

Chapter 5: Limiting the Oxide Phase

5.1: Introduction

5.1.1: Conventional Methods for Limiting Oxide Phase Formation

The processing of non-oxidic materials, such as AlMgB_{14} , is fraught with the formation of oxide phases. The formation of these oxide phases is often deleterious to the integrity of the material and failure through fracture often occurs at the site of oxidation.

It is easy to predict whether or not a specific material will oxidise or not. The prediction is based on thermodynamic arguments involving the electrochemical potentials for the oxidation of that specific material⁵⁹. When the oxidation potential is coupled with the reduction potential of the medium in which the material functions or is synthesised, the sum of these two potentials will indicate the spontaneity of the redox reaction. The oxidation of a material can thus be inferred prior to its synthesis and application. Deciding on how to synthesise the material or whether or not to use that material for the desired application thus, in principle is possible.

However, kinetic issues can dominate over thermodynamic issues and minimising the extent of the oxidation of a material then involves retarding the kinetics of the oxidation reaction in some way. Any strategy that is employed to minimise the effect of the oxidation of a material will exploit one of the factors that affect the rate of a reaction. Examples of procedures to minimise kinetic factors and thus to slow down oxide formation abound in the literature⁶⁰. A summary of these methods is now given.

1. Inert Conditions

The most obvious way to reduce any oxidation reaction will be to remove the oxidant. This is most successfully applied during the synthesis of the material. The procedure to achieve this entails the use of an inert atmosphere. Once synthesised the material can be stored in an inert atmosphere until the point of application.

2. Temperature

The synthesis of dense ceramic materials via powder metallurgical routes is preferably achieved at the lowest possible temperatures⁶¹. Lower temperatures reduce the grain growth of the materials during processing. Larger grains have a negative impact on the strength of the material⁶¹. The rate of oxidation can be described by an Arrhenius equation where the rate dependence on temperature is exponential. As the temperature is increased the rate of oxidation increases exponentially. Dense materials at low temperatures are not always achievable for non-oxidic ceramics as densification temperatures for many non-oxidic ceramic materials occur at temperatures greater than 1000°C⁶².

3. Surface Area

The surface area of the reacting materials also affects the rate of a reaction. Thus, the finer the starting powders, the larger the surface area, the faster the rate of the reaction when synthesising the material. However, finer particle sizes of the starting powders with their corresponding larger surface areas are themselves more prone to oxidation. Thus, using starting powders of finer particle size is not always beneficial for example, Mogilevsky *et al* have shown that SiC whiskers in an Al₂O₃ matrix are more prone to oxidation when the SiC whiskers have smaller volumes and larger surface areas⁶³.

4. The Nature of the Reacting Substances

The nature of the reacting substances can minimise the amount of oxidation that takes place. Additives to the starting powders can provide oxidative resistance by forming a passive oxidation layer around grains. A passive oxidation layer is a surface layer that is chemically bonded to the bulk matrix of the grain but prohibits the diffusion of oxygen into the grain⁶⁴. The surfaces of certain oxidisable materials can themselves behave as passive oxidation layers⁶⁵. Process control agents (PCA's) are often used during the milling cycle. Paraffin is one such PCA. Its role is to coat the particles that are being milled. The paraffin coated particles are resistant to further oxidation because the paraffin layer acts as a diffusion barrier to oxygen.

Diffusion barriers are vital to the longevity of most materials that are prone to oxidation. The addition of B₄C and SiC to diamond vastly improves the oxidation

resistance of the diamond at temperatures above 1200°C in oxidising environments. The oxidation resistance is achieved by the formation of borosilicate layers at the carbon surface undergoing oxidation. The borosilicate layer acts as a diffusion barrier to the oxidant⁶⁶.

5.1.2: Measuring the Oxygen Content

There are a variety of methods used to determine the oxygen content in materials. One of the most frequently used methods is a technique in which carbon is used as a reducing agent. Ellingham diagrams⁶⁷, which indicate the relative stability of many oxide phases, allow for the determination of the reductive temperature and necessary partial pressures required for the reduction of the respective metal oxide in the presence of a reducing agent such as carbon.

This technique requires the addition of a fixed amount of carbon to a sample. The temperature at which spontaneous reduction occurs is determined from the Ellingham diagram, and then the sample is heated in an inert atmosphere to this temperature and the amount of CO/CO₂ evolution is measured in order to determine the amount of oxide present in the sample⁶⁸.

X-ray diffraction (XRD) techniques using Rietveld refinement can be used to determine the amount of crystalline oxide phases that are present in a material⁶⁹. Thus, the amount of oxide phase, once determined from the refinement, can be used to infer the amount of oxide phase that must have been present in the starting materials.

Scanning electron microscopy (SEM) or transmission electron microscopy (TEM) in conjunction with energy dispersive spectrometry (EDS) can also be used to determine the amount of oxygen present in a sample⁷⁰.

5.1.3: Limiting the Formation of the Spinel Phase in $AlMgB_{14}$ materials

5.1.3.1: The $MgAl_2O_4$ system

The family of spinels takes its name from the 1:1 reaction product of the two refractories MgO and Al_2O_3 , equation 5.1.



The spinel itself is a useful industrial material, used mostly for furnace linings and other thermal insulative applications. $MgAl_2O_4$ has a melting point of $2135^\circ C$ a hardness ($H_{V5} = 2.89 \text{ GPa}-7.79 \text{ GPa}$), fracture toughness of $2.5-5.82 \text{ MPam}^{1/2}$ and good thermal shock resistance^{71, 72}.

The structure of the spinel consists of a unit cell comprising of thirty-two oxygen anions, all of which are equivalent and form a close-packed structure⁷³. Eight A cations occupying tetrahedral sites and sixteen B cations occupying octahedral sites. This close packed array generates sixty-four tetrahedral and thirty-two octahedral sites for the twenty-four cations to occupy. The formula unit is $MgAl_2O_4$ and thus the charges on the cations can consist of $(A^{2+}, 2B^{3+})$, $(A^{4+}, 2B^{2+})$, $(A^{6+}, 2B^{1+})$ to compensate for the total charge of the four O^{2-} anions. Spinel is named as (2,3) spinel, (4,2) spinel and (6,1) spinel respectively. A normal spinel has all the eight A ions in tetrahedral positions and the sixteen B ions in octahedral sites. This produces an overall structure for the spinel as shown in figure 5.1.1.

