Thermal Analysis and Phase Equilibria in the Mg-B System

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Outline

• Introduction
• Thermal Analysis of the Mg/B Reaction
• Smith Thermal Analysis Method in the Mg/B System
• Synthesis of Mg-B-C Alloys
Introduction

- MgB$_2$ known since ~19$^{th}$ century

- Originally used by chemists to make boron hydrides by dissolving the compound in acid

- Mislabeled as Mg$_3$B$_2$ until 1954 when correct stoichiometry was determined by Jones and Marsh to be MgB$_2$ and structure was determined to be isomorphous with AlB$_2$ (P6/mmm)

- Discovered to be superconducting with $T_c$ of 39 K by Nagamatsu et al. in 2001

- Continuous development as applied material for superconducting applications since 2001
Thermal Analysis of the Mg/B Reaction
Low Temperature MgB$_2$ Synthesis

- Low temperatures required due to Mg volatility (Mg boils at 1090 °C)
- This requires a fine boron powder since the boron never melts (pure boron melts at 2092 °C)
- Presumably, the reaction proceeds by formation of MgB$_7$ first, MgB$_4$ second, and finally MgB$_2$ (see phase diagram – next slide)
- Numerous authors reported two exothermic events in the reaction of Mg powder and amorphous Boron powder by DTA and DSC (see below)

TA Instruments Differential Scanning Calorimeter 2920
Instrument Response – Pure Mg

10 °C/minute ramp rate

Baseline Drift

Mg melting

DSC Temperature Limit

Universal V4.7A
Mg powder and Mg + B powder

Two Exothermic Events

Mg Powder Melting

10 °C/minute ramp rate
Mg powder and Mg + B powder

Small Exothermic Event in Mg coincides with Mg + B reaction at low temperature
Mg Powder – multiple runs

10 °C/minute ramp rate
Mg from MgH$_2$

Both Mg and MgH$_2$ after decomposition have a repeatable exothermic peak at ~425-475 °C after air exposure.
XRD on MgH$_2$ exposed to air
XRD on MgH$_2$ after decomposition
Proposed Mechanism for Mg DSC Behavior

- Mg(OH)$_2$ forms on Mg and MgH$_2$ exposed to air

- At ~425-475 °C Mg(OH)$_2$ decomposes

- This leads to Mg(OH)$_2$ + Mg $\rightarrow$ 2MgO + H$_2$ which starts a low temperature reaction in the Mg/B powder mixture

- A source of clean Mg with no hydroxide may provide a means to study the Mg/B powder reaction without the initial low temperature event (i.e. clean MgH$_2$)
MgH$_2$ + amorphous B

MgH$_2$ $\rightarrow$ Mg + H$_2$

Mg + 2B $\rightarrow$ MgB$_2$
Kinetic Analysis

Assuming an elementary reaction and known initial and final states then we can use the general rate equation:

\[ \frac{d\alpha}{dt} = k(T) \cdot (1 - \alpha) \]

where

\[ k(T) = A \cdot e^{-\frac{E_A}{kT}} \]

which becomes

\[ \beta \frac{d\alpha}{dT} = A \cdot e^{-\frac{E_A}{kT}} \cdot (1 - \alpha) \]

where

\[ \beta = \frac{dT}{dt} \]
$E_A = -2.303 \cdot R \cdot \frac{d(\log \beta)}{d(1/T)}$

$E_A = ~241 \text{ kJ/mole}$
MgH$_2$ + B with air exposure

Possible Mg(OH)$_2$ decomposition
Conclusions

• “Intrinsic” reaction of Mg + amorphous B starts at ~575 °C with activation energy of ~241 kJ/mole
• The reaction starts below the Mg melting point of 650 °C.
• The first reaction observed in standard Mg/B powder mixtures is likely initiated by Mg(OH)$_2$ decomposition
• The thermal events in the Mg/B powder mixture are kinetic events and thus this study is only relevant for this particular boron powder (99% pure amorphous boron)

Smith Thermal Analysis Method in the Mg/B System
Problems in Low Temperature Synthesis

- Mg is volatile
- MgO contamination almost always present
- Homogenous doping is very difficult
- Porosity always exists

Fracture SEM on MgB$_2$ filament in commercial wire

Voids where Mg powder used to be
High Pressure and High Temperatures

What about using pressure to increase the boiling point of Mg?

