phases commonly found in AlMgB_{14} materials with TiB_2 alloying additives, and these peaks also do not change. The intensity of the AlMgB_{14} peaks were lower than the TiB_2 peaks. The reason for this is that the powder analyzed may have had a much higher content of TiB_2 and smaller amount of AlMgB_{14} . In addition variation in the amount of boron may have contributed to the difference in intensity. The higher number of boron atoms the lower the intensity peaks in XRD. The diffraction patterns show no observable changes occurred as temperature increases.

7.4 The Effects Caused by TiC Additives

The analysis of the effects caused by TiC alloying additives consisted of hardness, density, SEM and EDS, 4-point probe, van der Pauw, and TMA measurements. Five samples with TiC alloying additive were made: one at 12.7 wt%, two at 20wt%, and two at 40 wt%. The five samples were designated 48, 49, 52, 53, and 54. Two other samples, 50 and 51, were made with 30 wt% of TiC, but these samples were contaminated and gave poor results in both hardness and density. Table 18 shows the wt% of TiC additive, the maximum hardness, the minimum hardness, and the average density. Figure 60 shows a plot of average hardness versus composition of TiC alloying additive. Table 18 shows that AlMgB_{14} materials with TiC alloying additives had about the same hardness values as baseline samples, but samples with TiC alloying additives had higher densities. Also shown was that AlMgB_{14} samples made with 20 wt% of TiC had the highest hardness measurements for AlMgB_{14} materials made with TiC alloying additives. The beginning point of the plot in Figure 60 was the average hardness of AlMgB_{14} baseline material and the ending point was

Figure 59: X-ray diffraction patterns at various temperatures for sample 67. Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997].

the average density for 100% TiC bulk material taken from the literature (see Table 1 in Chapter 1). Figure 60 shows that hardness for AlMgB₁₄ materials made with TiC additives do not follow a rule of mixture relationship and shows no meaningful pattern. The hardness and density variation seen in among these five specimens is thought to reflect processing and porosity differences rather than true variations attributable to the TiC content.

Table 18: Shows hardness and density for various AlMgB₁₄ samples with TiC alloying additives.

Sample ID #	Amount of TiC (wt%)	Minimum Hardness (Vickers)	Maximum Hardness (Vickers)	Density (g/cm ³)
48	20.00	2622	3261	3.767
49	20.00	3193	3513	3.745
52	40.00	2349	3065	3.507
53	40.00	2526	3160	3.5816
54	12.71	2191	3035	3.01

Figure 60: Shows average measured hardness versus composition of TiC alloying additive. The hardness value at 100% TiC is from the literature.

XRD was not attempted on AlMgB_{14} materials that had TiC alloying additives. However, extensive analysis by SEM and EDS was done. Figure 61 shows SEM and EDS scans for Sample 54, which had 12.71 wt% TiC. The EDS scans performed on the various phases within the microstructures in Figure 61 were typical for the different samples that had different amounts of TiC additives. Each arrow indicates the location of the EDS scan taken within the SEM picture. The SEM was unable to detect boron, since boron 2-5 is too light to give a measurable x-ray signal. EDS scan (a) in Figure 61 shows the elements of the darkest phase, assumed to be AlMgB_{14} . EDS scan (b) shows the elements of a white phase that has some iron impurities. EDS scan (c) shows the elements of a light grey phase that has high amounts of Ti and C. EDS scan (.) shows the elements of a dark grey phase that was also assumed to be AlMgB_{14} with Ti impurities.

Comparing this SEM picture to previous baseline pictures, the TiC alloying additives refine the phase size within these AlMgB_{14} materials. It was also observed from SEM photographs of AlMgB_{14} samples with TiC additives that most of the phases contained Al, Mg, B, Ti, O, and C. None of the phases contained had TiC exclusively. This was different from the materials made with TiB_2 additives, because those samples had larger TiB_2 particles that were large enough to contain the entire electron activated volume within one phase. Figure 62 shows SEM pictures of AlMgB_{14} materials that had different amounts of TiC alloying additives. Picture (a) shows a SEM photograph of a sample that had 12.71 wt% of TiC alloying additive, picture (b) shows a SEM photograph of a sample that had 20 wt% of TiC alloying additive, and picture (c) shows SEM photograph of a sample that had 40 wt% of TiC alloying additive. Figure 63 shows that the microstructures in picture (b) had finer phase size than the microstructures in photograph (a). The microstructures in photograph (c) were smaller than both (a) and (b). Photograph (c) had the least amount of dark phase particles, while picture (a) had the most dark phase particles. This means that as the amount of TiC increased, the size of phases in the microstructures decreased, and the number of dark phase particles decreased. This pattern was different from the materials with TiB_2 alloying additives. As the amount of TiB_2 increased, larger TiB_2 phase regions were observed.

Figure 61: SEM and EDS pictures of Sample 54, which had 12.71 wt% of TiC alloy additives. Each EDS plot shows elements of a different phase. SEM micrograph was taken in backscattered electron mode at 1000X. (a.)-Black Phase, (b.)-White Phase, (c.)-Light Grey Phase, and (d.)-Dark Grey Phase.

Figure 62: SEM of AlMgB_{14} samples with different amounts of TiC alloying additives. SEM pictures were taken in backscattered electron mode at 1000X. (a.)-Sample 54 had 12.71 wt% of TiC, (b.)-Sample 48 had 20 wt%, and (c.)-Sample 52 had 40 wt% TiC.

TiC alloying additives also had a major effect on the electrical properties. Table 1 in Chapter 1 shows that single phase TiC has a resistivity of $1.05 \times 10^{-6} \Omega\text{-m}$. Four AlMgB_{14} samples out of the five with TiB_2 alloying additive were analyzed using the 4-point probe and van der Pauw techniques described in Chapter 6. Table 19 shows the result from 4-point probe analysis and Table 20 shows the results from van der Pauw analysis, which is on page 105. Table 19 presents the amount of TiC alloying additive, thickness, correction factor (F), and average resistivity found for the 4 samples using 4-point probe. The overall average resistivity for samples with 12.71 wt% of TiC was $7.56 \times 10^{-5} \Omega\text{-m}$, for samples with 20 wt%

Table 19: Shows 4-point probe results for TiC alloying additive samples.

Sample ID #	Amount of TiC (wt%)	Thickness (mm)	F	Average Resistivity ($\Omega\text{-m}$)
48	20	1.47	0.581	9.51×10^{-6}
52	40	1.60	0.618	7.51×10^{-6}
53	40	1.75	0.658	7.71×10^{-6}
54	12.71	1.75	0.663	7.56×10^{-5}

of TiC was $9.51 \times 10^{-6} \Omega\text{-m}$, and for samples with 40 wt% of TiC was $7.61 \times 10^{-6} \Omega\text{-m}$. A plot of these overall average resistivities versus composition is shown in Figure 64. These overall averages and the values shown in Table 19 suggest that as more TiC was added to AlMgB_{14} resistivity decreased, which was similar to the results of the TiB_2 additive materials. Table 20 shows the van der Pauw results for the same samples and the percent difference between the 4-point probe and van der Pauw techniques for each sample. The average percent difference between the two techniques was 22%. The overall average resistivity measured by the van der Pauw method for samples with 12.71 wt% of TiC was $5.96 \times 10^{-5} \Omega\text{-m}$, for samples with 20 wt% of TiC was $7.81 \times 10^{-6} \Omega\text{-m}$, and for samples with 30 wt% of TiC $5.75 \times 10^{-6} \Omega\text{-m}$. A plot of these overall average resistivities versus composition is shown in Figure 63. These overall averages and the values shown in Table 20 also suggest that as more TiC was added to AlMgB_{14} the resistivity decreased markedly. Samples with TiC tended to have much lower resistivities than samples that were AlMgB_{14} baseline in Chapter 6, which is to be expected in light of the low resistivity of the TiC phase. The data in Table 20 show that with increasing amounts of TiC, the material becomes p-type, because the Hall coefficients increased. Also the hole (p) concentration and the mobility increased.

TMA was done on one sample that had TiC alloying additive, Sample 49, which had 20 wt% of TiC. Figure 64 shows the TMA plot of this sample. All the thermal expansion coefficients were calculated from Figure F8 in Appendix F. Sample 49's TMA plot shows similar results to the baseline AlMgB_{14} samples' TMA plots. Sample 49's TMA plot can be

Table 20: Shows van der Pauw results for TiC alloying additive samples.

Sample ID#	Amount of TiC (wt%)	Average Resistivity ($\Omega\text{-m}$)	Percent Difference Between Methods (%)	Hall Coefficient (cm^3/C)	$n(p)$ (cm^{-3})	Hall Mobility ($\text{cm}^2/\text{V-s}$)
48	20	7.81×10^{-6}	17.9	1.01×10^{-3}	$2.40\text{E}+21$	1.29
52	40	5.85×10^{-6}	22.1	2.18×10^{-4}	$2.73\text{E}+21$	3.95
53	40	5.66×10^{-6}	26.5	2.13×10^{-3}	$2.96\text{E}+21$	3.75
54	12.71	5.96×10^{-5}	21.1	-4.17×10^{-3}	$1.50\text{E}+21$	0.70

Figure 63: Average resistivities versus composition of TiC alloying additive. The y-axis is a log scale and the x-axis is linear scale.

split into three regions, because at two different locations in the plot noticeable changes to the thermal expansion coefficient occurred. Region 1 was from 50°C to 390°C, and the thermal expansion coefficient for that region was $7.55 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Region 2 was from 390°C to 755°C, and the thermal expansion coefficient for this region was $14.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. Region 3 was from 755°C to 950°C, and the thermal expansion coefficient for this region was $10.4 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. The overall thermal coefficient from the TMA plot was $10.9 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$.

Figure 64: TMA plot of Sample 49. Sample 49 contained 20 wt% of TiC of alloying additive. Heating rate was 10C°/min, in flowing helium gas from 50°C to 950°C.