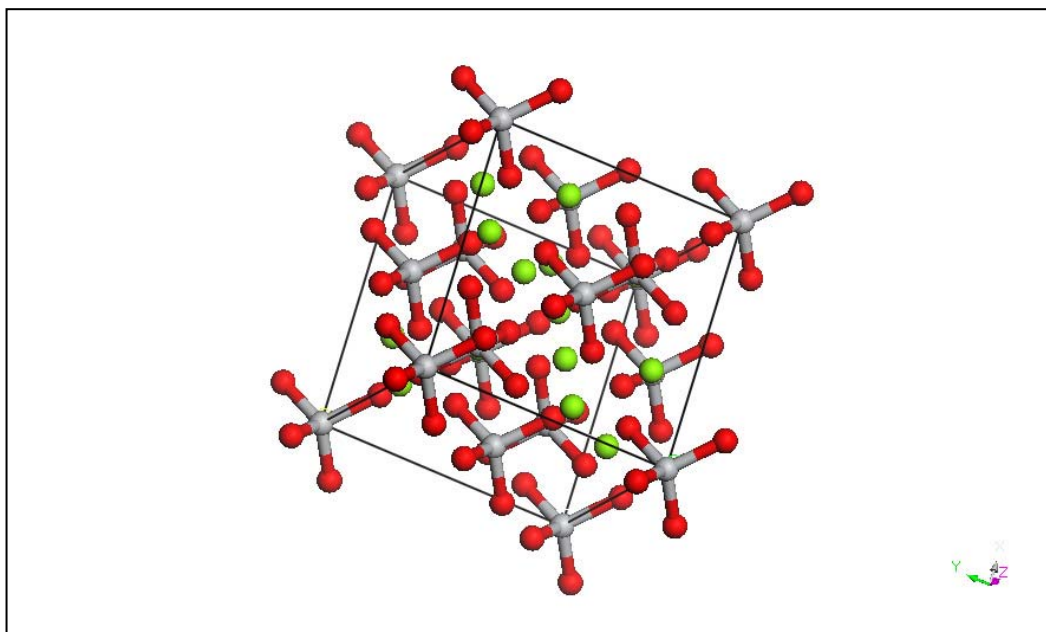
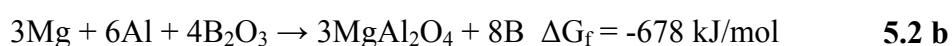
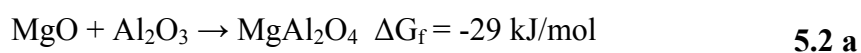


Figure 5.1.1: The structure of MgAl_2O_4 the grey coloured atoms are magnesium cations, the green coloured atoms are the aluminium cations and the red atoms are the oxygen anions

The processing of AlMgB_{14} involves the reaction of the elemental powders of magnesium, aluminium and boron. However, each one of the starting elemental powder particles (B, Al, Mg) contain a thin oxide layer viz. B_2O_3 ; Al_2O_3 and MgO .

During the processing of Al, Mg and B the formation of the spinel phase is expected from the reactions listed in equations 5.2 a and b.



The Gibbs free energy quoted in reactions 5.2 a and b is favourable at 1400°C ^{17, 74}. Spinel formation, from both reactions, can be shown to be spontaneous at temperatures in excess of 675°C ⁷⁴.

5.1.3.2: The AlMgB₁₄ compound

The specific reference to the synthesis of AlMgB₁₄ and the subsequent publication by the Ames group on their discovery of the super hard ceramic material AlMgB₁₄ created a stir amongst the hard materials fraternity^{75, 2}. Many articles carried the news^{76, 77} and interest in the material spread via the internet⁷⁸. However, the initial report by Cook *et al* did not report on the presence of any “impurity phase”, specifically the formation of the spinel phase. The hardness of the spinel phase is between 2.89-7.79 GPa⁷¹. The presence of this phase in a material that is reported to have a hardness of 35 GPa would almost certainly result in a lower hardness of the AlMgB₁₄ material. Thus, the hardness of AlMgB₁₄ reported may have been the hardness of AlMgB₁₄ + MgAl₂O₄ and thus an even higher value may be associated with pure AlMgB₁₄. Presumably the spinel phase was produced, but no mention was made of it in the initial publication² or in the patent filed with the US patent office⁷⁵.

Subsequently a paper was published by the Ames group that corrected their initial report²⁷. They reported that specimens prepared from elemental powders of the highest purity, milled in a helium glove box and sintered under vacuum, contained about 2-3 wt.% impurities, primarily consisting of MgAl₂O₄ and FeB. Cook *et al* suggested that the impurities arose from adsorbed atmospheric oxygen and H₂O, and the steel vials and steel ball milling media used during the mechanical alloying. Furthermore, specimens that were prepared from elemental powders of lower purity that had experienced greater exposure to atmospheric oxygen and H₂O resulted in samples that had an impurity content of as much as 30 wt.%²⁷.

The approach used by the Ames group, for limiting the amount of oxide phase present in the final non-oxidic ceramic, followed the procedure laid out in section 5.1.1. Firstly they used the highest purity starting materials that were available, thus limiting the amount of impurity oxide phase in the initial starting powders. Secondly, they used aluminium and magnesium pieces as opposed to powders. This had the effect of lowering the surface area and thus the rate of oxidation of their starting powders prior to mechanical alloying. Thirdly, the authors did all their processing in an inert atmosphere thereby reducing the concentration of any oxidising agent (O₂ or H₂O).

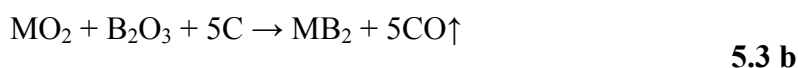
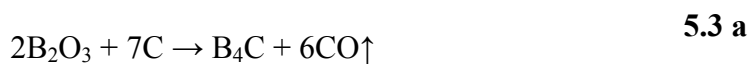
Finally, they determined the lowest temperature and shortest soak time required to produce a completely dense compact with the optimal mechanical properties.

Notwithstanding this, the Ames group still could not totally restrict spinel formation. In an attempt to further reduce spinel formation in AlMgB₁₄ we employed a procedure to remove the oxide layer from the boron starting powder. This process and the results obtained are discussed in section 5.2 and 5.3.

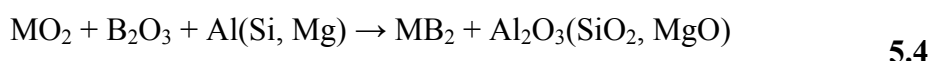
5.1.4: Boron Oxide as an oxidising agent

The boiling point of boron oxide (B₂O₃) is 1500°C⁷⁹. The removal of the surface layer of B₂O₃ at elevated temperatures disrupts the passive oxidation layer thereby allowing further oxidation of the boron to occur if exposed to an oxidising environment.