Clausius-Clapeyron Equation: \[ \frac{dP}{dT} = \frac{L}{T\Delta V} \]

1 bar  
10 bar  
100 bar  

1090 °C
~1475 °C
~2200 °C
High Temperature High Pressure Vessel

Eurotherm 3504 Temperature Controller

99.998% Argon

Type C thermocouples (W-Re)

Monel Pressure Vessel (1500 psi maximum pressure)

Lepel 5 kW Induction Power Supply

Conax High Pressure Feedthroughs

Burst Disc and Pressure Relief Valve
Induction Coil and Hot Zone
Hot Zone Design

- Type C thermocouples
- 9 turn copper induction coil
- Fused Silica tube
- MgO
- Graphite Felt Insulation
- 9 in. (22.9 cm)
- 1 in. (2.5 cm)
- MgB$_2$
- Graphite Tube
- 2.75 in. (7 cm)
- Graphite Felt Insulation
The sample thermocouple is passive and not part of the temperature control loop.
The sample and graphite thermocouples are part of the temperature control loop and a temperature difference is maintained.
Smith Thermal Analysis Protocol

• Under manual control, heat the sample to some temperature near the region of interest.
• Determine the temperature difference between the graphite thermocouple and sample thermocouple
• Switch to automatic control and input a temperature difference set point that is either higher or lower than the equilibrium value determined above to either heat or cool the system.
Smith Thermal Analysis on Aluminum

Equilibrium Difference: ~20 °C

- Al Melting: 35 °C difference (~4 °C/min. cool)
- Al Freezing: 8 °C difference (~2 °C/min. heat)

Date/Time vs Graphite
Date/Time vs Aluminum
Advantages over DTA and DSC

- Sample is closer to equilibrium during first order phase transitions
- Small thermal events can be observed by increasing the sample size
- Large samples (10-100 grams) make it easy to use other characterization methods afterwards such as XRD
- Specific heat and latent heats can be obtained if suitable calibration runs are done beforehand
- Low capital investment (a fraction of a new DTA or DSC which is ~$60k)
Smith Thermal Analysis Run on AlB$_2$

15 °C difference (~2-5 °C/min. heat)

Date/Time vs Graphite
Date/Time vs AlB$_2$

Induction Power Supply turned off
Endothermic Event
Aluminum solidification
Smith Thermal Analysis Run on AlB$_2$ (15 °C difference)

Date/Time vs Graphite
Date/Time vs AlB$_2$
Predicted Mg-B Phase Diagram (CALPHAD)

MgB_2 \rightleftharpoons \text{Mg}_L + \text{MgB}_4

Peritectic: $\beta \leftrightarrow \text{Liquid} + \alpha$

Pressure: $10^7$ MPa (~1450 psi or 98 bar)

Second Ramp/Dwell/Cool in Mg-B Mixture

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:30:00</td>
<td>1400</td>
</tr>
<tr>
<td>11:40:00</td>
<td>1420</td>
</tr>
<tr>
<td>11:50:00</td>
<td>1440</td>
</tr>
<tr>
<td>12:00:00</td>
<td>1460</td>
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<tr>
<td>12:10:00</td>
<td>1480</td>
</tr>
<tr>
<td>12:20:00</td>
<td>1500</td>
</tr>
</tbody>
</table>

Graph showing temperature change over time with endotherm and exotherm indicated.

10 °C/min.
Smith Thermal Analysis Run on Mg-B Mixture

~1490 °C

40 °C difference
(~2-5 °C/min. heat)
Ramp, Dwell, Cool on Mg/B mixture (99.9999% B)

Time
11:30:00  11:50:00  12:10:00  12:30:00  12:50:00  13:10:00  13:30:00

Temperature (°C)
0  200  400  600  800  1000  1200  1400  1600  1800

Date/Time vs Graphite
Date/Time vs Sample

Thermocouple Failure

Endothermic Event

Mg Melting
MgB$_2$ from High Purity Boron

Time

12:25:00  12:26:00  12:27:00  12:28:00  12:29:00  12:30:00  12:31:00  12:32:00

Temperature (°C)

1430
1440
1450
1460
1470
1480

Date/Time vs Graphite
Date/Time vs Sample
Col 6 vs Col 5

[Graph showing temperature changes over time with multiple data points and trend lines]
Expected Microstructure for Peritectic