CHAPTER 8: HOT ISOSTATIC PRESSING VERSUS HOT UNIAXIAL PRESSING

8.1 Description of Pressing Techniques

All of the experimental research for this project described in the previous chapters has been performed on samples that were made by hot uniaxial pressing (HUP). The HUP system consists of a hydraulic press, vacuum system, induction furnace coil, graphite dies, h-BN lubricant aerosol spray and push rods. Figure 65 shows a schematic of the HUP system, which is positioned inside a vacuum chamber. The HUP system used for this research was

Figure 65: Schematic of the hot uniaxial pressing system. Force is applied along the vertical axis on the specimen.

designed and constructed by Bruce Cook and Joel Harringa at Iowa State University. Mechanical alloying was used to produce AlMgB_{14} powder batches. Before the powder was placed into the die between the push rods, the graphite push rods and the die were coated with h-BN lubricant. This prevented the carbon graphite from reacting with the AlMgB_{14} and helped to release the sample from the graphite die when the pressing was done. The specimen powder was placed into the graphite die and rod apparatus in a He filled glove box. The loaded assembly was then removed from the glove box and placed within the vacuum chamber of the press directly under the steel push rod. Once in place, an induction furnace coil was set around the die. The hydraulic press applied pressure on the steel push rod, which applied pressure on the graphite rods and compressed the powder. The induction furnace coil supplied the heat. The vacuum system consisted of a rotary pump and a diffusion pump. Pressures of $10^{-5} - 10^{-7}$ torr were obtained. The HUP method produced 1 to 3 gram samples.

For AlMgB_{14} materials to be useful in industry, AlMgB_{14} needs to be produced in larger amounts, while maintaining good quality. A method that can produce a larger quantity of material is the hot isostatic pressing technique. "Hot isostatic pressing (HIP) is the process of forming or bonding materials at high temperatures with high pressures acting on all surfaces simultaneously and equally [Zimmerman, 1983]." The process consists of putting a sealed vessel full of the material to be pressed into a high temperature furnace enclosed in a pressure chamber. The system is evacuated. Then an inert gas is applied in the pressure chamber to establish an initial pressure. A HIP run begins by heating the material to a certain temperature and holding it there.

For the HIP trials performed on AlMgB_{14} materials in this research, the heating rate was $10^{\circ}\text{C}/\text{min}$, and the maximum temperature of the pressing was between 1400 and 1450°C . At maximum temperature, more inert gas was put into the system, which applies high pressure to all the external surfaces of the sealed vessel. The maximum pressure was 44.5 ksi. At higher temperatures the sealed vessel becomes more ductile, making it more susceptible to deformation. After a certain time at high temperature and high pressure, the furnace is allowed to cool, the inert gas is evacuated from the pressure chamber, and air is allowed back into the pressure chamber. The sealed vessel is then opened and the pressed material is taken out and examined. Figure 66 shows a schematic of a HIP. The closures

Figure 66: Schematic of a HIP Furnace System [Zimmerman, 1983].

on the figure are the entrances to the pressure vessel. The work piece is the sealed vessel containing the pressed material. The element is the heating source of the system. The thermal barrier isolates the heat from the pressure chamber. The major advantage to the HIP technique is that more material can be produced than in the HUP method, and products from HIP are more completely densified. This improves the mechanical properties. The main disadvantage with HIP is that a suitable material has to be chosen for the sealed vessel that doesn't react with the material being pressed. It must also withstand the temperature and pressure applied during a press run. Another disadvantage is that seals on the vessel holding

the material must be free from defects or holes, and they need to be strong enough to withstand the temperature and pressure applied during a press run.

The HIP system used in this research was an Eagle HIP constructed by International Pressure Service. The gas used to apply the pressure was high purity argon. The system can apply pressures up to 44.5 ksi. The furnace used was a cylindrical graphite furnace. The highest temperature this furnace can reach is 1850°C [Wheelock, 2001]. The material used for the sealed vessel was tantalum. The sealed vessel dimensions were approximately 1 inch in height and 3/4 inch in diameter. A graphite film was placed within the sealed vessel to be a barrier between the powdered material and the tantalum. The powdered material was either a mixture of the elemental constituents or a mechanically alloyed mixture of the elemental constituents of AlMgB₁₄ materials. Once the powder was placed in the tantalum vessel, the vessel was sealed by electrical beam welding (EBW).

8.2 Processing Parameters and Success/Failure of Each HIP Sample

HIP was attempted on a total of seven samples. Three samples were made of turbula mixed powder, two samples were made with material processed by planetary mechanical alloying, and two samples were made with material processed by Spex mechanical alloying. The specific processing parameters of each sample are shown in Table I1 and Table I2 in Appendix I. Six of the samples were made from powder batches weighed out for baseline AlMgB₁₄, and the seventh sample was made from powder batches with 30wt% TiB₂ alloying additive. The TiB₂ alloying additive sample was HIP-7. The three HIP samples (HIP-1, HIP-2, and HIP-3) were made from a single batch of turbula mixed that was blended for 30 minutes. The two HIP samples, HIP-4 and HIP-5, made with Planetary powder came out of the same batch, which was milled for 100 hours. Sample HIP-6 was made from six Spex milled powder batches that were milled for 12 hours each. Sample HIP-7 was made from a combination of several Spex milled powder batches that were milled for a total of 16 hours. Each of the powder batches used to make HIP-7 had 30 wt.% of TiB₂ and followed the processing Procedure 1 described in section 7.1 of Chapter 7. Table 21 shows the pressing temperature, the success of making the sample, and, in those specimens that failed, the cause of the failure. Each sample had about 5 g of powdered materials loaded into the can, was pressed for 1 hour at the pressing temperature, and the maximum applied pressure was 44.5

ksi. One failure type that was observed was that the vessels did not compress during the run. Two possible reasons could cause this failure. The first possible reason was that the turbula mixed powder had a large amount of moisture. The moisture evaporated and caused the tantalum vessel to expand and not contract. This is believed to be the case for HIP-1 and HIP-2. For HIP-3 the turbula powder was heated in an oven and out gassed before loading it in the tantalum vessel to remove any moisture. The second reason that the tantalum vessel

Table 21: Pressing temperatures and results in AlMgB₁₄ HIP trial materials.

Sample ID #	Pressing Temperature (°C)	Success/Failure	Description of Failure
HIP-1	1400	Failure	vessel did not compress.
HIP-2	1400	Failure	vessel did not compress.
HIP-3	1450	Success	N/A
HIP-4	N/A	Failure	Had a bad weld on the vessel's seals.
HIP-5	N/A	Failure	Had a bad weld on the vessel's seals.
HIP-6	1450	Failure	vessel did not compress.
HIP-7	1450	Partial-Success	N/A

did not shrink would be either a hole or crack in the tantalum vessel or its weldmelt hat allows the inert gas into the can thereby relieving the pressure on the tantalum vessel and the powder within. The second reason seemed applicable to HIP-6. The other type of failure was a bad weld before the run was started. Specimens HIP-4 and HIP-5 had bad welds; the material was exposed to the air and press run was not attempted. It was assumed the Mg and Al oxidized, and the material would form Al₂MgO₄-spinel. The bad welds occurred because small powder particles clung to the edges of the seal, and that prevented the weld from forming properly. Sample HIP-3 was successful and sample HIP-7 was partially-successful. The explanation for HIP-7 will be discussed in the characterization section.

8.3 Characterization of Successful HIP Samples

After the HIP runs, samples HIP-3 and HIP-7 were removed from their tantalum vessels. The tantalum vessels were very brittle after the press run. Pliers were used to break the tantalum vessels away from the samples. The HIP samples were sanded off with a Dremel tool to remove the adhering graphite foil. The samples were cut into flat segments

by a high-speed diamond saw. The flat segments of each sample were polished and characterized for hardness and density and by XRD, SEM and EDS, and TMA. Table 22 shows the range of hardness and an average density. This table shows that the HIP specimens' hardness values lie within the usual range of hardness of baseline specimens, but do not reach extreme hardness values. HIP-7 was a TiB_2 alloying additive sample but did not reach the high hardness observed in the TiB_2 additive samples produced by the HUP technique.

Table 22: Shows maximum and minimum hardness and average density measured for the two successful HIP samples.

Sample ID #	Minimum Hardness (Vickers)	Maximum Hardness (Vickers)	Density (g/cm^3)
HIP-3 (baseline)	2480	2723	2.61
HIP-7 (w. 30% TiB_2)	2647	3096	3.37

Figure 67 shows a SEM picture and EDS scans at different location within the SEM picture for sample HIP-3. The SEM picture shows that large and small white phases appeared through out the microstructure. EDS scan (a.) shows the elements in the dark phase (matrix). This phase was assumed to be AlMgB_{14} . EDS scan (b.) shows the elements in the white phase. This phase was assumed to be Al_2MgO_4 -spinel. SEM analysis of HIP-3 showed that it had phases similar to those seen in the baseline samples produced by the HUP techniques. Figure 68 shows a SEM picture and EDS scans for sample HIP-7. The SEM picture shows that HIP-7 had large TiB_2 phases throughout its microstructure. These TiB_2 phases were larger than the phases found in the TiB_2 alloying additive samples produced by the HUP technique. EDS scan (b.) shows the elements in a dark grey phase. This grey phase had Al, Mg, Fe, and Ti. It was assumed that this phase was AlMgB_{14} with Fe and Ti impurities although the activated volume beneath the sample surface may include unseen TiB_2 particles that are contributing to the Ti peak intensity. EDS scan (c.) was taken from the darkest phase found in HIP-7. The scan shows only Al, and Mg. This was assumed to be the purest form of AlMgB_{14} in HIP-7. It was difficult to find any Al_2MgO_4 -spinel phase within the microstructures in HIP-7.

Figure 67: SEM micrograph in backscattered mode for sample HIP-3. EDS scans (a.) and (b.) were taken from the locations indicated by the arrows.

Figure 68: SEM micrograph in backscattered mode for sample HIP-7. EDS scans (a.), (b.), and (c.) were taken from the locations indicated by the arrows.

