Dissertation Overview

Thermal Analysis and Phase Equilibria in the Mg-B System

By S. D. Bohnenstiehl

Presented in partial fulfillment of the requirements for the Doctor of Philosophy degree in Materials Science & Engineering at The Ohio State University

Committee:
Dr. Michael Sumption (co-advisor)
Dr. Suliman Dregia (co-advisor)
Dr. John Morral

Acknowledgements: This work was supported by the U. S. Dept. of Energy, Office of High Energy Physics under Grant No. DE-FG02-95ER40900.

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 ~19th century
- Originally used by chemists to make boron hydrides by dissolving the compound in acid
- Mislabeled as Mg_3B_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

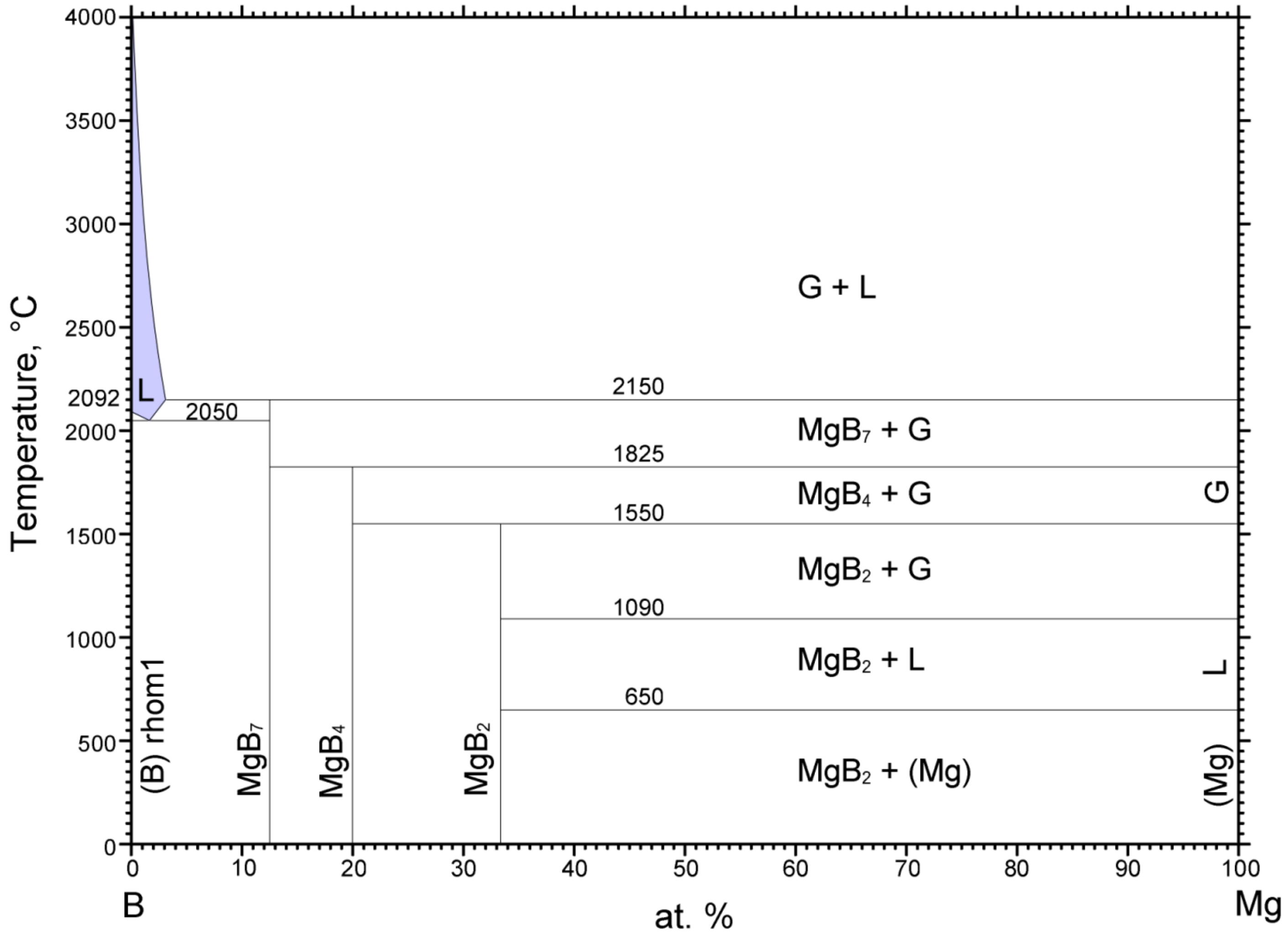
Thermal Analysis of the Mg/B Reaction

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)

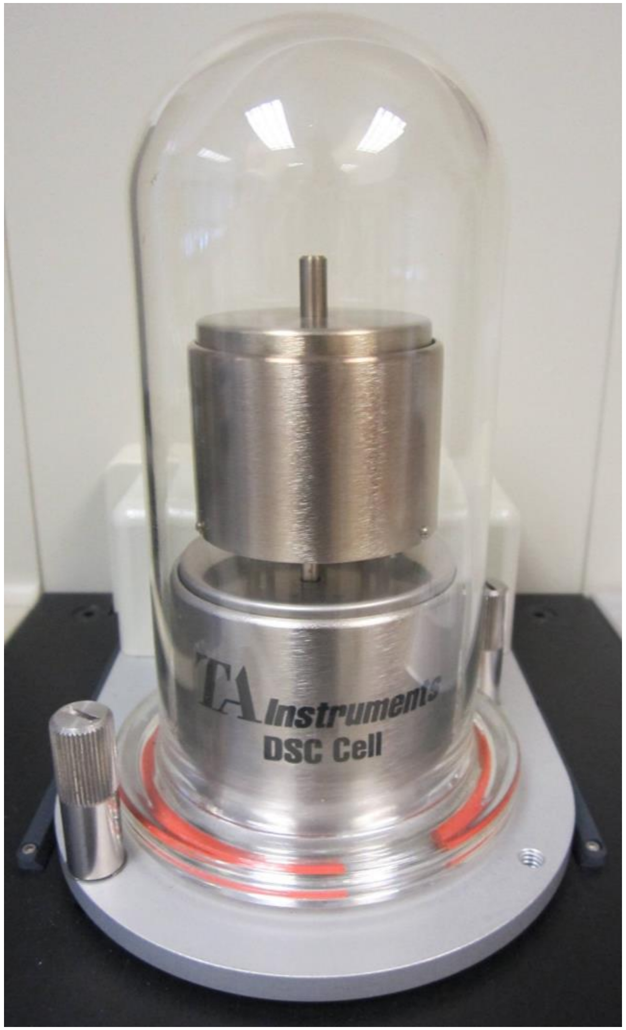
1. Meng et al., *Materieals Research Society Symposia Proceedings* **689** (2002) 39-46.
2. Goldacker et al., *Supercond. Sci. Technol*. **17** (2004) S490.
3. Kim et al., *Journal of Applied Physics* **100** (2006) 013908.