B₂O₃ can be reacted with carbon to form B₄C⁸⁰ as well as the transition metal diborides⁸¹ according to equations 5.3 a and b.



Aluminium, silicon and magnesium can reduce boron oxides, see equation 5. 4. The product is usually contaminated by residual metals or oxides and the product has to be purified by subsequent leaching, or a high temperature vacuum treatment⁸².



5.1.5: Boron as a reducing agent

High quality transition metal borides can be synthesised from a metal oxide and boron. The reaction is termed a borothermic reduction⁸³ of the metal oxide and the reaction scheme is laid out in equation 5. 5.

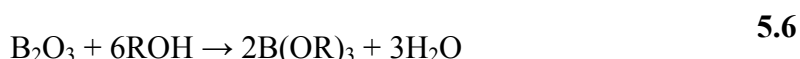


The formation of the transition metal diborides from the reductive elimination of the metal oxides to form the volatile sub-oxide B_2O_2 indicates the readiness with which boron forms metal diborides⁸². Thus, any surface layer of B_2O_3 that is removed from the starting boron powder grains will expose elemental boron which when reacted with metals preferentially forms the borides.

5.1.6: Boron oxide and the formation of boron esters

The formation of the spinel phase can further be reduced by eliminating the surface boron oxide layer from the starting boron powders. Disruption of the surface boron oxide layer can occur if direct reaction of the oxide layer with some reactant results in the formation of a volatile boron species. This would be even more beneficial if the reactant did not react with elemental boron and/or re-oxidise the surface of the exposed boron. Better yet would be a situation in which a reaction product would volatilise at moderate temperatures.

Boron esters are readily formed from boron oxide and any organic alcohol⁸⁴, see equation 5.6.



Boron esters are formed under reflux in benzene at temperatures of around 80°C ⁸⁴. Furthermore, no reaction occurs between an organic alcohol and elemental boron i.e. boron does not oxidise to the ester or to the oxide in the presence of organic alcohols⁸⁴. Boron esters are themselves volatile and evaporate at atmospheric pressure and at temperatures below 150°C . The volatility of the boron ester generally decreases with the increasing length of the alkyl chain, R.

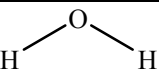
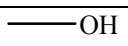
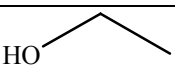
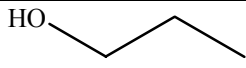
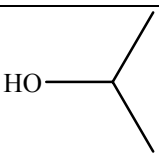
In this chapter we report a method to limit the formation of the spinel phase by reacting B_2O_3 with a range of alcohols to form boron esters. By milling the elemental powders in alcohols of various polarities the formation of these boron esters during milling and/or subsequently during solvent extraction in the rotary evaporator will reduce the amount of boron oxide present in the green compacts. Equation 5.2 b indicates that the removal of boron oxide will result in the reduction of the amount of the spinel phase present in the final sintered compacts.

5.2: Experimental

5.2.1: Solvent Properties

Table 5.2.1 indicates the structures, polarities, boiling points and purities of the solvents used in this study. The choice of alcohols was determined by the availability of the alcohols as well as the length of the alcohol alkyl chain.

TABLE 5.2.1: Properties of some organic compounds

Organic compound	Boiling Point (°C)	Dipole Moment	Purity Supplier
 water	100	1.85	distilled and deionised
 methanol	65	1.70	99.5% Saarchem
 ethanol	78.3	1.69	Abs. 99.9% Saarchem
 1-propanol	97.4	1.68	99.7% Saarchem
 iso-propanol	82.4	1.66	99.7% Saarchem

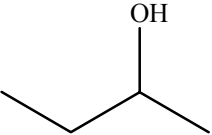
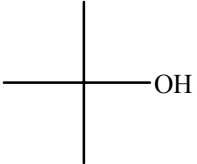
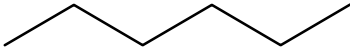
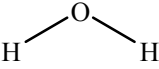
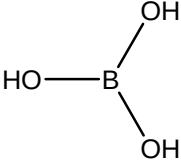
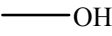
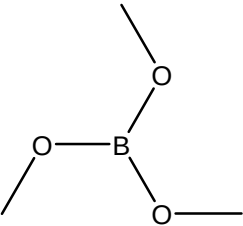
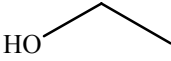
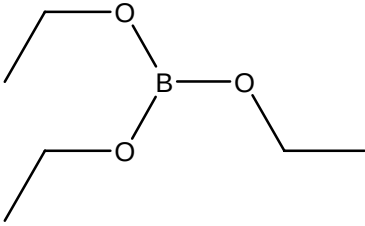
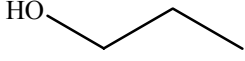
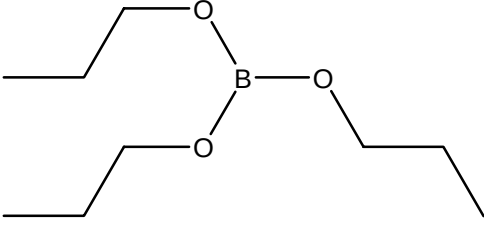
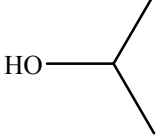
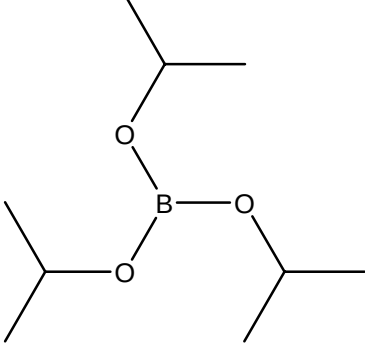
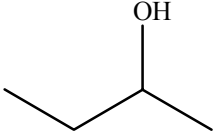
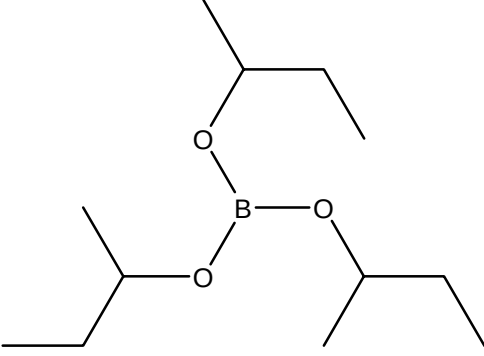
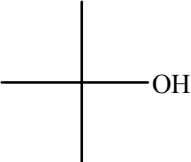
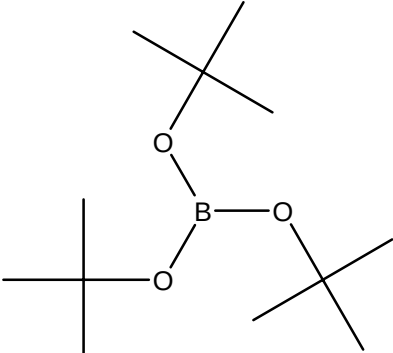
 2-butanol	99.5	1.66	99.5% Saarchem
 tert-butyl alcohol	82.2	1.64	99.5% Saarchem
 hexane	69	0	99.99% Saarchem

Table 5.2.2 indicates the boron ester formed from the corresponding alcohol and the respective boiling points of the ester at room pressure.