Figure 69 shows the XRD patterns for HIP-3 and HIP-7. Figure 69 also shows XRD reference patterns. The XRD pattern for HIP-3 only shows the peaks for AlMgB₁₄ and the Al₂MgO₄-spinel. The AlMgB₁₄ peaks were the most intense from this pattern. This XRD pattern, the SEM, EDS, hardness and density show that it was possible to make AlMgB₁₄ by using HIP with mixed powder of elemental constituents. Two peaks were not identified as shown in the figure. Also within these XRD patterns a peak was caused by the diffractometer, which was labeled as machine peaks. The HIP-7 XRD pattern shows that TiB₂ had the most intensity. HIP-7's XRD pattern shows only the TiB₂, and FeB peaks. Table 22 shows that the density of the HIP-7 sample was greater than the average density of TiB₂ additive samples produced by HUP, in Chapter 7, in Table 13. The XRD pattern would suggest that sample HIP-7 had more TiB₂ content to the point that the AlMgB₁₄ intensity peaks were not viewable in the XRD pattern. The SEM showed that only a few areas had AlMgB₁₄. Thus, HIP-7 was only considered a partial-success, because it had relatively good hardness, a higher density, a larger amount of TiB₂ phase in the SEM analysis, and the XRD does not show the AlMgB₁₄ intensity peaks.

TMA was done on both samples. Figure 70 shows the TMA plots of HIP-3 and HIP-7 where the initial probe size was subtracted from the TMA plots. The thermal expansion coefficients were calculated from Figures 12F and 13F in Appendix F. It was observed that both HIP-3 and HIP-7 exhibited a large contraction occur. HIP-3 had a thermal expansion coefficient of $7.25 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ over the temperature range of 50°C to 513°C. HIP-3 contracted from 513°C to 861°C with a thermal expansion coefficient of $-61.4 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. HIP-3 expanded from 861°C to the end of the run and had a thermal expansion coefficient of $6.01 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. HIP-7 had a thermal expansion coefficient of $7.87 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ over the temperature range of 50°C to 481°C. HIP-7 contracted from 481°C to 730°C with a thermal expansion coefficient of $-29.7 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. HIP-7 expanded from 730°C to the end of the run and had a thermal expansion coefficient of $11.04 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. One possible reason for this major contraction is that Al has a melting point of 660°C and Mg has a melting point of 650°C. Figure 2 in Chapter 1 shows that the Al and Mg phase diagram have intermetallics as

Figure 69: Measured X-ray Diffraction patterns for HIP samples. Reference XRD patterns are also shown [International Centre For Diffraction Data, Card Numbers: 39-0459, 21-1152, 26-1136, 08-0121, 07-0275, 1997]

Figure 70: Shows the TMA plots of HIP-3 and HIP-7 where the initial probe was subtracted from each plot.

low as 457°C. Thus, when the HIP samples reached around 500°C, Al and/or Mg that had not reacted to form AlMgB_{14} materials melted, become a gas, and/or turned into a different compound, reducing specimen volume in the process. After each run the quartz stage was black, and it appeared that some Mg out gassing occurred.

CHAPTER 9: CONCLUSION AND FUTURE SUGGESTIONS

9.1 Conclusions

- Baseline AlMgB₁₄ shows highest hardness when sample density is highest. This conclusion was found from plotting density, hardness, and specific ID # data from Appendix E. The plot of these data is shown in Figure 71.
- Al₂MgO₄ spinel and iron compound impurities are common byproducts of AlMgB₁₄ production. These impurities have a major effect on hardness, density, electrical properties, and thermal properties. This was shown throughout the research.
- Heating AlMgB₁₄ appears to alter the XRD patterns of the impurity phases but not the diffraction pattern of the AlMgB₁₄ itself. This was discovered from the TMA analysis of AlMgB₁₄ baseline materials and the XRD at various temperatures presented in Chapter 5 sections 5.3 and 5.5.
- Heat treatment of AlMgB₁₄ baseline materials causes physical, mechanical and microstructure properties to change. Specifically, the higher the temperature and the longer the heat treatment of AlMgB₁₄ the larger the degradation of the hardness. This was presented in Chapter 5 section 5.2.
- At room temperature, AlMgB₁₄ baseline materials have a range of electrical resistivity from 10⁻⁵ to 100 Ω-m. These materials have both n-type and p-type characteristics. This was shown in Chapter 6 sections 6.1 and 6.2.
- TiB₂ and TiC alloying additives have substantial effect on the various properties of AlMgB₁₄. TiB₂ increases the hardness of AlMgB₁₄, and TiB₂ and TiC causes AlMgB₁₄ to be more conductive. Chapter 7 sections 7.3 and 7.4 describes these effects.

Figure 71: Shows various AlMgB₁₄ Baseline Samples as a function of density and hardness.

- AlMgB₁₄ can be produced by hot isostatic pressing techniques. This was shown in Chapter 8 section 8.2 and 8.3.

9.2 Future Suggestions

For future research, probably the most important challenge is to find methods to make larger amounts of AlMgB₁₄ with quality properties. This would include experimenting with different single crystal techniques, hot pressing methods, and variations of mechanical alloying. Finding easier methods to produce ultra hard materials would benefit many different industries. Also more mechanical property characterization is needed. Very little is known about the tensile strength, shear strength, various moduli, and crack propagation characteristics of AlMgB₁₄. More DTA analysis is needed to expand TMA and x-ray diffraction results and to find the melting temperature of AlMgB₁₄. Further investigation of different alloying additives is needed to find the best material composition for specific applications. Lastly, research into making this material applicable to coatings would be very important. Most abrasives in industry are used as coatings.

APPENDIX A: X-RAY DIFFRACTION DATA AND PHASE DIAGRAMS

A.1 X-ray Diffraction Data Tables

Table A1: X-ray Diffraction and Crystallography Data for AlMgB₁₄ Using Cu-K α Radiation
[International Centre For Diffraction Data, 1997].

d-Spacing (Å)	Bragg's Angle (degrees)	Diffraction Angle (degrees)	Lattice Plane	Relative Intensity
6.3705	6.95	13.89	0,1,1	75
4.7413	9.35	18.70	1,1,0	29
3.4903	12.75	25.50	1,1,2	44
3.1874	13.99	27.97	0,2,2	13
2.6574	16.85	33.70	2,1,1	24
2.616	17.12	34.25	0,3,1	8
2.5426	17.64	35.27	2,0,2	22
2.4538	18.30	36.59	1,3,0	1
2.3927	18.78	37.56	1,2,3	27
2.2647	19.88	39.77	1,1,4	8
2.2155	20.35	40.69	1,3,2	65
2.1757	20.74	41.47	0,2,4	25
2.1543	20.95	41.90	2,2,2	56
2.148	21.01	42.03	2,1,3	100
2.1248	21.26	42.51	0,3,3	39
2.0278	22.33	44.65	0,4,0	1
1.9985	22.67	45.34	0,1,5	2
1.9494	23.28	46.55	2,3,1	1
1.9337	23.48	46.95	2,0,4	3
1.8953	23.98	47.96	3,1,0	3
1.8838	24.14	48.27	1,4,1	9
1.7775	25.68	51.36	1,3,4	2
1.7537	26.06	52.11	1,2,5	13
1.7456	26.19	52.37	2,2,4	10
1.7318	26.41	52.82	3,2,1	4
1.7188	26.63	53.25	0,0,6	32
1.6662	27.54	55.07	2,4,0	15
1.6499	27.83	55.66	2,1,5	12
1.6399	28.02	56.03	0,3,5	4
1.6027	28.73	57.45	0,5,1	9
1.5853	29.07	58.14	2,4,2	13
1.5816	29.15	58.29	3,3,0	24
1.5635	29.52	59.03	1,5,0	11
1.527	30.30	60.59	3,1,4	2
1.5116	30.64	61.27	3,3,2	2
1.4816	31.33	62.65	2,0,6	9
1.462	31.79	63.59	4,0,0	12

Table A1: (continued)

d-Spacing (Å)	Bragg's Angle (degrees)	Diffraction Angle (degrees)	Lattice Plane	Relative Intensity
1.4493	32.11	64.21	0,1,7	2
1.425	32.72	65.44	4,1,1	7
1.4054	33.24	66.47	2,5,1	16
1.3996	33.39	66.78	2,4,4	6
1.3921	33.60	67.19	3,4,1	6
1.3753	34.06	68.12	4,2,0	1
1.3519	34.74	69.47	0,6,0	2
1.3475	34.87	69.73	1,2,7	10
1.3373	35.17	70.34	3,2,5	17
1.3287	35.43	70.86	4,2,2	7
1.3273	35.48	70.95	4,1,3	6
1.3114	35.97	71.94	2,5,3	10
1.308	36.08	72.16	0,6,2	8
1.3006	36.32	72.64	3,4,3	6
1.2985	36.39	72.77	2,1,7	8
1.275	37.17	74.34	0,5,5	19
1.2468	38.16	76.31	3,5,0	1
1.2439	38.26	76.52	1,1,8	4
1.2297	38.79	77.57	1,6,3	2
1.2271	38.88	77.77	2,6,0	5
1.2134	39.41	78.81	4,2,4	5
1.2045	39.76	79.51	4,3,3	9
1.1963	40.08	80.17	2,4,6	8
1.1936	40.19	80.39	2,6,2	8
1.1859	40.51	81.02	4,4,0	2
1.1799	40.76	81.51	4,1,5	3
1.1681	41.26	82.52	1,4,7	1
1.1613	41.55	83.11	3,4,5	1
1.1516	41.98	83.96	0,7,1	1
1.1411	42.46	84.92	1,3,8	3
1.1325	42.86	85.71	2,2,8	1
1.1289	43.03	86.05	3,2,7	1
1.1225	43.33	86.67	3,5,4	1
1.1136	43.77	87.53	4,0,6	1
1.11	43.94	87.89	1,7,2	3
1.1077	44.06	88.12	2,6,4	2
1.1051	44.19	88.38	3,6,1	1
1.0981	44.55	89.09	0,7,3	1
1.0906	44.94	89.87	0,5,7	3