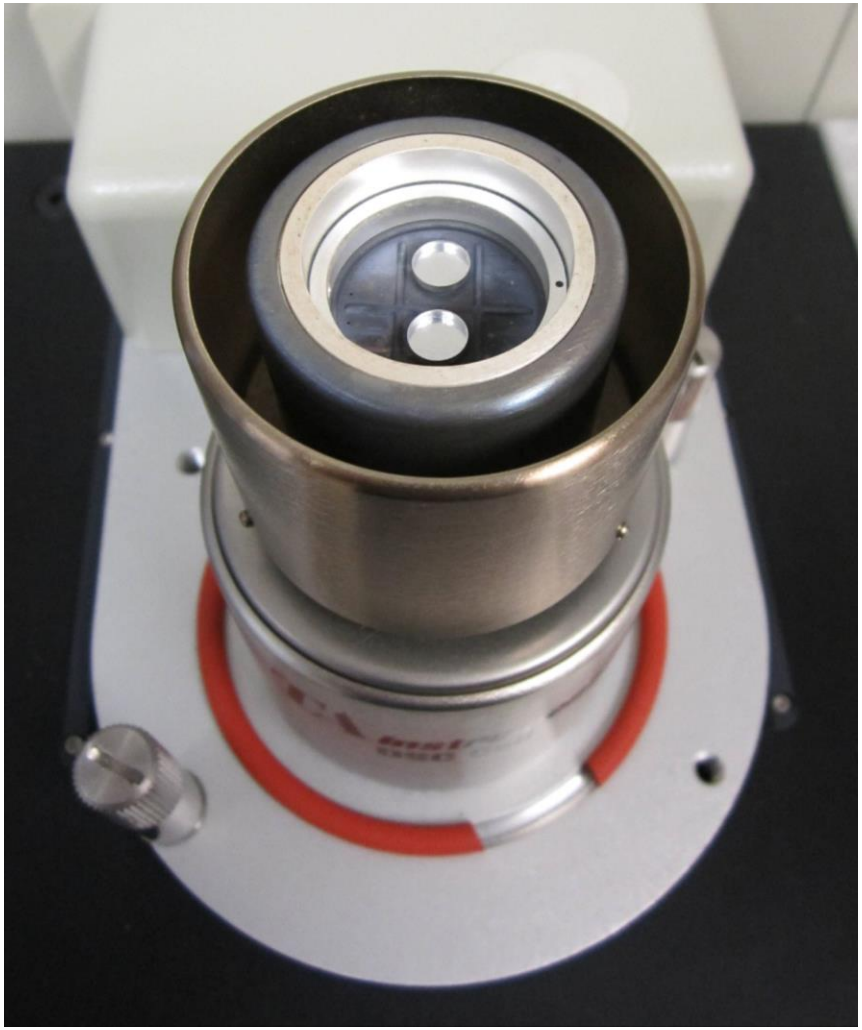
Mg-B Phase Diagram – 1 atm



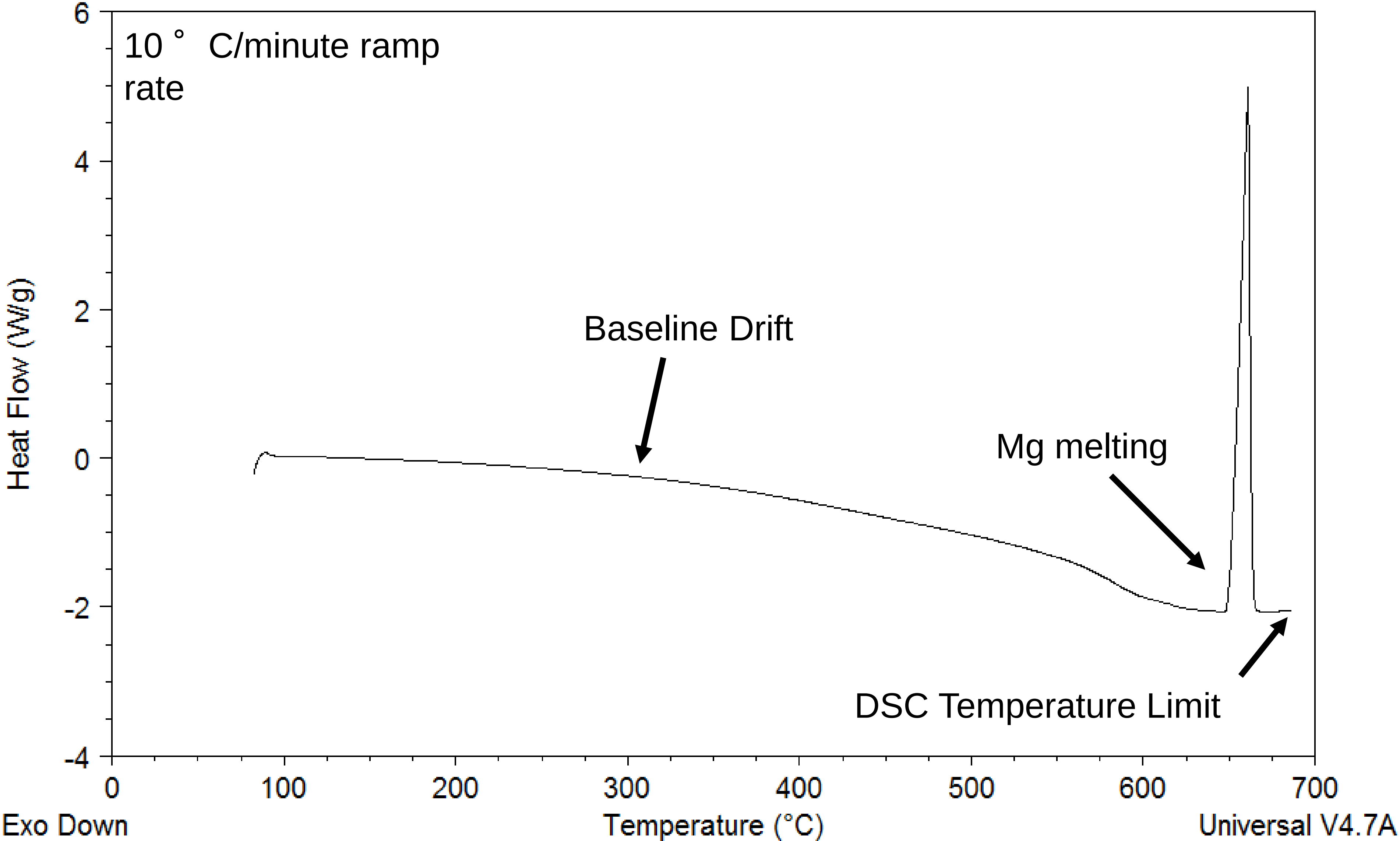
© ASM International 2006. Diagram No. 900297