TABLE 5.2.2: The corresponding boron esters

Organic Compound	Boron Ester	Boiling Point (°C)
 water	 boric acid	Decomposes 169 ⁸⁵ $2\text{B}(\text{OH})_3 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$
 methanol	 trimethyl borate	69 ⁸⁶

 ethanol	 triethyl borate	112 ⁸⁷
 1-propanol	 tri-n-propyl borate	177 ⁸⁶
 iso-propanol	 triisopropyl borate	137 ⁸⁸
 2-butanol	 tri(2-butyl) borate	196 ⁸⁹

 tert-butyl alcohol	 tritertbutylborate	164⁸⁹
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The use of water as a solvent required a slightly different processing procedure. The boron powder was first washed in hot water, heated to 60°C, by stirring the powder and water with a teflon stirrer bar for 20 minutes. The water was then removed by centrifuge and the boron powder was dried under vacuum. This boron powder was then milled with aluminium and magnesium in hexane as per usual.

5.2.2: TEM analysis

In order to prepare the powders for elemental analysis in the TEM, 25 ml methanol was placed in a 100 ml glass beaker. The solvent was stirred with a teflon magnetic stirrer bar. Argon gas was (simultaneously) bubbled through the methanol. After 30 min, 1 g of boron powder was added to the solvent and the solvent was brought to boil. Freshly degassed methanol was constantly added to the contents of the beaker as the contents boiled away for 2 hours under a steady flow of argon gas.

About 2 ml. of this mixture was loaded onto a polymer coated copper grid for TEM analysis. Aluminium and magnesium powders were loaded onto the TEM copper grids by dispersing these metal powders in ethanol by ultrasound.

An energy dispersive spectrometer (EDS) analyser attached to the TEM was used to analyse for oxygen, boron, magnesium and aluminium. Quantitative analysis of the elements was done using the Cliff-Lorimer ratio for thin sections⁹⁰. This method requires that the particles being analysed are very thin (< 5 µm).

In order to get a correct oxygen analysis in the sample as determined by the EDS analyser it was necessary to remove the contribution to the oxygen content from the organic polymer support on which the powders were loaded. This was done by finding the ratio of the at.% oxygen and the at.% carbon for the polymer support as was determined by the EDS analyser on the pure polymer support film. Using the ratio obtained from this calculation the amount of oxygen contributed by the polymer could be removed from the oxygen in the sample. It is assumed that the only contribution for carbon comes from the polymer support itself. The oxygen content calculated in this way will be referred to as the normalised oxygen content.

5.3: Results and Discussion

5.3.1: Carbothermal Reduction

Temperatures for the reduction of alumina and magnesium oxide are above 1800°C. Magnesium boils at 1100°C and temperatures higher than this result in sputtering of the metal. This sputtering is often minimised for many metals by the use of a suitable flux. However, no suitable flux for minimising the effect of the sputtering of the magnesium metal could be found during this work.

The carbothermal analysis of samples yielded results that were difficult to interpret. Figure 5.3.1 is a plot of the oxygen content determined eleven times for the same batch of magnesium powder.

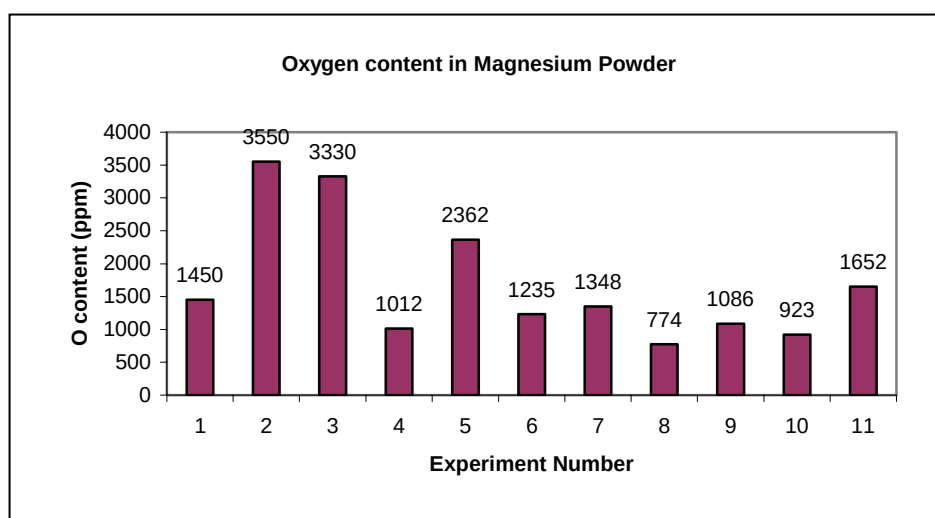


Figure 5.3.1: Oxygen content in Mg powder determined by carbothermal reduction

From figure 5.3.1 it is clear that the results from the carbothermal reduction of magnesium powder produces results that are unreliable. Similarly, no trend was evident in the results obtained from the carbothermal reduction of the aluminium and boron starting powders. During the carbothermal reduction both aluminium and boron powders were also prone to sputtering at the high temperatures that are required for the reduction of the respective oxide in the presence of carbon. Therefore carbothermal reduction was not suitable for determining the oxide content in the starting powders.

5.3.2: X-ray diffraction techniques

XRD analysis was used to evaluate whether a reduction in the spinel phase content relative to the boride phase content, as a result of the alcohol washing process, was discernable. The XRD technique was used to evaluate the effect of milling aluminium and magnesium in the oxidising solvents and the resulting appearance of any additional oxide phases after hot-pressing.