Table A2: X-ray Diffraction and Crystallography Data for Al_2MgO_4 Spinel Using Cu-K α Radiation [International Centre For Diffraction Data, 1997].

d-Spacing (Å)	Bragg's Angle (degrees)	Diffraction Angle (degrees)	Lattice Plane	Relative Intensity
4.66	9.52	19.04	1,1,1	35
2.858	15.64	31.28	2,2,0	40
2.437	18.43	36.87	3,1,1	100
2.336	19.26	38.52	2,2,2	4
2.02	22.42	44.85	4,0,0	65
1.65	27.84	55.68	4,2,2	10
1.5554	29.70	59.39	5,1,1	45
1.4289	32.63	65.27	4,4,0	55
1.3662	34.33	68.67	5,3,1	4
1.278	37.08	74.16	6,2,0	4
1.233	38.68	77.35	5,3,3	8
1.2187	39.22	78.43	6,2,2	2
1.1666	41.34	82.67	4,4,4	6
1.132	42.90	85.79	5,5,1	2
1.0802	45.50	91.01	6,4,2	6
1.0524	47.07	94.13	7,3,1	12
1.0104	49.69	99.38	8,0,0	8
0.9527	53.97	107.94	6,6,0	2
0.9334	55.63	111.26	7,5,1	8
0.9274	56.18	112.36	6,6,2	2
0.9038	58.48	116.96	8,4,0	6
0.8872	60.27	120.54	9,1,1	2
0.88	61.10	122.21	8,4,2	2
0.8616	63.40	126.80	6,6,4	2
0.8474	65.39	130.77	9,3,1	8
0.8249	69.05	138.10	8,4,4	18
0.8123	71.51	143.02	7,7,1	2
0.7927	76.35	152.71	10,2,0	2
0.7814	80.33	160.66	9,5,1	12

Table A3: X-ray Diffraction and Crystallography Data for Fe₃O₄ Using Cu-K α Radiation
 [International Centre For Diffraction Data, 1997].

d-Spacing (Å)	Bragg's Angle (degrees)	Diffraction Angle (degrees)	Lattice Plane	Relative Intensity
4.67	9.49	18.99	1,1,1	10
2.86	15.62	31.25	2,2,0	30
2.439	18.41	36.82	3,1,1	100
2.335	19.26	38.52	2,2,2	10
2.023	22.38	44.76	4,0,0	30
1.651	27.81	55.62	4,2,2	20
1.557	29.65	59.30	5,1,1	40
1.43	32.59	65.19	4,4,0	50
1.234	38.63	77.25	5,3,3	10

Table A4: X-ray Diffraction and Crystallography Data for TiB₂ Using Cu-K α Radiation
 [International Centre For Diffraction Data, 1997].

d-Spacing (Å)	Bragg's Angle (degrees)	Diffraction Angle (degrees)	Lattice Plane	Relative Intensity
3.22	13.84	27.68	0,0,1	20
2.62	17.10	34.20	1,0,0	60
2.033	22.27	44.53	1,0,1	100
1.613	28.53	57.05	0,0,2	14
1.514	30.58	61.17	1,1,0	20
1.374	34.10	68.20	1,0,2	16
1.37	34.21	68.42	1,1,1	10
1.311	35.98	71.97	2,0,0	8
1.215	39.35	78.69	2,0,1	14
1.104	44.25	88.49	1,1,2	12
1.02	49.04	98.08	2,0,2	12
0.9956	50.69	101.38	1,0,3	8
0.9479	54.35	108.71	2,1,1	10
0.8773	61.41	122.81	1,1,3	4
0.8746	61.73	123.46	3,0,0	4
0.84	66.49	132.99	2,1,2	6
0.83	68.14	136.27	2,0,3	6
		145.131	0,0,4	1

Table A5: X-ray Diffraction and Crystallography Data for FeB Using Cu-K α Radiation
 [International Centre For Diffraction Data, 1997].

d-Spacing (Å)	Bragg's Angle (Degrees)	Diffraction Angle (Degrees)	Lattice Plane	Relative Intensity
3.269	13.63	27.27	1,1,0	16
2.752	16.26	32.52	0,2,0	32
2.384	18.86	37.72	1,0,1	50
2.2768	19.78	39.56	1,2,0	33
2.1888	20.61	41.23	1,1,1	72
2.0116	22.52	45.05	0,2,1	100
1.9043	23.87	47.74	2,1,0	67
1.8018	25.32	50.64	1,2,1	28
1.6716	27.45	54.90	1,3,0	33
1.6335	28.15	56.29	2,2,0	5
1.5995	28.80	57.60	2,1,1	27
1.4736	31.53	63.05	0,0,2	22
1.4542	32.00	63.99	1,3,1	3
1.3435	35.00	69.99	1,1,2	3
1.303	36.25	72.51	1,4,0	10
1.2993	36.37	72.75	0,2,2	6
1.2466	38.18	76.36	0,4,1	17
1.2374	38.51	77.03	1,2,2	16
1.2354	38.59	77.17	2,3,1	25
1.2297	38.80	77.60	3,0,1	8
1.2141	39.39	78.79	3,2,0	5
1.1999	39.95	79.91	3,1,1	12
1.1917	40.28	80.57	1,4,1	4
1.1653	41.39	82.79	2,1,2	22
1.1224	43.35	86.71	3,2,1	9
1.1054	44.19	88.38	1,3,2	9
1.0889	45.04	90.08	3,3,0	7
1.0621	46.51	93.01	2,4,1	4
1.0147	49.40	98.81	4,0,0	6

A.2 Phase Diagrams

Figure A1: Phase Diagram of Al-B from ASM Binary Phase Diagrams [ASM, 1986].

Figure A2: Phase Diagram of Mg-B from ASM Binary Phase Diagrams [ASM, 1986].

Figure A3: Phase Diagram of Al-Mg from ASM Binary Phase Diagrams [ASM, 1986].

APPENDIX B: REFERENCE HARDNESS DATA

B.1 Hardness Test Descriptions

Table B1: Hardness Techniques and Descriptions. Descriptions are taken verbatim from "Ceramic Hardness," by I. J. McColm pages 1-3.

Hardness Technique	Description
Scratch	Test where one observes whether one material scratches another material.
Ploughing	Test where a hard blunt material is loaded and pulled across a surface to make a groove. The width and depth of the groove are a measure of hardness.
Cutting	Test where a sharp tool is used to cut or chip specimen material at certain standard dimensions.
Abrasion	Test where a sample is loaded against a rotating disk and the rate of wear is determined optically or by weight loss to measure hardness.
Erosion	A test similar to the abrasion test where abrasive grains are fired onto the sample surface and the loss of weight in a given time is the hardness measurement.
Damping	Test where a pendulum that has a very hard pivot is set rocking on the sample surface and the time to decrease the amplitude of the swing by 50% is the measurement of hardness.
Rebound	Test where a ball is bounced off a surface of a sample and the height of the rebound is the measurement of hardness.
Static Indentation	Test where a ball, cone, or pyramid is forced into a surface and the load per unit area of impression is the hardness measurement.

B.2 ASM Data Chart – Conversion Data

Table B2: These Data came from ASTM E 18 and Granta Design website:

<http://www.granta.co.uk/resources/materials/hardnesscharts.html>.

ROCKWELL C	VICKERS	KNOOP	ROCKWELL C	VICKERS	KNOOP
79.4	1800		35	345	351
74.9	1400		34	336	342
72.2	1200		33	327	334
69	1000	955	32	318	326
68	940	920	31	310	318
67	900	895	30	302	311
66	865	870	29	294	304
65	832	846	28	286	297
64	800	822	27	279	290
63	772	799	26	272	284
62	746	776	25	266	278
61	720	754	24	260	272
60	697	732	23	254	266
59	674	710	22	248	261
58	653	690	21	243	256
57	633	670	20	238	251
56	613	650			
55	595	630			
54	577	612			
53	560	594			
52	544	576			
51	528	558			
50	513	542			
49	498	526			
48	484	510			
47	471	495			
46	458	480			
45	446	466			
44	434	452			
43	423	438			
42	412	426			
41	402	414			
40	392	402			
39	382	391			
38	372	380			
37	363	370			
36	354	360			

B.3 Theoretical Hardness Derivation

Table B3: Theoretical Hardness. Comes from "Ceramic Hardness," by I. J. McColm pages 20-24.

Math Step	Derivation
1	Derive a Model for the Indentation: Where P = load
2	$H = \frac{P}{Area}$ where P = load and Area = cross-sectional of one structural unit.
3	<p>Need to derive a potential energy between structural units: Use Lennard-Jones 6-12 Potential:</p> $E = \frac{V_e}{m - n} \left[m \left(\frac{r_e}{r_2} \right)^n - n \left(\frac{r_e}{r_1} \right)^m \right]$ <p>where V_e = is the equilibrium potential, m and n = are constants related to bond type, r_e = distance where $E = 0$ and r_1 and r_2 = distances.</p> <p>Need to add structure factors:</p> $E = \frac{V_e}{m - n} \left[m \frac{z}{b_1} \left(\frac{r_e}{r_2} \right)^n - n \frac{z}{b_2} \left(\frac{r_e}{r_1} \right)^m \right]$ <p>where z = coordination b_1 and b_2 = constants based on structure factors.</p>
4	<p>Need to take the derivative of E with respect to r_1 and r_2 to get the load:</p> $\frac{dE}{dr_1} = \frac{V_e z}{m - n} \frac{nm}{b_2 r_e} \left(\frac{r_e}{r_1} \right)^{m+1} \left(\frac{r_e - r_2}{r_1} \right)$ <p>where $\left(\frac{r_e - r_2}{r_1} \right)$ comes from the angle of deformation.</p>

Table B3: (continued)