TA Instruments Differential Scanning Calorimeter 2920





Instrument Response – Pure Mg



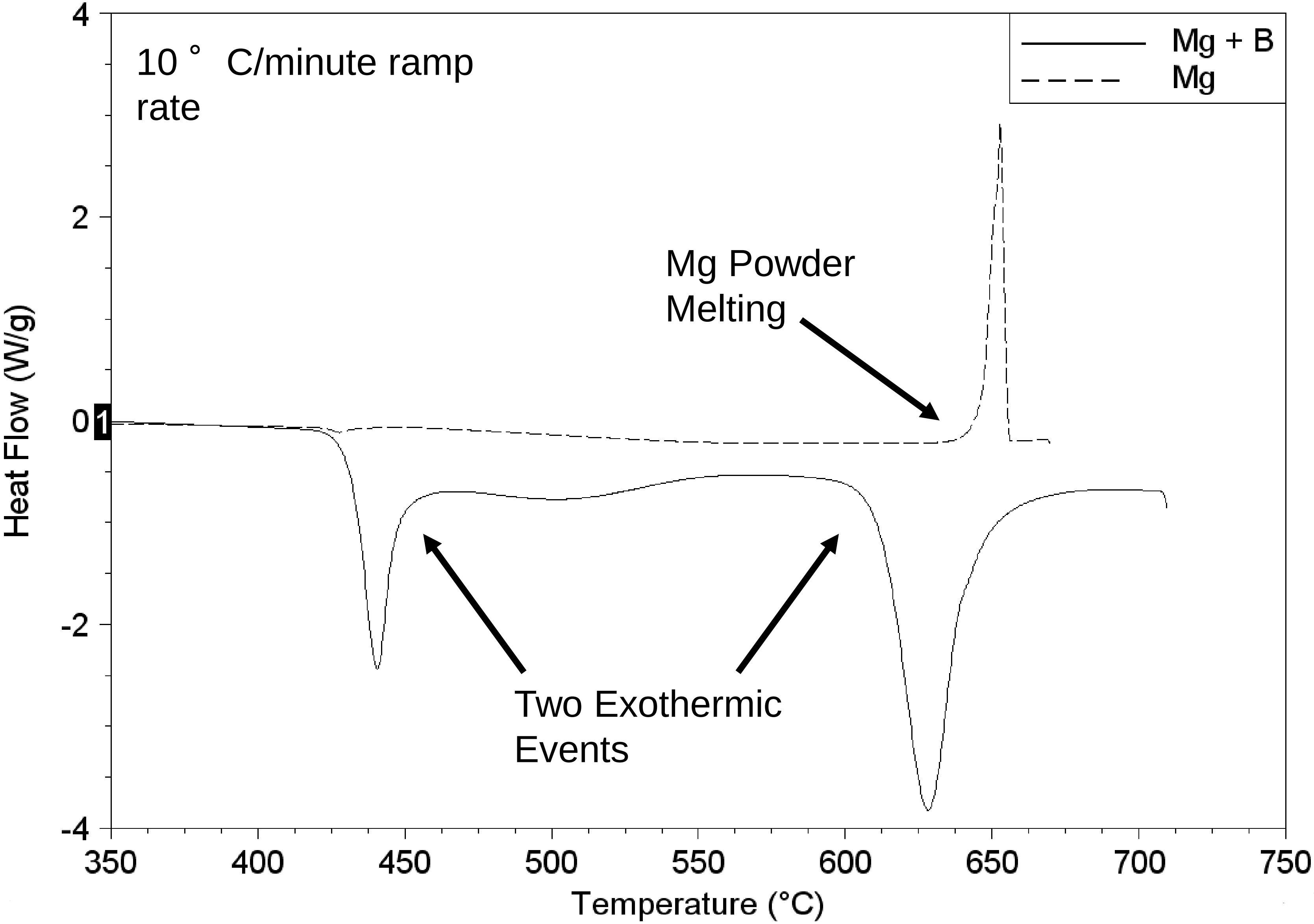
10 ° C/minute ramp rate

Baseline Drift

Mg melting

DSC Temperature Limit

Mg powder and Mg + B powder