5.3.2.1: The baseline material

In order to determine the amount of spinel phase present using XRD, a baseline material composed of a 1:1:14 mole ratio of Al:Mg:B respectively was prepared in hexane. Rietveld analysis was used to measure the amount of the various phases present in a 1:1:14 mole ratio (Mg : Al : B) sample prepared according to the method laid out in section 2.3. Figure 5.3.2 shows a diffractogram of the baseline material and the corresponding Rietveld analysis is presented in figure 5.3.3. A summary of the phase content of the baseline material is given in table 5.3.1. The main phases were AlMgB_{14} , MgAl_2O_4 , some unreacted Al and W_2B_5 .

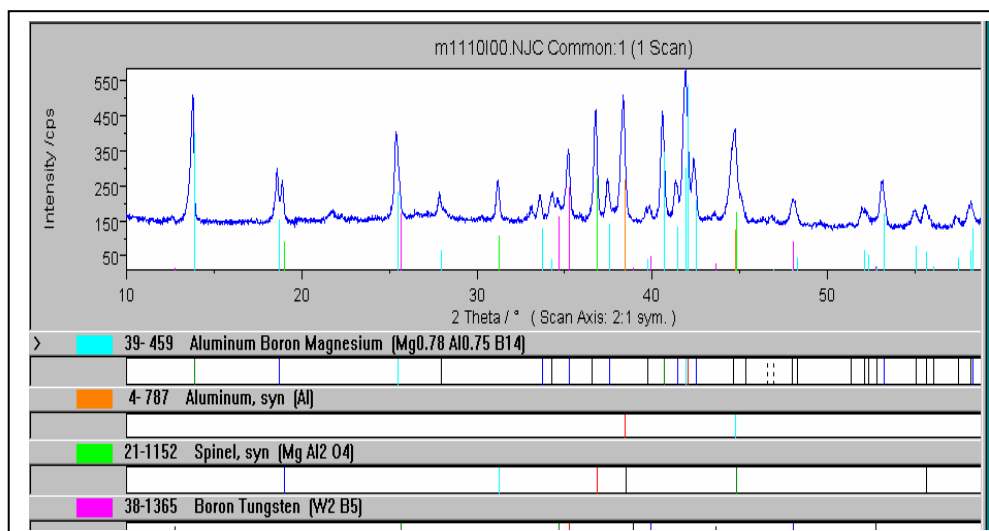


Figure 5.3.2: X-ray diffractogram for Rietveld analysis of phase content

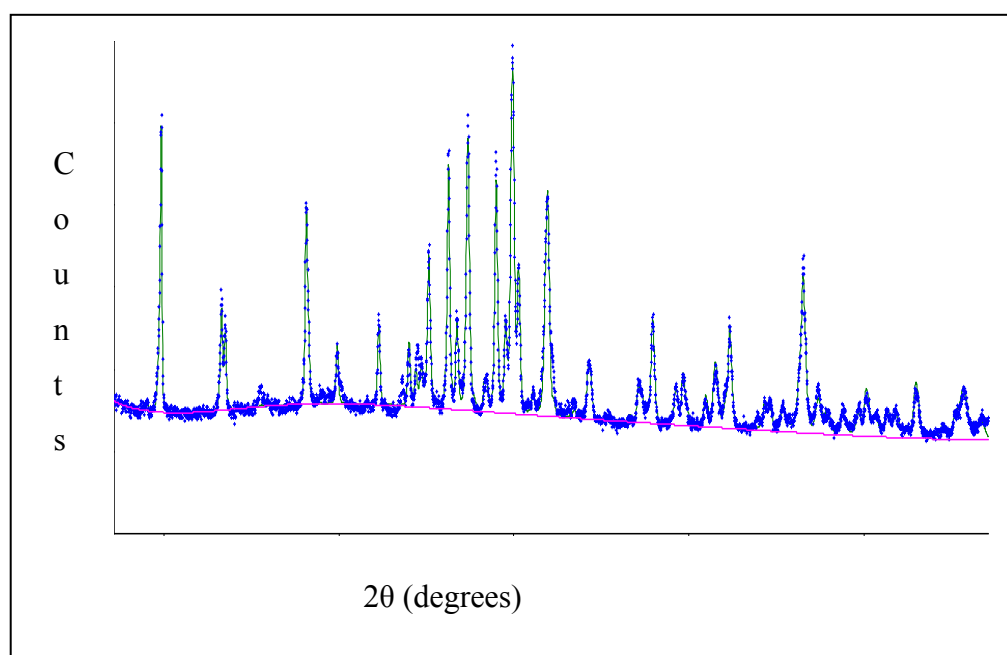


Figure 5.3.3: Rietveld analysis diffractogram

Table 5.3.1 indicates the phase content as determined from the Rietveld analysis.

TABLE 5.3.1: Table of phase content of baseline AlMgB₁₄ determined by Rietveld analysis

Phase	% Mass
Al	5.2 ± 0.8
MgAlB ₁₄	83.5 ± 2
MgAl ₂ O ₄	10.4 ± 1.2
W ₂ B ₅	0.8 ± 0.3

The presence of W₂B₅ is expected as it was formed during the sintering cycle by reaction of WC with B at elevated temperatures. WC is picked up from the milling vessel during milling. The presence of unreacted aluminium in a 1:1:14 composition of Al:Mg:B is explained from the migrating solid solution boundary that allows an equilibrium to exist between Al and AlMgB₁₄ at 1400°C, see chapter 4. the analysis shows that samples produced from a 1:1:14 atomic ratio of Al:Mg:B and prepared at 1400°C have about a 10 wt.% spinel phase content.

5.3.2.2: Washing the boron powder versus milling the boron powder in the solvent

An alternative strategy to limit the formation of the spinel phase is to remove boron oxide from the starting boron powder by reaction with an organic alcohol. It is necessary to establish if less spinel phase is produced when the boron powder is first washed in the solvent, then dried and finally milled in an inert solvent with all the other ingredients. Or if all the ingredients, when milled together in the respective alcohol, without a prior washing of the boron powder, produce less spinel than the baseline material. This comparison is necessary to confirm if milling all the ingredients in an alcohol oxidises Al and Mg thus negating the overall aim of this method which is to limit the amount of the spinel phase in the final product. Figure 5.3.4 indicates the diffractograms for the respective samples prepared in 1-propanol. The major boride peak (AlMgB₁₄) and major oxide (Al₂MgO₄) are indicated in the figure.