Math Step	Derivation
4 continue	$\frac{dE}{dr_2} = -\frac{V_e z}{(m-n)} \frac{nm}{b_1 r_e} \left(\frac{r_e}{r_2}\right)^{n+1}$
5	<p>Combine the derivatives to get the load (P):</p> $P = \frac{V_e z n m}{(m-n)r_e} \left[\frac{1}{b_2} \left(\frac{r_e - r_2}{r_1}\right) \left(\frac{r_e}{r_1}\right)^{m+1} + \frac{1}{b_1} \left(\frac{r_e}{r_2}\right)^{n+1} \right]$
6	<p>Defining r_e and V_e:</p> $r_e = \frac{V_m}{N_o K} \quad V_e = \frac{U_L}{z N_o W} \quad \text{where } V_M = \text{molar volume, } N_o =$ <p>Avogadro's Number, K = structure factor related to coordination number, z = coordination number, U_L = lattice energy, and W = number of atoms per formula unit.</p>
7	<p>To get rid of r_1 and r_2 have to take a double derivative of E with respect to r_1:</p> $\frac{d^2 E}{dr_1^2} = 0 = (n+1) \left(\frac{r_e}{r_1}\right)^{n+2} - (m+1) \left(\frac{r_e}{r_1}\right)^{m+2}$ $\frac{r_e}{r_1} = \left[\frac{m+1}{n+1} \right]^{1/(n-m)}$ <p>To find r_e/r_2 assume that $E = 0$ when at equilibrium:</p> $E = 0 = m \left(\frac{r_e}{r_2}\right)^n - n \left(\frac{r_e}{r_1}\right)^m$ $\frac{r_e}{r_2} = \left[\frac{n+1}{m+1} \right]^{1/(n-m)}$

Table 3B: (continued)

Math Step	Derivation
8	<p>Substitute everything into math step 2 gives the theoretical hardness:</p> $H_{th} = \frac{nmU_L K}{(n-m)V_m} \left(\frac{1}{b_2} \left\{ \left(\frac{m+1}{n+1} \right)^{(m+1)/(n-m)} * \left[\left(\frac{m+1}{n+1} \right)^{1/(n-m)} - 1 \right] \right\} + \frac{1}{b_1} \left(\frac{m+1}{n+1} \right)^{(m+1)/(n+m)} \right)$

B.4 Metals Development – Gilman Machine Data

Table B4: Hardness Data for A Study of Hardness Variation Between Two Hardness Machines.

Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)	Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)
Alumina	1350	1930	SiC	2450	2560
	1460	1980		2450	2630
	1600	2030		2540	2630
	1630	2030		2640	2640
	1840	2090		2640	2720
		2150		2640	2990
		2210		2690	3310
		2410		2850	3680
C-BN	3580	4280	ASC	1340	1530
	3750	4450		1450	1560
	4640	4450		1492	1560
	4640	4640		1490	1570
	4750	4640		1510	1570
	5270	5500		1540	1620
				1560	1640
				1680	1650

Table B4: (continued)

Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)	Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)
#1	2743.00	2598.00	#6	2640.44	2804.00
Baseline	2743.00	2859.00	TiB ₂ Add	2796.50	3425.00
Pressed	2796.00	2915.00	30 wt%	2796.50	3425.00
At 1500°C	2908.00	3003.00	Pressed	2851.60	3549.00
	2908.00	3004.00	At 1400°C	2908.34	3678.00
	2966.00	3034.00		2966.80	3814.00
	3027.00	3097.00		2966.80	3816.00
	3027.00	3401.00			3817.00
#7	2742.97	3962.00	#8	2854.60	3308.00
TiB ₂ Add	2796.50	4068.00	Baseline	2966.80	3425.00
30 wt %	3089.10	4115.00	Pressed	2966.80	3679.00
Pressed	3089.10	4116.00	At 1400°C	3089.10	3679.00
At 1400°C	3089.10	4116.00		3153.20	3817.00
	3219.20	4165.00		3287.00	3962.00
	3430.20	4279.00		3430.20	3962.00
	3582.70	4279.00			4115.00
#9	1652.26	1696.00	#10	435.52	409.00
Baseline	1677.20	1783.00	Baseline	467.18	440.00
Pressed	1868.73	1927.00	Pressed	498.32	451.00
At 1400°C	1961.00	2407.00	At 1300°C	502.43	529.00
	2167.28	2407.00		506.59	560.00
	2167.28	2479.00		515.10	620.00
	2591.32	2717.00		523.76	629.00
	2796.49	3092.00			748.00
#11	764.50	813.00	#12	2451.00	2526.00
Baseline	839.41	903.00	Baseline	2543.00	2622.00
Pressed	848.41	937.00	Pressed	2591.00	2697.00
At 1300°C	866.85	1029.00	At 1400°C	2851.60	2776.00
	1130.47	1113.00		2851.60	2831.00
	1203.62	1183.00			2916.00
	1492.28	1259.00			2974.00
		1344.00			3034.00

Table B4: (continued)

Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)	Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)
#14	2365.00	2858.00	#15	1188.45	1615.00
Baseline	2451.00	2915.00	Baseline	1234.88	1696.00
Pressed	2497.00	2916.00	Pressed	1513.60	1696.00
At 1450°C	2543.00	2944.00	At 1400°C	1557.87	2147.00
	2543.00	3004.00		1580.70	2338.00
	2640.00	3004.00		2204.80	2407.00
	2690.00	3065.00		2282.90	2479.00
	2796.00	3128.00		3089.10	2555.00
#16	2407.92	2289.00	#17	2591.32	3092.00
Baseline	2543.55	2598.00	Baseline	2742.97	3308.00
Pressed	2640.44	2697.00	Pressed	2742.97	3425.00
At 1400°C	2690.98	2886.00	At 1450°C	2851.60	3425.00
	2690.98	2944.00		2908.34	3426.00
	2690.98	2944.00		3153.20	3429.00
	2796.49	3034.00		3287.00	3549.00
	2796.49	3129.00			3679.00
#23	1929.50	2154.00	#26	2543.00	2776.00
Baseline	2204.82	2503.00	Baseline	2591.00	2803.00
Pressed	2243.33	2672.00	Pressed	2690.00	2887.00
At 1300°C	2323.44	2749.00	At 1415°C	2743.00	2887.00
	2407.92	2776.00		2851.00	2915.00
	2497.10	2858.00		2996.00	2974.00
	2543.55	2858.00		3027.00	3034.00
	2543.55	2944.00		3027.00	3096.00
#27	2690.98	2503.00	#28	2591.00	2840.00
Baseline	2690.98	2647.00	Baseline	2591.00	2920.00
Pressed	2690.98	2697.00	Pressed	2640.00	3329.00
At 1425°C	2742.97	2746.00	At 1415°C	2640.00	3416.00
	2796.49	2776.00		2960.00	3587.00
	2851.60	3193.00		3027.00	
	2851.60	2803.00			
	3027.04	2915.00			

Table B4: (continued)

Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)	Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)
#30	1158.91	1829.00	#31	1755.00	1982.00
Baseline	1604.02	2210.00	Baseline	1929.50	2083.00
Pressed	1702.71	2288.00	Pressed	1961.00	2154.00
At 1400°C	1728.80	2329.00	At 1400°C	1993.00	2414.00
	2095.05	2503.00		2130.00	2414.00
	2095.05	2526.00		2407.00	2457.00
		2574.00		2544.00	2458.00
		2622.00		2743.00	2672.00
#32	2451.00	2598.00	#37	2026.00	2435.00
Baseline	2497.00	2671.00	Baseline	2243.00	2435.00
Pressed	2543.00	2724.00	Pressed	2243.00	2550.00
At 1400°C	2591.00	2776.00	At 1400°C	2283.00	2598.00
	2640.00	2831.00		2283.00	2672.00
	2690.00	2915.00		2323.00	2830.00
	2743.00	3097.00		2365.00	2887.00
	3357.00	3128.00		2407.00	3004.00
#38	3089.00	3301	#39	2908.34	3275
TiB ₂ Add	3089.13	3587	TiB ₂ Add	3089.13	3347
20 wt%	3153.15	3599	20 wt%	3089.13	3536
Pressed	3219.18	3599	Pressed	3089.13	3572
At 1400°C	3252.98	3663	At 1400°C	3089.13	3631
	3287.31	3696		3219.18	3692
	3287.31	3729		3357.63	3863
	3505.20	3938		3430.22	3986
#40	2365.00	2640.00	#42	2591.00	3096.00
TiB ₂ Add	2407.00	2646.00	TiB ₂ Add	2640.00	3096.00
10 wt%	2451.00	2944.00	30 wt%	2690.00	3227.00
Pressed	2543.00	3004.00	Pressed	2690.00	3261.00
At 1400°C	2543.00	3065.00	At 1400°C	2743.00	3366.00
	2543.00	3096.00		2743.00	3475.00
	2591.00	3096.00		2796.00	3552.00
	2796.00	3129.00		3027.00	3630.00

Table B4: (continued)

Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)	Sample I.D.	Gilman (Vickers)	Metals Development (Vickers)
AlN Add	2060.28	1815.00	#75	2407.90	2895.00
20 wt%	2060.30	2015.00	Baseline	2407.90	2991.00
Pressed	2130.00	2100.00	Pressed	2543.60	3092.00
At 1400°C	2204.82	2136.00	At 1400°C	2543.60	3197.00
	2243.33	2191.00		2543.60	3198.90
	2282.86	2191.00		2591.31	3308.00
	2323.44	2248.00		2640.40	3549.00
	2365.11	2350.00		2966.80	3549.00

B.5 Rockwell C – Vickers Relation

Figure B1: A Plot of the data in Table 2B between Rockwell C and Vickers Hardness. Also a trend line was used to get a relationship.

APPENDIX C: BASELINE PROCESSING PARAMETERS

C.1 Sample Identifications

Table C1: Shows Sample ID Number that matches with sample identification used in experimental research.