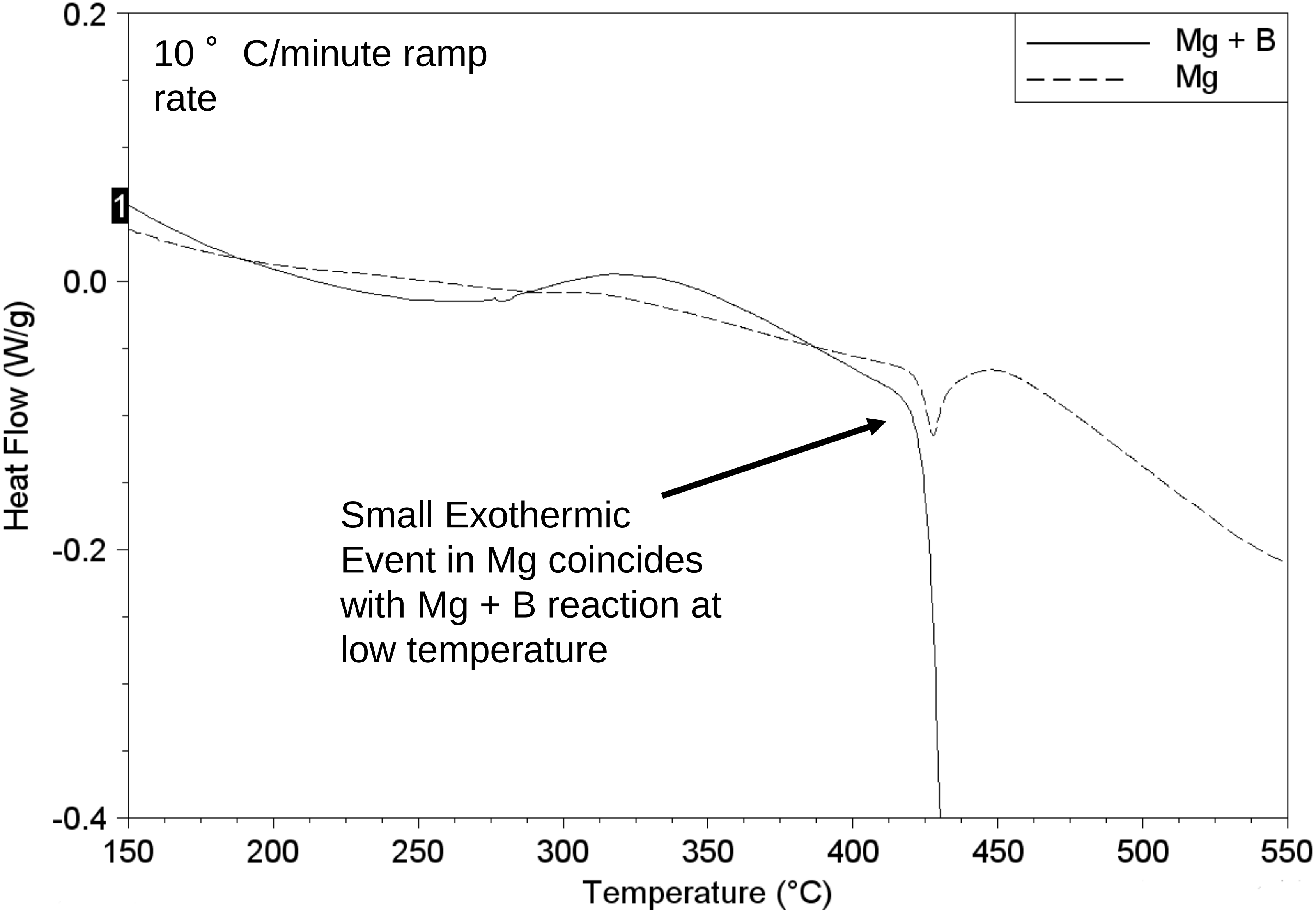


10 ° C/minute ramp rate

Mg Powder Melting

Two Exothermic Events

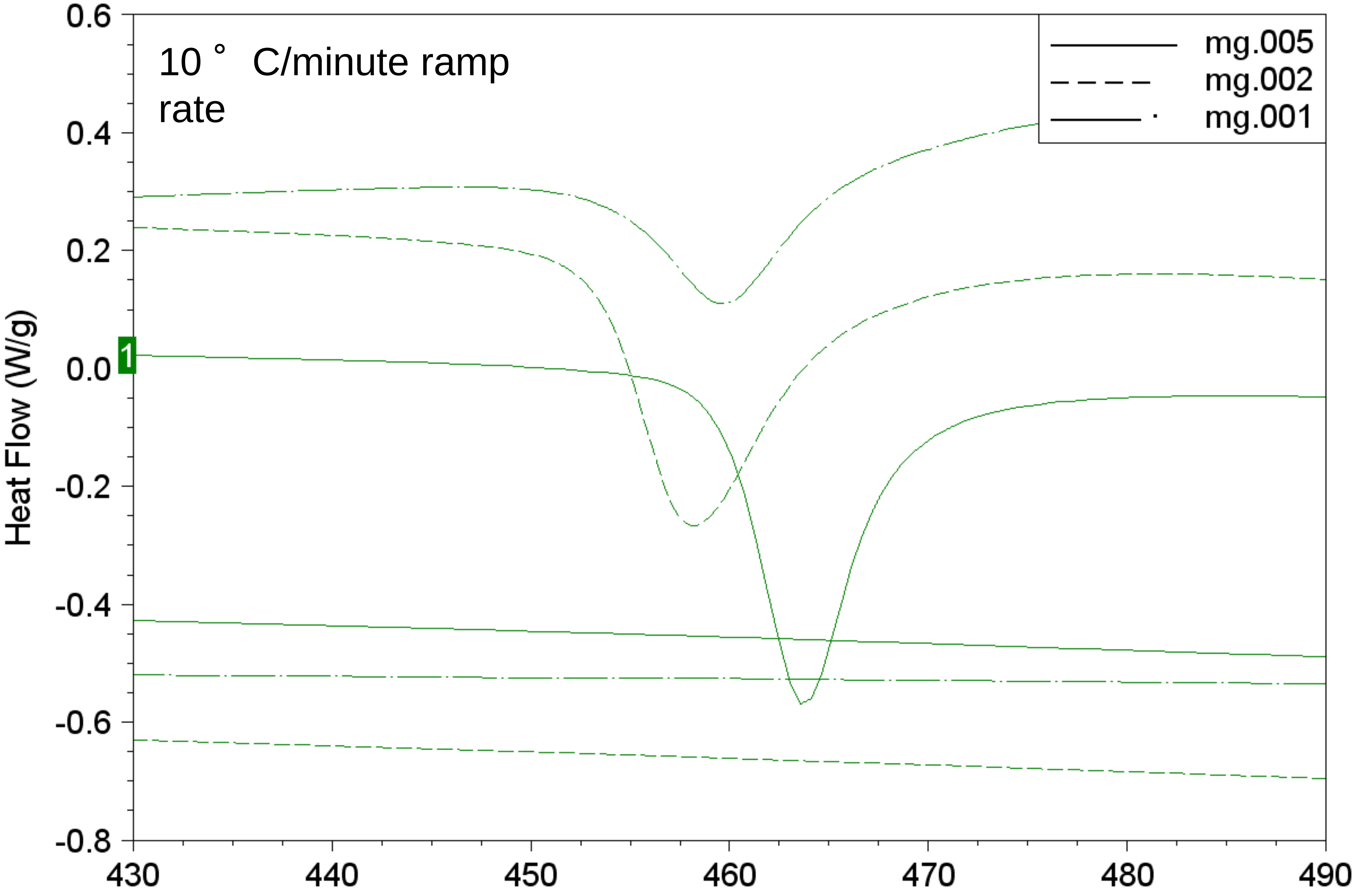
Mg powder and Mg + B powder



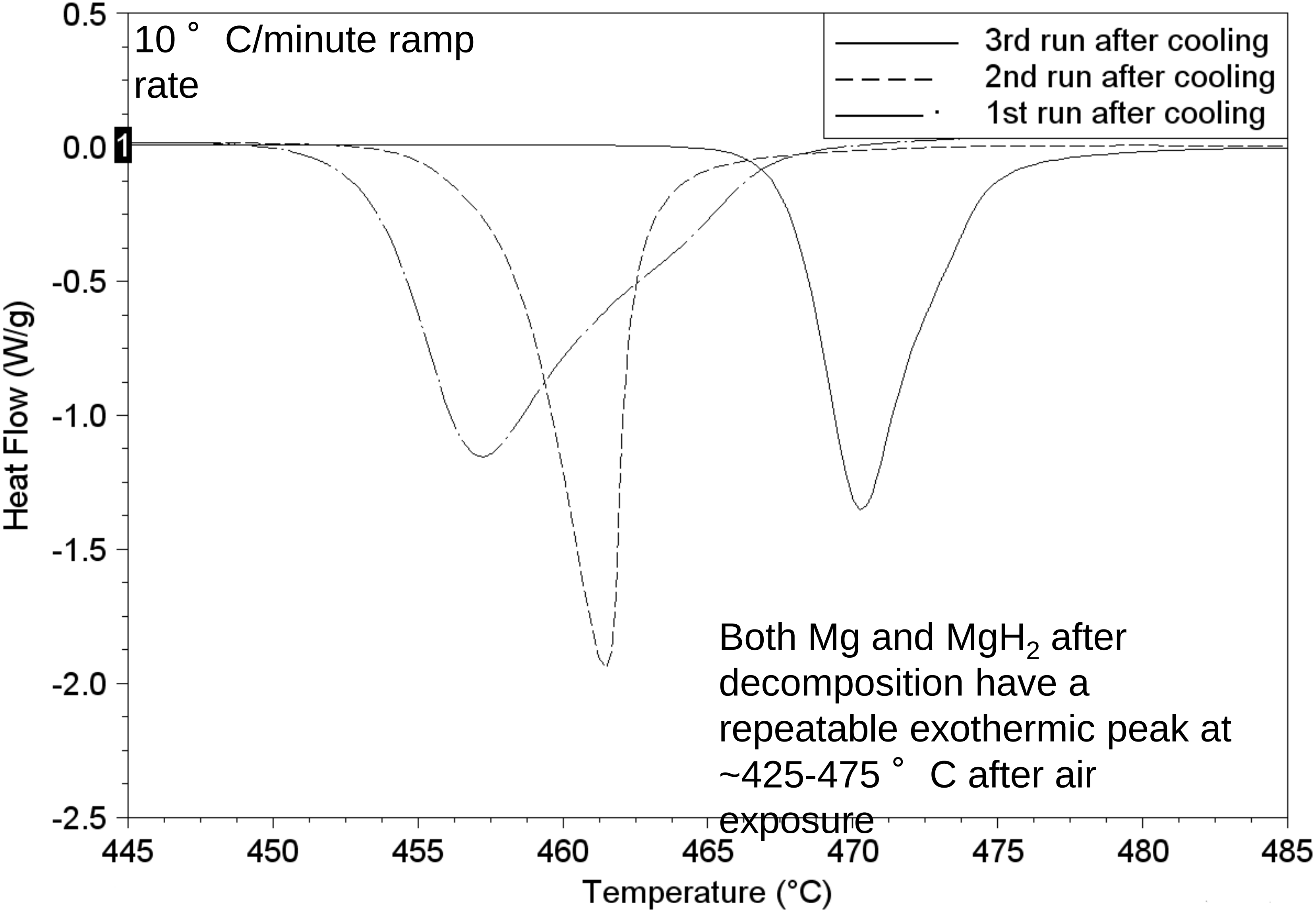