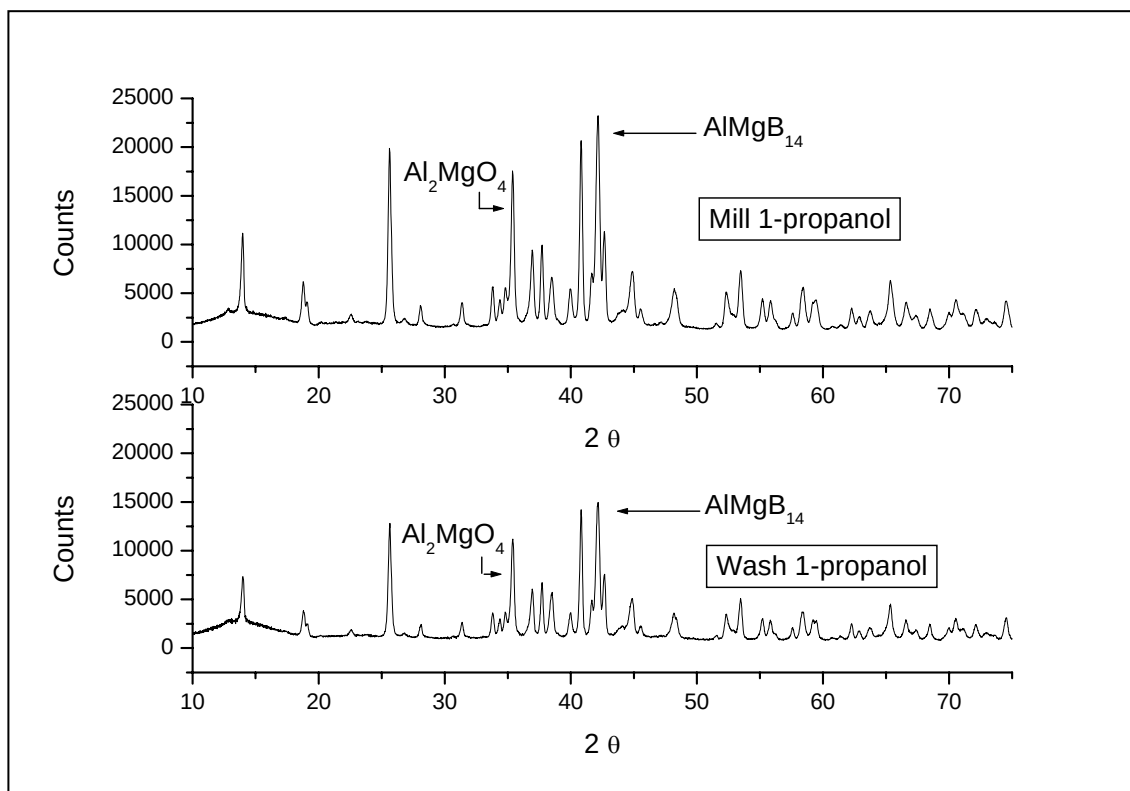


Figure 5.3.4: X-ray diffractograms for samples prepared by different methods hot-pressed at 1400°C, 20 MPa, 1 hour

From figure 5.3.4 it is clear that there are no significant differences in the phases produced from either procedure. More importantly the respective ratios of the AlMgB_{14} and MgAl_2O_4 major peak heights are 2.86 ± 0.18 and 2.80 ± 0.15 for the samples produced from the milling and washing procedures respectively. Figure 5.3.5 reveals the phase content of the milled sample presented in figure 5.3.4.

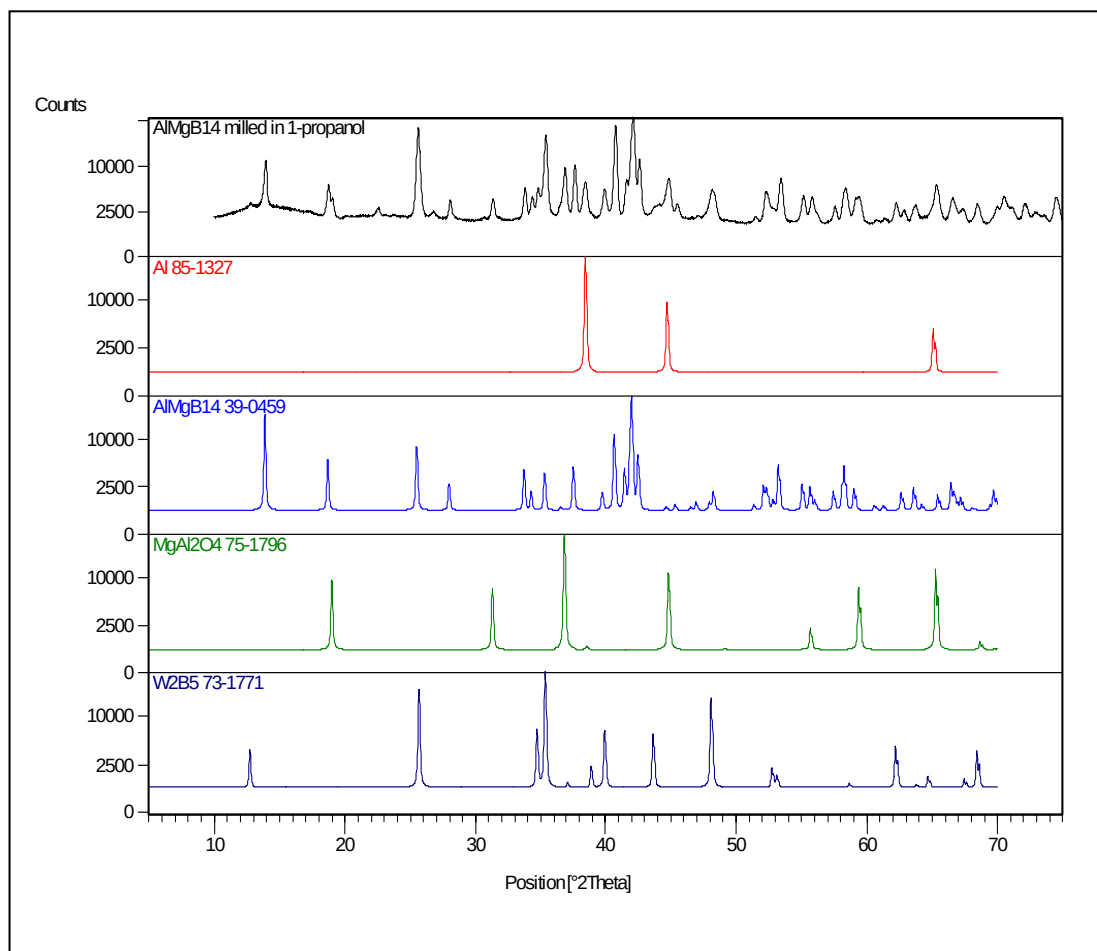


Figure 5.3.5: Diffractogram for the milled sample hot-pressed at 1400°C, 20 MPa, 1 hour

It is not clear what phase produces the peak that appears at about 23° 2θ. Because the intensity of this one peak is very small the phase can at best be present in trace amounts only.