Sample ID#	Experimental Sample Identification	Sample ID#	Experimental Sample Identification
1	AlMgB-1B	35	AlMgBSh-40
2	AlMgBHB-1	36	AlMgBSh-41
3	AlMgB-5A	37	AlMgBSh-Mix
4	AlMgB-5B	38	AlMgB-TiB-3A
5	AlMgBSh-5	39	AlMgB-TiB-3B
6	AlMgBSh-6	40	AlMgB-TiB-4A
7	AlMgBSh-12	41	AlMgB-TiB-4B
8	AlMgBSh-16	42	AlMgB-TiB-5
9	AlMgBSh-17A	43	AlMgB-TiB-6
10	AlMgBSh-17B	44	AlMgB-TiB-7
11	AlMgBSh-17C	45	AlMgB-AlN-1A
12	AlMgBSh-18	46	AlMgB-AlN-1B
13	AlMgBSh-20	47	AlMgB-AlN-2A
14	AlMgBSh-20-2	48	AlMgB-TiC-1A
15	AlMgBSh-21	49	AlMgB-TiC-1B
16	AlMgBSh-22	50	AlMgB-TiC-2A
17	AlMgBSh-23-2	51	AlMgB-TiC-2B
18	AlMgBSh-24	52	AlMgB-TiC-3A
19	AlMgBSh-25	53	AlMgB-TiC-3B
20	AlMgBSh-26	54	AlMgB-TiC-4
21	AlMgBSh-27	55	AlMgB-hBN-1A
22	AlMgBSh-28	56	AlMgB-hBN-1B
23	AlMgBSh-29	57	AlMgB-hBN-1C
24	AlMgBSh-30	58	AlMgB-AP-3
25	AlMgBSh-31	59	AlMgB-AP-4
26	AlMgBSh-32	60	AlMgB-AP-7
27	AlMgBSh-33	61	AlMgB-AP-8
28	AlMgBSh-34	62	AlMgB-AP-9
29	AlMgBSh-35-L	63	AlMgB-AP-10/11
30	AlMgBSh-35-CH	64	AlMgB-AP-12/6
31	AlMgBSh-36	65	AlMgB-AP-13
32	AlMgBSh-37	66	AlMgB-AP-15
33	AlMgBSh-38	67	AlMgB-AP-16
34	AlMgBSh-39	68	AlMgB-AP-19

Table C1: (continued)

Sample ID#	Experimental Sample Identification	Sample ID#	Experimental Sample Identification
69	AlMgB-AP-25	78	AlMgB-SB-1
70	AlMgBSi-11A	79	AlMgB-TM-Hip-3
71	AlMgBSi-13A	80	AlMgB-SB-9
72	AlMgBSi-14A	81	AlMgB-SB-12
73	AlMgB-TM	82	AlMgB-PM
74	AlMgB-Ti-1	83	AlMgBSi-PM-1C
75	AlMgBSh-15	84	AlMgBSi-PM-1D
76	AlMgB-T-2	85	AlMgBSi-PM-2A
77	AlMgB-T-3	86	AlMgB-AP-Hip

C.2 Processing Properties and Conditions for Baseline Samples

It is assumed that a baseline sample has less than 1 wt% of other material compared to AlMgB₁₄-Al₂MgO₄ spinel. Assume these samples were made by hot uniaxial pressing.

Table 2C-a: Shows type of Mixing, Alloying Process, and elemental constituents for baseline samples.

Sample ID#	Mixing / Mechanical Alloying Technique	Boron (g)	Magnesium (g)	Aluminum (g)
1	Spex Milling	3.7384	0.6003	0.6664
2	Spex Milling	3.000	0.4818	0.5348
3	Spex Milling	3.7384	0.6003	0.6664
4	Spex Milling	3.7384	0.6003	0.6664
5	Spex Milling	3.000	0.4818	0.5348
8	Spex Milling	2.2432	0.3602	0.4002
9	Spex Milling	2.243	0.3602	0.4001
10	Spex Milling	2.243	0.3602	0.4001
11	Spex Milling	2.243	0.3602	0.4001
12	Spex Milling	2.243	0.3603	0.3997
13	Spex Milling	2.2429	0.3602	0.400
14	Spex Milling	2.2429	0.3602	0.400
15	Spex Milling	2.2429	0.3603	0.3997
16	Spex Milling	2.2430	0.3602	0.399
17	Spex Milling	2.2491	0.3603	0.3999
18	Spex Milling	2.2429	0.3603	0.3998
19	Spex Milling	2.2431	0.3603	0.400
20	Spex Milling	2.2431	0.3602	0.3997
21	Spex Milling	2.2429	0.3603	0.3997
22	Spex Milling	2.2431	0.3600	0.3997

Table C2: (continued)

Sample ID#	Mixing / Mechanical Alloying Technique	Boron (g)	Magnesium (g)	Aluminum (g)
23	Spex Milling	2.243	0.3602	0.3999
24	Spex Milling	2.2429	0.3603	0.3998
25	Spex Milling	2.2429	0.3602	0.400
26	Spex Milling	2.2431	0.3603	0.4001
27	Spex Milling	2.243	0.3998	0.3602
28	Spex Milling	2.2429	0.3603	0.3997
29	Spex Milling	2.2429	0.3603	0.400
30	Spex Milling	2.2429	0.3603	0.400
31	Spex Milling	2.2431	0.3600	0.400
32	Spex Milling	2.2746	0.3259	0.3997
33	Spex Milling	2.2746	0.3258	0.3998
34	Spex Milling	2.7483	0.326	0.3997
35	Spex Milling	2.243	0.3601	0.3999
36	Spex Milling	2.2429	0.36	0.3997
37	Spex Milling	N/A	N/A	N/A
70	Spex Milling	2.2401	0.3596	0.3793
71	Spex Milling	2.2402	0.3599	0.3795
72	Spex Milling	2.2400	0.3598	0.3797
73	Turbula Mixed	34.12	5.97	4.87
74	Spex Milling	2.2429	0.3601	0.3996
75	Spex Milling	2.2432	0.3602	0.4002
76	Spex Milling	2.2432	0.3602	0.4000
77	Spex Milling	2.2431	0.36	0.4000
78	Spex Milling	2.243	0.3601	0.3999
80	Spex Milling	2.2428	0.3602	0.3997
81	Spex Milling	2.2429	0.3603	0.3999
82	Planetary Milling	11.2003	1.7986	1.8969
83	Planetary Milling	11.2003	1.7986	1.8969
84	Planetary Milling	11.2003	1.7986	1.8969
85	Planetary Milling	11.2003	1.7986	1.8969

Table C3: Shows mixing or milling time, the amount of powder loaded into the hot uniaxial press, the temperature used for the hot uniaxial press and the time at the pressing temperature used for baseline samples.

Sample ID#	Milling/ Mixing Time (hr)	Pressing Load (g)	Pressing Temperature (°C)	Pressing Time (min)
1	22	1.00	1500	30
2	12	1.00	1400	60
3	23	1.00	1350	30
4	23	1.00	1350	30
5	12	1.00	1400	60
8	12	1.16	1400	60
9	20	0.85	1400	60
10	20	0.85	1300	60
11	20	0.62	1300	120
12	12	0.76	1400	60
13	12	0.85	1400	60
14	12	0.9766	1450	60
15	12	0.85	1400	60
16	12	0.838	1400	60
17	12	0.8552	1450	60
18	12	0.8594	800	60
19	12	0.8584	900	60
20	12	0.8553	1000	60
21	12	0.8527	1100	60
22	12	0.866	1200	60
23	15	0.8536	1300	60
24	12	0.8672	1450	60
25	12	0.9954	1415	60
26	12	0.9443	1415	60
27	12	0.8518	1425	60
28	12	1.1425	1415	60
29	12	1.092	1400	60
30	12	1.0021	1400	60
31	13	1.015	1400	60
32	12	0.9733	1400	60
33	12	1.0007	1400	60
34	12	1.003	1400	60
35	32	1.000	1400	60
36	32	1.0947	1450	60

Table C3: (continued)

Sample ID#	Milling/ Mixing Time (hr)	Pressing Load (g)	Pressing Temperature (°C)	Pressing Time (min)
37	N/A	0.9953	1400	30
70	12	1.00	1400	60
71	12	1.00	1400	30
72	12	1.00	1400	30
73	0.5	0.9985	1400	60
75	21.3	1.04	1400	60
77	12	0.9998	800	60
78	12	1.01	1400	60
80	12	0.978	1400	60
81	12	0.9745	1425	60
82	50	1.100	1400	60
83	50	1.000	1450	60
84	50	1.000	1400	60
85	100	1.000	1450	60

Sample 84 was a 1 inch diameter disc, that had a lot less applied uniaxial stress, which caused this sample to have a lot of porosity.

APPENDIX D: ADDITIVES PROCESSING PARAMETERS

D.1 Processing Procedures

Table D1: The three procedures used to make the powders to be loaded into the hot uniaxial press. The first procedure was for AlMgB₁₄ standard baseline and the other two to were for AlMgB₁₄ with additive materials.

Procedure	Description
Standard Baseline	<p>First, all the elemental constituents needed to be turned into a powder. Each elemental chunk material was put into its own separate spex vial and milled for a few minutes. Some samples were made with elemental constituents that came as powder from the vendor. All the powders were kept in a glove box.</p> <p>Powder for a standard baseline sample consisted of weighing out loads of 74.69 wt% of boron, 13.31 wt% of aluminum and 12 wt% of magnesium and putting the material in the mechanical alloying vial. Then the mechanical alloying vial is milled for a period of time and brought back into the glove box. Powder loads made by spex milling had milling times ranging from 12 to 32 hours. Loads made with planetary milling had milling times ranging from 50 to 100 hours. After the milling all the contents were cleaned out of the vial. The contents would be separated as loose and chunk material.</p>
Procedure 1 (Joel's Method)	<p>A load of loose standard baseline powder was put into a spex vial. An amount of additive material was put into the spex vial. Then the spex vial would be milled for about 30 minutes. All the material was cleaned out of the spex vial and separated as loose and chunk material.</p>
Procedure 2 (Theron's Method)	<p>A load of both loose and chunk standard baseline powder was put into a spex vial. An amount of additive material was put into the spex vial. Then the spex vial would be milled for about 4 hours. All the material was cleaned out of the spex vial and separated as loose and chunk material.</p>

D.2 Processing Parameters for Alloying Additive Samples

All the following AlMgB₁₄ with additive samples was made with spex milling and hot uniaxial pressing.