10 ° C/minute ramp rate

Small Exothermic Event in Mg coincides with Mg + B reaction at low temperature

Mg Powder – multiple runs



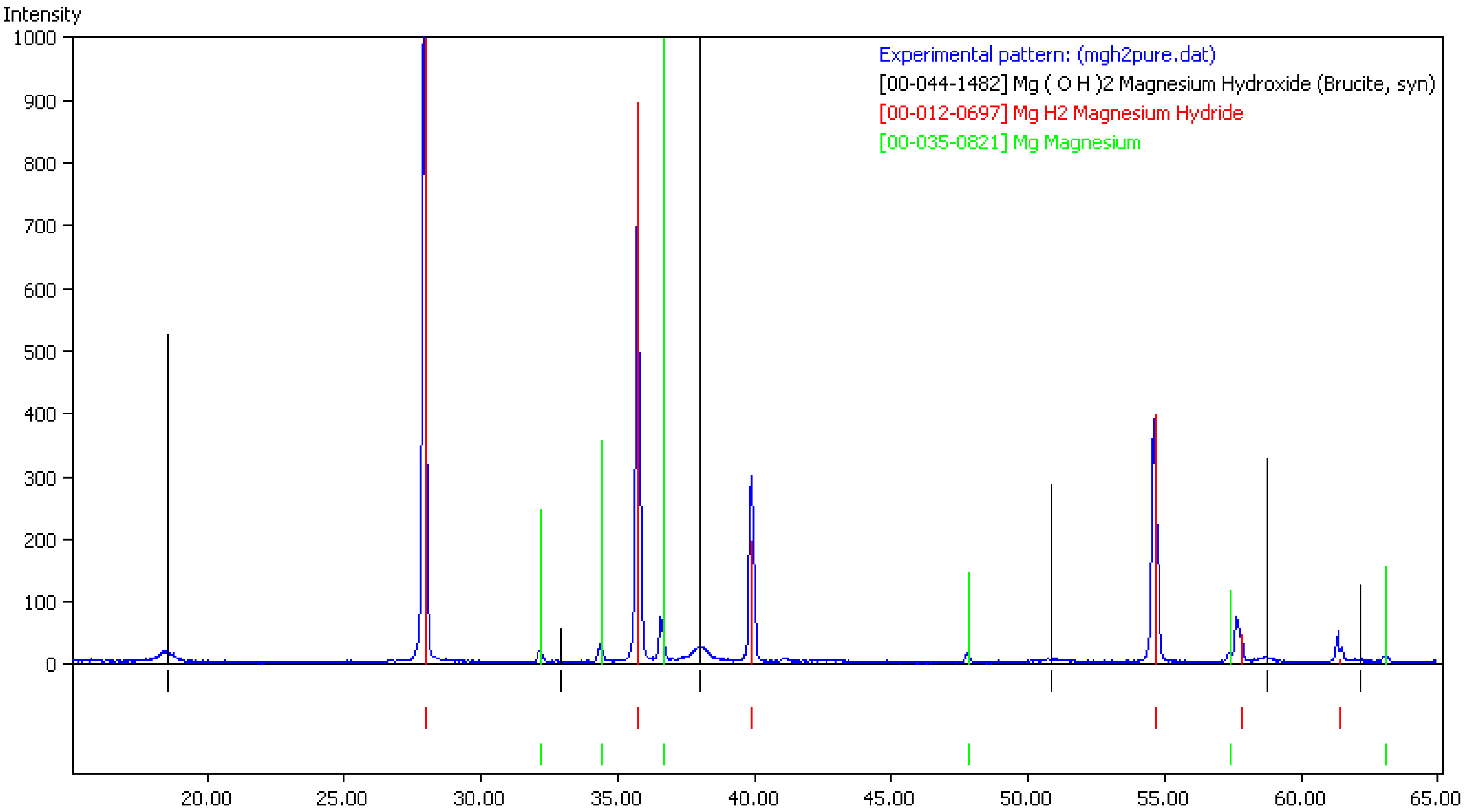
Mg from MgH_2



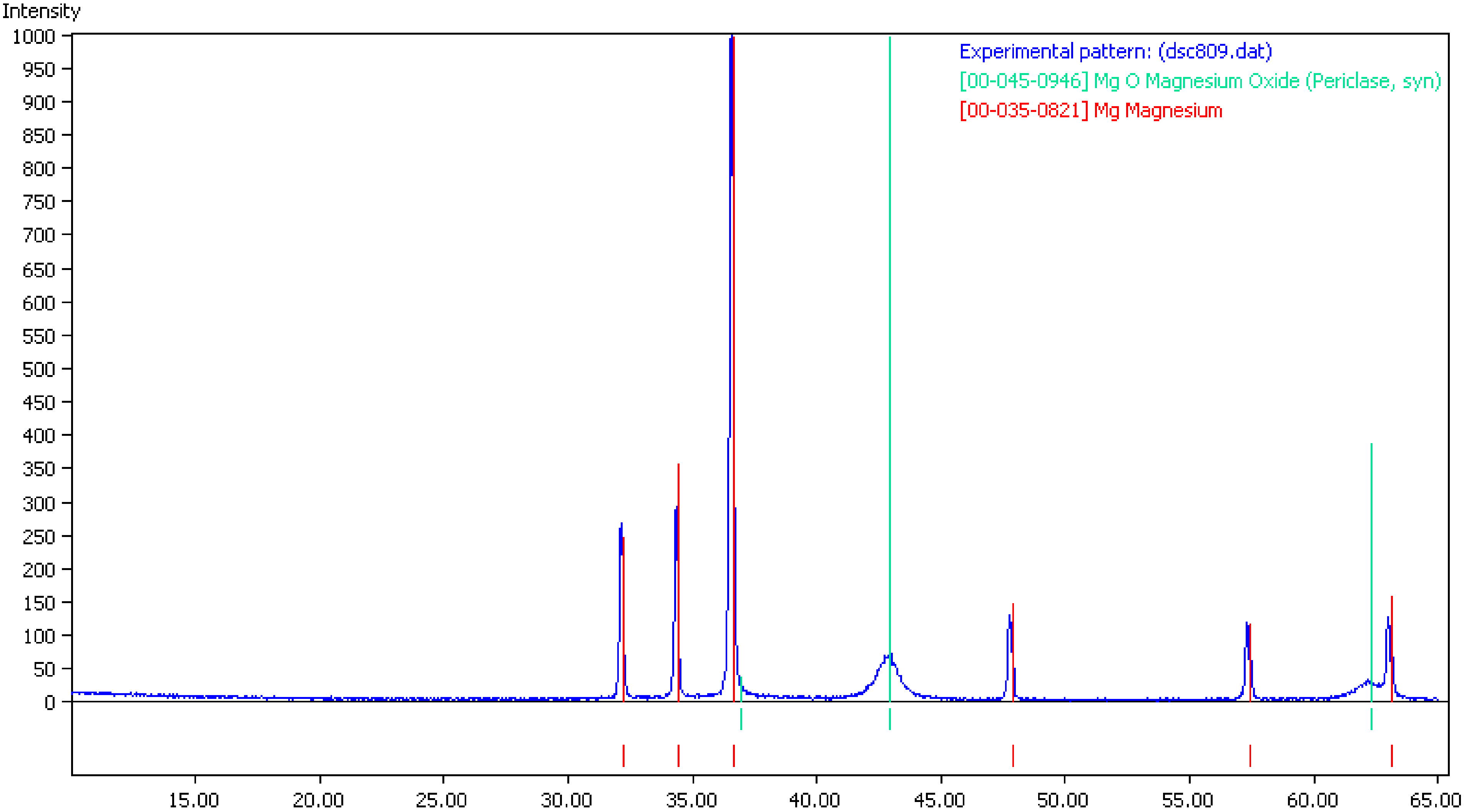
10 ° C/minute ramp rate