5.3.2.3: The effect of milling Al, Mg and B in various solvents

The milling of the ingredients, 2 hours at 200 rpm in a planetary mill, was performed in the range of solvents shown in table 5.2.1. The XRD powder diffractograms were recorded for each of the samples after hot-pressing at 1400°C. The milling process was held constant for each solvent.

The ratio of the intensities of the major peak heights of AlMgB_{14} and MgAl_2O_4 were calculated from the diffractograms for each of the products. The values are presented in table 5.3.2.

TABLE 5.3.2: Values used in figures 5.3.6a-b

Solvent	Ratio Boride/Oxide	Polarity ⁹¹
Hexane (1400°C)	0.93	0
t-butanol	1.64	1.64
Isopropanol	2.25	1.66
2 butanol	2.48	1.66
1-propanol	2.86	1.68
Ethanol	3.20	1.69
Methanol	3.25	1.7
Water*	3.74	1.85

* procedure described section 5.2.1

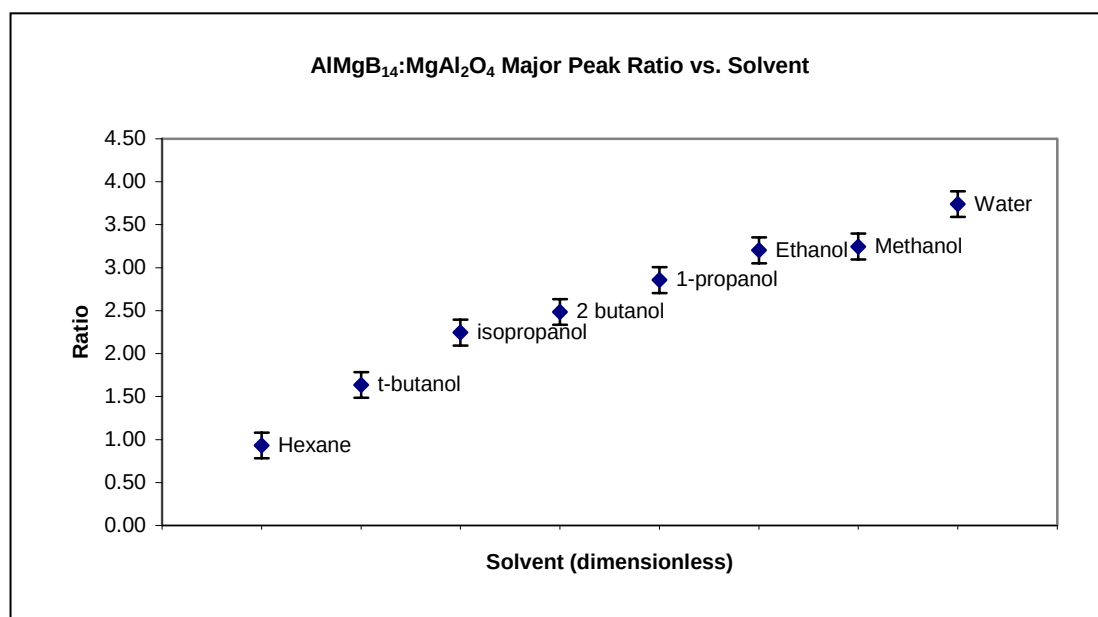


Figure 5.3.6 a: Ratio of Boride/Oxide vs. solvent

It can be seen that by arranging the alcohol solvents in terms of their chain length that as the boride to oxide ratio decreases, the length of the alcohol alkyl chain increases.

Since the length of the alkyl chain is related to the polarity of the solvent a plot of alcohol polarity against the ratio reveals a similar correlation, figure 5.3.6 b.

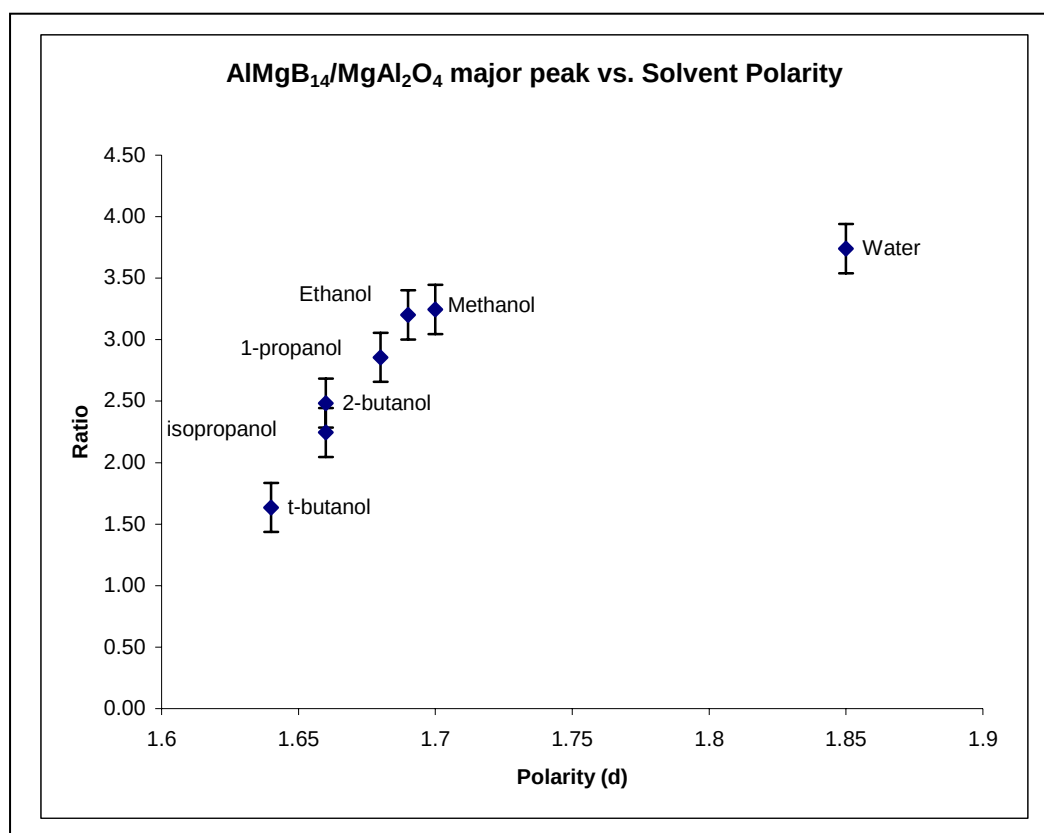


Figure 5.3.6 b: Ratio of Boride/Oxide vs. alcohol solvent polarity

The upper limit of the boron to oxide ratio will obviously be the point at which all of the boron oxide is removed and the contribution to the oxide phase will then only be made by the other metals (magnesium and aluminium). The lower limit of this ratio will obviously be set by the total amount of oxide phases that contribute to the spinel formation.