Table D2: Samples produced by Procedure 1. Shows elemental constituents and additives for each sample.

Sample ID#	Boron (g)	Magnesium (g)	Aluminum (g)	Type of Additive	Weight Percent of Additive (wt %)
6	3	0.4818	0.5348	TiB ₂	30
7	2.2433	0.400	0.3601	TiB ₂	30
58	2.243	0.3601	0.400	TiB ₂	30
59	2.2432	0.3603	0.3998	TiB ₂	30
60	2.2432	0.3601	0.3997	TiB ₂	30
61	2.2432	0.3603	0.3998	TiB ₂	30
62	2.2431	0.3603	0.3998	TiB ₂	30
63	2.2429	.3601	.3998	TiB ₂	30
64	2.2428	.3600	.3998	TiB ₂	30
65	2.2426	0.4001	0.3604	TiB ₂	30
66	2.243	0.3600	0.3996	TiB ₂	30
67	2.2428	0.3602	0.3997	TiB ₂	30
68	2.2428	0.3601	0.399	TiB ₂	30
69	2.2428	0.3604	0.399	TiB ₂	30

Table D3: Samples produced by Procedure 2. Shows elemental constituents and additives for each sample.

Sample ID#	Boron (g)	Magnesium (g)	Aluminum (g)	Type of Additive	Weight Percent of Additive (wt %)
38	2.243	0.3602	0.3999	TiB ₂	20.00
39	2.243	0.3602	0.3999	TiB ₂	20.00
40	2.243	0.3602	0.400	TiB ₂	10.00
41	2.243	0.3602	0.400	TiB ₂	10.00
42	2.2431	0.3603	0.3999	TiB ₂	30.00
43	2.2432	0.3603	0.3997	TiB ₂	11.75
44	2.243	0.3601	0.399	TiB ₂	40.01
45	2.2431	0.3602	0.3999	AlN	20.00
46	2.2431	0.3602	0.3999	AlN	20.00
47	2.243	0.36	0.3998	AlN	30.01
48	2.2429	0.3603	0.399	TiC	20.00
49	2.2429	0.3603	0.399	TiC	20.00
50	2.2429	0.3603	0.3997	TiC	30.01

Table D3: (continued)

Sample ID#	Boron (g)	Magnesium (g)	Aluminum (g)	Type of Additive	Weight Percent of Additive (wt %)
51	2.2429	0.3603	0.3997	TiC	30.01
52	2.2432	0.3602	0.3999	TiC	40.00
53	2.2432	0.3602	0.3999	TiC	40.00
54	2.243	0.3602	0.400	TiC	12.71
55	2.2431	0.3602	0.3999	h-BN	20.00
56	2.2431	0.3602	0.3999	h-BN	20.00
57	2.2431	0.3602	0.3999	h-BN	20.00

Table D4: Shows mixing or milling time, the amount of powder loaded into the hot uniaxial press, the temperature used for the hot uniaxial press and the time at the pressing temperature used for additive samples.

Sample ID#	Milling/ Mixing Time (hr)	Pressing Load (g)	Pressing Temperature (°C)	Pressing Time (min)
6	12.5	1.000	1400	60
7	12.5	0.7400	1400	60
38	16	0.8503	1400	60
39	16	0.925	1400	60
40	16	0.945	1400	60
41	16	0.9868	1400	60
42	16	0.9867	1400	60
43	16	0.9746	1400	60
44	16	0.9898	1400	60
45	16	0.9118	1400	60
46	16	0.9334	1400	60
47	16	1.001	1420	60
48	16	0.9944	1400	60
49	16	0.9978	1400	60
50	16	0.9877	1400	60
51	16	0.9876	1400	60
52	16	0.9538	1400	60
53	16	1.0011	1430	60
54	16	0.9001	1400	60
55	16	0.986	1400	60
56	16	0.9602	1400	60

Table D4: (continued)

Sample ID#	Milling/ Mixing Time (hr)	Pressing Load (g)	Pressing Temperature (°C)	Pressing Time (min)
57	16	0.999	1420	60
58	12.5	1.0007	1400	60
59	12.5	1.000	1400	60
60	12.5	0.9959	1400	60
61	12.5	1.000	1400	60
62	12.5	1.000	1400	60
63	12.5	0.9625	1400	60
64	12.5	0.985	1430	60
65	12.5	0.9967	1400	60
66	12.5	0.9826	1400	60
67	12.5	1.0011	1430	100
68	12.5	0.9456	1400	60
69	12.5	1.0475	1410	60

APPENDIX E: HOT UNIAXIAL PRESSING CHARACTERIZATION

E.1 Simple Characterization Data for HUP Samples

Table E1: Shows the density and hardness measured for various samples.

Sample ID #	Density (g/cm ³)	Metals Development Machine		Gilman Machine	
		Average Hardness (Vickers)	Maximum Hardness (Vickers)	Average Hardness (Vickers)	Maximum Hardness (Vickers)
1	2.585	2988.88	3401	2889.75	3027
2	2.715	2674	2974	N/A	N/A
3	N/A	3053	N/A	N/A	N/A
4	N/A	2160	2452	N/A	N/A
5	N/A	3428	N/A	2885	3027
6	3.169	3541	3817	2847	2966
7	3.17	3914	4831	3130	3582
8	N/A	3743.4	4115	3106.8	3430.2
9	2.525	2313.5	3092	2110.2	2794.5
10	2.148	548.25	748	492.7	523.8
11	N/A	1072.6	1344	1020.7	1492.3
12	N/A	2797	3034	2609	2852
14	2.6336	2979	3128	2657	2796
15	2.466	2116.6	2555	1831.5	3089
16	2.663	2815.13	3129	2657.2	2796.5
17	N/A	3416	3679	2896.7	3287
23	N/A	2689.25	2944	2336.7	2543.6
24	2.691	2865	3004	2940.6	3153.2
25	2.705	2966	3366	2721.8	2908.3
26	2.859	2921	3096	2808	3027
27	3.015	2784	3193	2792.83	3027.04
28	2.869	3218.4	3587	2741.5	3027
29	2.842	N/A	N/A	2842	3089
30	2.479	2360.13	2622.00	1730.8	2095.1
31	2.667	2329.3	2672	2182	2743
32	3.197	2842.5	3128	2689	3357
33	3.123	2744.3	2915	N/A	N/A
34	3.986	2751	3330	N/A	N/A
35	3.416	2572	2944	N/A	N/A

Table E1: (continued)

		Metals Development Machine		Gilman Machine	
Sample ID #	Density (g/cm ³)	Average Hardness (Vickers)	Maximum Hardness (Vickers)	Average Hardness (Vickers)	Maximum Hardness (Vickers)
36	3.101	2817	2944	N/A	N/A
37	2.712	2676.38	3004	2107.7	2407
38	3.069	3639	3938	3074.1	3505.2
39	3.118	3612.8	3968	3159	3430.2
40	2.913	2952.5	3129	2529.9	2796
41	2.858	2792	3128	N/A	N/A
42	3.25	3337	3630	2740	3027
43	3.36	2852	3128	N/A	N/A
45	2.792	2131	2350	2092.5	2365.1
46	2.76	2122	2413	N/A	N/A
48	3.767	2943	3261	N/A	N/A
49	3.745	3386	3513	2726.6	3027
50	3.542	1983	2309	N/A	N/A
51	3.191	1926	2136	N/A	N/A
52	3.507	2690	3065	N/A	N/A
53	3.5816	2724	3160	N/A	N/A
54	3.01	2658	3035	N/A	N/A
55	2.532	893	1066	700	734
56	2.376	657	794	N/A	N/A
57	2.356	754	955	N/A	N/A
58	3.146	3223.9	3475	2687	3089
59	3.33	3237.5	3632	2679.6	2851
60	3.0099	2657	3065	N/A	N/A
61	3.304	3114.9	3476	2783.9	3089
62	3.04	2848.6	3128	2536	2796
63	3.2941	3015	3401	N/A	N/A
64	3.118	2920	3261	N/A	N/A
65	3.11	3165	3591	N/A	N/A
66	3.107	3232	3974	N/A	N/A
67	3.22	3572	4215	N/A	N/A
68	3.07	2883	3295	N/A	N/A
69	3.176	2902	3161	N/A	N/A

Table E1: (continued)

		Metals Development Machine		Gilman Machine	
Sample ID #	Density (g/cm³)	Average Hardness (Vickers)	Maximum Hardness (Vickers)	Average Hardness (Vickers)	Maximum Hardness (Vickers)
70	2.7256	2808	3226	N/A	N/A
71	2.708	2486	2915	N/A	N/A
72	2.8632	2726	2974	N/A	N/A
73	2.469	837.5	1349	N/A	N/A
75	N/A	2752.5	2767	N/A	N/A
77	1.945	N/A	N/A	N/A	N/A
78	3.076	2718	2886	N/A	N/A
80	3.101	2530	2830	N/A	N/A
82	2.447	1624	2100	N/A	N/A
83	2.643	3052	3295	N/A	N/A

Table E2: Pressing properties, density, hardness and the hardness for Sample 74. Hardness was measured by the Metals Development Machine. Sample 74 was spex milled for 12 hours and the amount time at the pressing temperature was 60 minutes.

Pressing Temperature (°C)	Pressing Load (g)	Density (g/cm³)	Average Hardness (Vickers)	Maximum Hardness (Vickers)
800	1.07	1.957	N/A	N/A
900	0.873	2.386	N/A	N/A
1000	0.8416	2.409	N/A	N/A
1100	0.7248	2.422	1117.3	2015
1200	0.6019	2.831	1522	2229

Table E3: Pressing properties, density, and hardness for Sample 76. Hardness was measured by the Metals Development Machine. Sample 76 was spex milled for 12 hours and the amount time at the pressing temperature was 60 minutes.