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



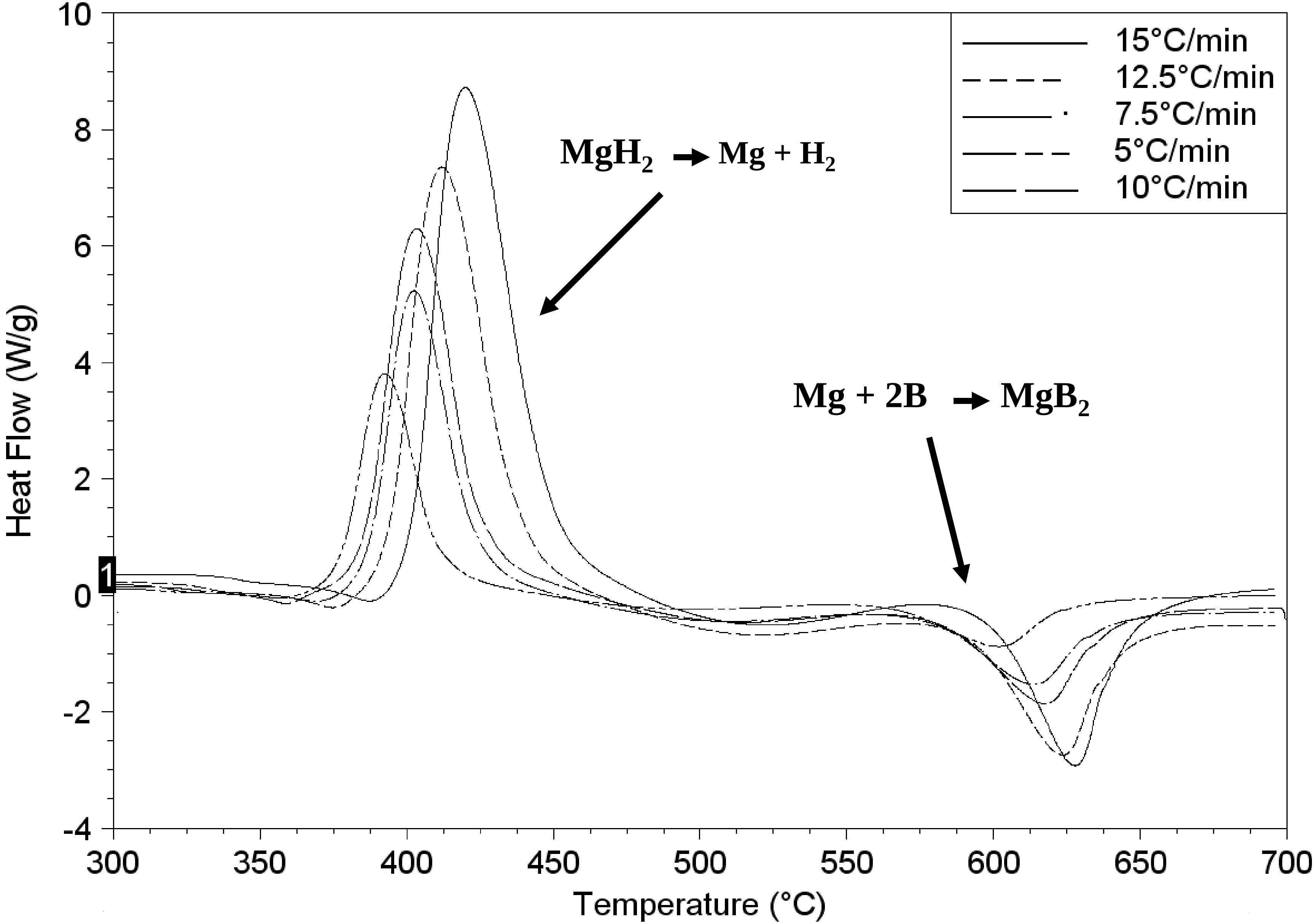
XRD on MgH_2 after decomposition



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:

$$\frac{d\alpha}{dt} = k(T)\cdot(1-\alpha) \qquad \textbf{where} \qquad k(T) = A\cdot e^{-E_A/kT}$$

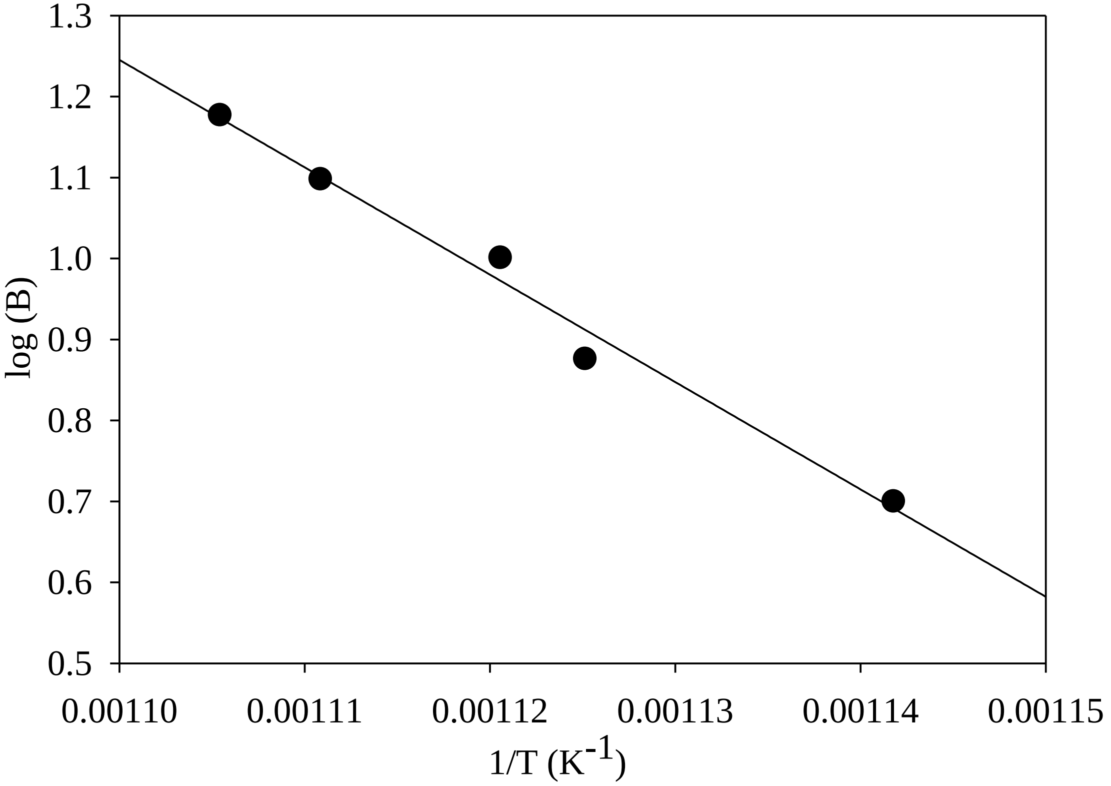
which becomes

$$\beta\frac{d\alpha}{dT} = A\cdot e^{-E_A/kT}\cdot(1-\alpha) \qquad \textbf{where} \qquad \beta = \frac{dT}{dt}$$