A more detailed investigation would need to be done to determine the limits of the amount of oxide which is removed from boron during the milling in the alcohols. Such parameters as temperature, time, stirring speed and polarity need to be optimised with respect to the yield of ester obtained in order to fully understand the limits of this procedure.

5.3.2.4: Predicting the amount of spinel phase present in AlMgB₁₄ samples milled in alcohol

Rietveld analysis was done on the sample prepared in hexane. It was assumed that the ratio calculated from the intensity of the major boride phase peak and the intensity of the major oxide phase peak indicate the relative amounts of the boride to oxide phase present. If the amount of spinel phase is assumed to be 10% in the sample prepared in hexane, then the % spinel present in a material prepared by milling in an alcohol can be calculated from equation 5.7.

$$\frac{R_k}{R_i} \times P_k = P_i \quad 5.7$$

R_k = ratio of known spinel content,

R_i = ratio of unknown spinel content, P_k = percentage known spinel content and

P_i = percentage unknown spinel content.

The values calculated are tabulated in table 5.3.3.

TABLE 5.3.3: The percentage by mass of the spinel phase

Solvent	Ratio Boride/Oxide	Polarity d	% spinel P _i
Hexane (1400°C)	0.93	0	10.0
t-butanol	1.64	1.64	5.7
isopropanol	2.25	1.66	4.1
2-butanol	2.48	1.66	3.7
1-propanol	2.86	1.68	3.3
Ethanol	3.20	1.69	2.9
Methanol	3.25	1.7	2.9
Water*	3.74	1.85	2.5

* procedure described in section 5.2.1

Based on the TEM analysis of boron powders milled in methanol, that will be presented in section 5.3.3, the lowering of the spinel phase content in AlMgB₁₄

samples prepared by milling in alcohols is the result of the lowering of the oxide content in the starting boron powder by the formation of boron esters when milling the starting powders in alcohol.

The least amount of spinel is formed for samples in which the boron powders is first washed in water, dried and then milled together with the other starting materials in hexane. The mechanism for this is assumed to be the solubility of B_2O_3 in water and not the formation of the boron esters⁹².

5.3.3: EDS analysis preformed by TEM on boron powders milled in hexane and methanol

To remove the effect of oxygen in the polymer coating of the copper grids used in the TEM analysis EDS analysis of the polymer coating was done. The values obtained for the oxygen and carbon content for the polymer coating are shown in table 5.3.4.

TABLE 5.3.4: Oxygen content in the polymer coating

Carbon	Oxygen	Normalised Oxygen
at %	at%	at%
92.8	7.2	0.08

EDS analysis was then done on boron particles taken from the starting boron powders prepared in hexane and methanol. The oxide content in the solvent prepared boron powders was converted from an atomic percent to a weight percent and the results are reported in table 5.3.5.

TABLE 5.3.5: Mass percent of oxygen in boron

Solvent	Boron (mass%)	Oxygen (mass%)
-	97.1 ± 0.6	2.9 ± 0.6
Hexane	96.9 ± 0.9	3.1 ± 0.9
Methanol	98.8 ± 0.4	1.2 ± 0.4

The error bars reported in table 5.3.5 are calculated from the values obtained for 5 analyses on 5 different particles. The samples prepared in methanol and hexane are reported because the sample prepared in methanol represents the best organic alcohol for limiting the amount of the spinel phase and the sample prepared in hexane is the baseline material.

No internal boron oxide standard was run in the TEM so the absolute value of the values quoted in the table is unknown.

5.3.4: TEM analysis of the starting Mg and Al powders

Analysis of thin edges of the perimeter of the magnesium and aluminium powders indicated that the outer layer of the metal powder consisted predominately of the respective metal oxide phase. Bulk analysis of the metal particles indicated pure metal only.

5.4: Summary

Traditional approaches for dealing with the oxidation problem of boron-based ceramic materials involves the stringent preparation of powders in inert atmospheres, the use of low reaction temperatures and hot-pressing under an inert atmosphere. That is, limiting the exposure of the starting powders to oxygen and/or other oxidising agents at all stages in the processing of the material.

The processing of AlMgB₁₄ by the Ames group involved the preparation and sintering of their material in oxidant free environments². The Ames group achieved total impurities content of less than 2.8 wt.% for samples prepared from the purest starting materials. For samples prepared from less pure starting powders the oxide phase content was as high as 30 wt.%.

A chemical solution to reduce the oxide content is also possible. In this process boron-based ceramics are prepared by milling the starting powders in an organic alcohol of high polarity. The alcohol removes some of the surface layer of oxide from

the boron powder by reacting with it to form the corresponding boron ester. The removal of the corresponding ester results in the lowering of the oxide content.

EDS analysis in a TEM further corroborate this conclusion. TEM and XRD analysis indicated that removal of the oxide occurs during (i) the washing of the boron powder and (ii) the subsequent solvent extraction under rotary evaporation. An additional increase might be achieved by the use of di-alcohols.

The amount of spinel phase remaining in the final sample is related to the polarity of the alcohol in which the starting powders were milled. At large polarities the trend is asymptotic achieving a maximum $\frac{AlMgB_{14}}{MgAl_2O_4}$ major peak ratio when boron was washed in water and then milled with Al and Mg in hexane. This limit is assumed to be determined by the amount of oxide phases present in the starting Al and Mg metal powders. However, TEM analysis indicates that there is some oxygen left in post-alcohol milled powders.

The use of this approach to minimising the oxide content in boron-based materials may apply to the processing of other non-oxidic-boron-based materials. This approach can be used to control residual oxide content present in boron by controlled removal of the oxide from a sample.