~1450 °C
Mg/B Microstructure – 99.9999% B
### EMPA Measurements by John Donovan

#### Dark Phase – MgB$_4$

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>20.9%</td>
<td>20%</td>
</tr>
<tr>
<td>B</td>
<td>78.7%</td>
<td>80%</td>
</tr>
<tr>
<td>O</td>
<td>0.4%</td>
<td>0%</td>
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</tbody>
</table>

#### Golden Phase – MgB$_2$

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>32.6%</td>
<td>33.3%</td>
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<tr>
<td>B</td>
<td>66.9%</td>
<td>66.6%</td>
</tr>
<tr>
<td>O</td>
<td>0.5%</td>
<td>0%</td>
</tr>
</tbody>
</table>
XRD on Mg-B High Purity Ingot

MgB₂

Mg

MgB₄
Remaining work on Mg-B binary

- Redo Smith Method with the high purity boron (99.9999%) and magnesium and obtain the peritectic temperature
- Characterize the sample
- ??
Synthesis of Mg-B-C Alloys

\[
\begin{align*}
\text{MgB}_2 \\
\text{MgB}_4 \\
\text{MgB}_7 \\
\text{MgB}_2\text{C}_2
\end{align*}
\]
Ternary Ingot from $B_4C$ Powder

$1500 \, ^\circ \text{C for 10 min.}, \, 2 \, ^\circ \text{C/min. cool}$

$Mg(B_{1-x}C_x)_2$

$MgB_2C_2$
XRD on Mg-B₄C Ingot

Mg(B₁₋ₓ°Cₓ)₂
Mg
MgB₂C₂
Peak Shift in XRD

<table>
<thead>
<tr>
<th>HKL</th>
<th>2θ Pure MgB$_2^*$</th>
<th>2θ Mg(B$_{1-x}$C$_x$)$_2$</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>25.266 (3.5221 Å)</td>
<td>25.332 (3.5131 Å)</td>
<td>+0.066</td>
</tr>
<tr>
<td>(100)</td>
<td>33.483 (2.6742 Å)</td>
<td>33.962 (2.6375 Å)</td>
<td>+0.479</td>
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<tr>
<td>(101)</td>
<td>42.412 (2.1295 Å)</td>
<td>42.796 (2.1113 Å)</td>
<td>+0.384</td>
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<tr>
<td>(002)</td>
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<td>51.941 (1.7590 Å)</td>
<td>+0.056</td>
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<td>(110)</td>
<td>59.886 (1.5433 Å)</td>
<td>60.697 (1.5246 Å)</td>
<td>+0.811</td>
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<tr>
<td>(102)</td>
<td>63.173 (1.4706 Å)</td>
<td>63.487 (1.4641 Å)</td>
<td>+0.314</td>
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<tr>
<td>(111)</td>
<td>66.044 (1.4135 Å)</td>
<td>66.817 (1.3990 Å)</td>
<td>+0.773</td>
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<tr>
<td>(200)</td>
<td>70.403 (1.3363 Å)</td>
<td>71.375 (1.3204 Å)</td>
<td>+0.972</td>
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<tr>
<td>(201)</td>
<td>76.125 (1.2494 Å)</td>
<td>77.051 (1.2367 Å)</td>
<td>+0.926</td>
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<tr>
<td>(112)</td>
<td>83.191 (1.1603 Å)</td>
<td>83.861 (1.1527 Å)</td>
<td>+0.670</td>
</tr>
</tbody>
</table>

*Pure MgB$_2$ based on PDF #00-038-1369 and Cu K$_{α1}$=1.5405982 Å

(00x) peaks do not shift very much indicating c lattice parameter has little change
**VSM Measurement at 100 Oe**

![Graph of VSM Measurement at 100 Oe with a sharp transition at approximately 21K.](image)

**Temperature (K)**

0 5 10 15 20 25 30

**Moment (emu)**

-0.06
-0.05
-0.04
-0.03
-0.02
-0.01
0.00
0.01

\(T_c \sim 21K\)
Preliminary TEM on Mg-B4C Ingot

HAADF Image from Tecnai TEM on FIB extraction sample

MgO inclusions
Work to be done on Mg-B-C Alloys

• Synthesis of a few (~3-4) different alloys with various carbon doping levels
• Characterization with XRD, SEM, TEM, etc.
• ??