Pressing Temperature (°C)	Pressing Load (g)	Density (g/cm³)	Average Hardness (Vickers)	Maximum Hardness (Vickers)
1100	1.015	2.0198	555	850
1200	1.0002	2.087	844.25	1017
1300	0.89	2.431	1681.6	1787

E.2 Electronic Properties Data for Baseline Samples

Table E4: Shows the 4-Point Probe results for the AlMgB₁₄ baseline samples.

Sample ID #	Thickness (mm)	F	Average Resistance (Ω)	Average Resistivity ($\Omega\cdot\text{m}$)
9	2.17	0.751	414.72	3.104
15	2.30	0.775	115.95	0.895
16	1.90	0.694	7.827	5.414×10^{-2}
35	1.69	0.642	0.0127	8.11×10^{-5}
36	1.53	0.599	0.141	8.400×10^{-4}
80	1.85	0.682	0.0367	2.496×10^{-4}
83	2.76	0.843	3248.82	27.30

Table E5: Shows results for AlMgB₁₄ baseline samples using van der Pauw method

Sample ID #	Average Resistivity ($\Omega\cdot\text{m}$)	Percent Error Resistivity Between 4-Point Probe/van der Pauw (%)	Hall Coefficient (cm^3/C)	n(p) (cm^{-3})	Hall Mobility ($\text{cm}^2/(\text{V}\cdot\text{s})$)
35	7.1345×10^{-5}	12.02	-0.001194	$5.872\text{E}+21$	0.1676
72	2.0653×10^{-3}	31.0	-0.0065625	$3.792\text{E}+20$	0.08125
80	2.164×10^{-4}	13.18	-0.00095	$2.044\text{E}+21$	0.15025

E.3 Volume Content of Other Phases in Baseline Samples

Table E6: Shows quantitative image analysis of phase areas for different baseline samples.

Sample ID #	Total Area (μm^2)	Phase Area (μm^2)	Percent Volume of Other Phases (%)	Percent Volume of AlMgB ₁₄ Phase
83	8007.54	586.63	7.33	92.67
83	7828.80	525.72	6.72	93.28
83	7812.90	578.91	7.41	92.59
83	7450.21	142.35	1.91	98.09
83	7702.48	328.26	4.26	95.74
83	7855.97	459.12	5.84	94.16
24	7735.14	1480.00	19.13	80.87
24	7657.95	1151.16	15.03	84.97
78	8041.84	669.75	8.33	91.67
78	7584.27	813.09	10.72	89.28
78	7941.36	1479.97	18.64	81.36
80	7688.13	1757.62	22.86	77.14
80	7688.13	2950.64	38.38	61.62
8	7958.44	1344.65	16.90	83.10
8	7610.94	3283.17	43.14	56.86
8	7689.12	659.93	8.58	91.42
8	7810.91	2379.46	30.46	69.54
12	7807.40	2703.70	34.63	65.37
12	7690.91	2062.84	26.82	73.18
27	7421.00	2037.45	27.46	72.54
28	7372.15	282.10	3.83	96.17
36	7943.48	2151.30	27.08	72.92

E.4 Electronic Properties for Alloying Additive Samples

Table E7: Shows 4-point probe results for TiB₂ alloying additive samples.

Sample ID #	Amount of TiB ₂ (wt%)	Thickness (mm)	F	Average Resistivity ($\Omega\text{-m}$)
7	30	1.4	0.560	4.86×10^{-5}
38	20	1.3	0.529	3.37×10^{-4}
39	20	1.78	0.665	2.22×10^{-4}
40	10	1.99	0.714	1.60×10^{-3}
41	10	2.3	0.774	5.59×10^{-3}
42	30	1.95	0.705	4.62×10^{-5}
43	30	1.77	0.663	1.80×10^{-5}
64	30	1.87	0.687	1.97×10^{-4}
65	30	1.84	0.680	8.55×10^{-5}

Table E8: Shows van der Pauw results for TiB₂ alloying additive samples.

Sample ID#	Amount of TiB ₂ (wt%)	Average Resistivity ($\Omega\cdot\text{m}$)	Percent Error (%)	Hall Coefficient (cm^3/C)	n(p) (cm^{-3})	Hall Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)
7	30	3.68×10^{-5}	24.4	4.87×10^{-3}	9.98E+20	1.704
38	20	1.61×10^{-4}	52.2	-2.98×10^{-4}	9.96E+20	0.395
39	20	1.59×10^{-4}	28.7	-4.25×10^{-4}	9.64E+20	0.411
40	10	1.94E-03	21.4	-2.31×10^{-3}	1.22E+21	0.044
41	10	4.33E-03	22.5	-0.135	8.50E+19	0.382
42	30	3.64×10^{-5}	21.2	5.44×10^{-4}	1.37E+21	1.280
43	30	1.52×10^{-5}	15.4	2.70×10^{-4}	1.65E+21	2.532
64	30	1.35×10^{-4}	31.4	3.49×10^{-3}	8.78E+20	0.529
65	30	7.84×10^{-5}	8.3	-3.05×10^{-3}	1.24E+21	0.652

Table E9: Shows 4-point probe results for TiC alloying additive samples.

Sample ID #	Amount of TiB ₂ (wt%)	Thickness (mm)	F	Average Resistivity ($\Omega\cdot\text{m}$)
48	20	1.47	0.581	9.51×10^{-6}
52	40	1.60	0.618	7.51×10^{-6}
53	40	1.75	0.658	7.71×10^{-6}
54	12.71	1.75	0.663	7.56×10^{-5}

Table E10: Shows van der Pauw results for TiC alloying additive samples.

Sample ID#	Amount of TiC (wt%)	Average Resistivity ($\Omega\cdot\text{m}$)	Percent Difference (%)	Hall Coefficient (cm^3/C)	n(p) (cm^{-3})	Hall Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)
48	20	7.81×10^{-6}	17.9	1.01×10^{-3}	6.40E+21	1.29
52	40	5.85×10^{-6}	22.1	2.18×10^{-4}	2.73E+21	3.95
53	40	5.66×10^{-6}	26.5	2.13×10^{-3}	2.96E+21	3.75
54	12.71	5.96×10^{-5}	21.1	-4.17×10^{-3}	1.50E+21	0.70

APPENDIX F: TMA PLOTS

Figure F1: Shows TMA of Sample 1 at a heating rate of 10°C/min. Baseline Sample.

Figure F2: Shows TMA of Sample 2 at a heating rate of 10°C/min. Baseline Sample.

Figure F3: Shows TMA of Sample 5 at a heating rate of 10°C/min. Baseline Sample.

Figure F4: Shows TMA of Sample 6 at a heating rate of 10°C/min. TiB₅ Additive Sample.

Figure F5: Shows first TMA profile of Sample 24 at a heating rate of 10°C/min. Baseline Sample.

Figure F6: Shows second TMA profile of Sample 24 at a heating rate of 10°C/min. Baseline Sample.

Figure F7: Shows TMA profile of Sample 26 at a heating rate of 10°C/min. Baseline Sample.

Figure F8: Shows TMA profile of Sample 49 at a heating rate of 10°C/min. TiC-Additive Sample.

Figure F9: Shows first TMA profile of Sample 67 at a heating rate of 10°C/min. TiB₂-Additive Sample.

Figure F10: Shows second TMA profile of Sample 67 at a heating rate of 10°C/min. TiB₂-Additive Sample.

Figure F11: Shows TMA profile of Sample 70 at a heating rate of 10°C/min. Baseline Sample.

Figure F12: Shows TMA profile of Sample HIP-3 at a heating rate of 10°C/min. HIP sample.

Figure F13: Shows TMA profile of Sample HIP-7 at a heating rate of 10°C/min. HIP sample that had 30wt% of TiB_2 .

APPENDIX G: X-RAY EXPOSURE IMAGES

Figure G1: Image plates for x-ray diffraction at various temperatures for Sample 24.

Figure G2: Image plates for x-ray diffraction at various temperatures for Sample 67.

Figure G3: Image plates for x-ray diffraction at various temperatures for Sample 84.

APPENDIX H: SEM AND EDS OF BASELINE SAMPLES

Figure 1H: SEM and EDS analysis in backscattered electron mode for Sample 9.

Figure H2: SEM and EDS analysis in backscattered electron mode for Sample 35.

Figure H3: SEM and EDS analysis in backscattered electron mode for Sample 36.

Figure H4: SEM and EDS analysis in backscattered electron mode for Sample 80.

Figure H5: SEM and EDS analysis in backscattered electron mode for Sample 83.

APPENDIX I: PROCESSING CONDITIONS FOR HIP SAMPLES

Table I1: Shows HIP Sample ID Number that matches with sample identification used in experimental research.

Sample ID #	Experimental Sample Identification
HIP-1	AlMgB-TM-HIP-1
HIP-2	AlMgB-TM-HIP-2
HIP-3	AlMgB-TM-HIP-3
HIP-4	AlMgB-PM-HIP-1
HIP-5	AlMgB-PM-HIP-2
HIP-6	AlMgB-SB-HIP
HIP-7	AlMgB-AP-HIP

Table I2: Shows type of number of powder batches used, mixing, alloying process, and elemental constituents.

Sample ID#	Number of Batches Used	Mixing / Mechanical Alloying Technique	Boron (g)	Magnesium (g)	Aluminum (g)
HIP-1	1	Turbula Mixed	34.12	5.97	4.87
HIP-2	1	Turbula Mixed	34.12	5.97	4.87
HIP-3	1	Turbula Mixed	34.12	5.97	4.87
HIP-4	1	Planetary Milling	11.20	1.80	1.90
HIP-5	1	Planetary Milling	11.20	1.80	1.90
HIP-6	6	Spex Milling	2.24	0.36	0.40
HIP-7	7	Spex Milling	2.24	0.36	0.40

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