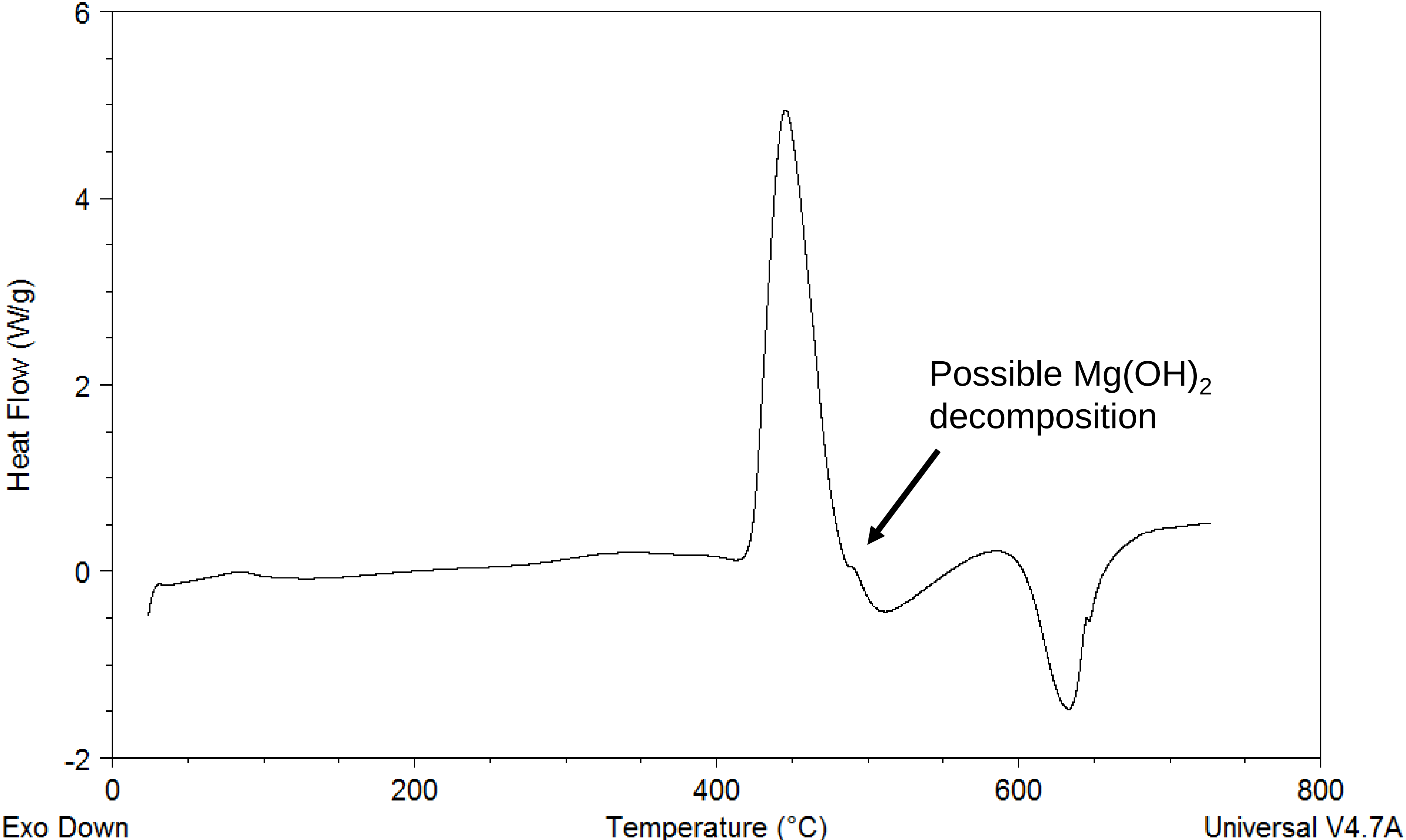
MgB_2 Activation Energy

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

E_A = ~241 kJ/mole



MgH_2 + B with air exposure



Possible $Mg(OH)_2$ decomposition

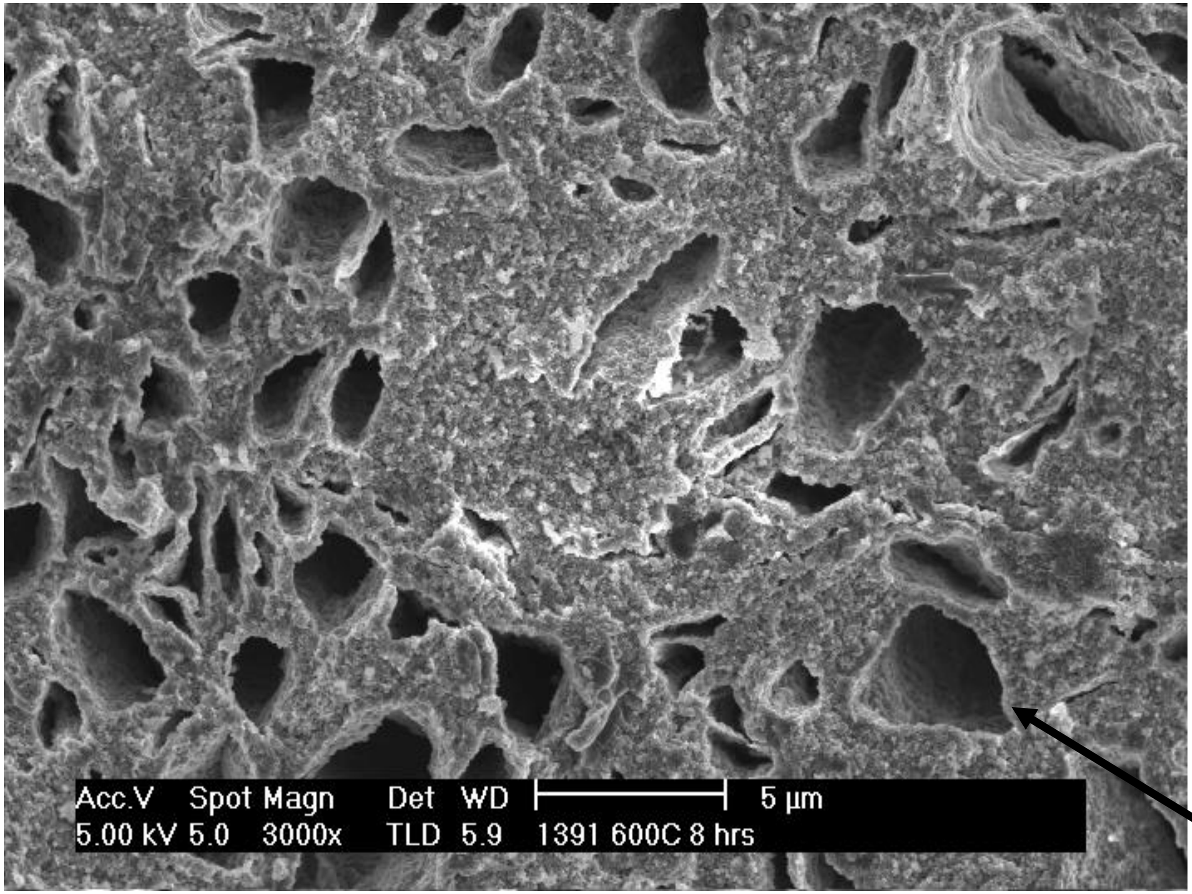
Conclusions

- “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)

Results Published in: S. Bohnenstiehl, S. A. Dregia, M. D. Sumption and E. W. Collings, “Thermal Analysis of MgB_2 Formation”, *IEEE Transactions on Applied Superconductivity* **17** (2007) 2754.

Smith Thermal Analysis Method in the Mg/B System

Problems in Low Temperature Synthesis



Voids where
Mg powder
used to be

Fracture SEM on MgB_2 filament in commercial wire

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

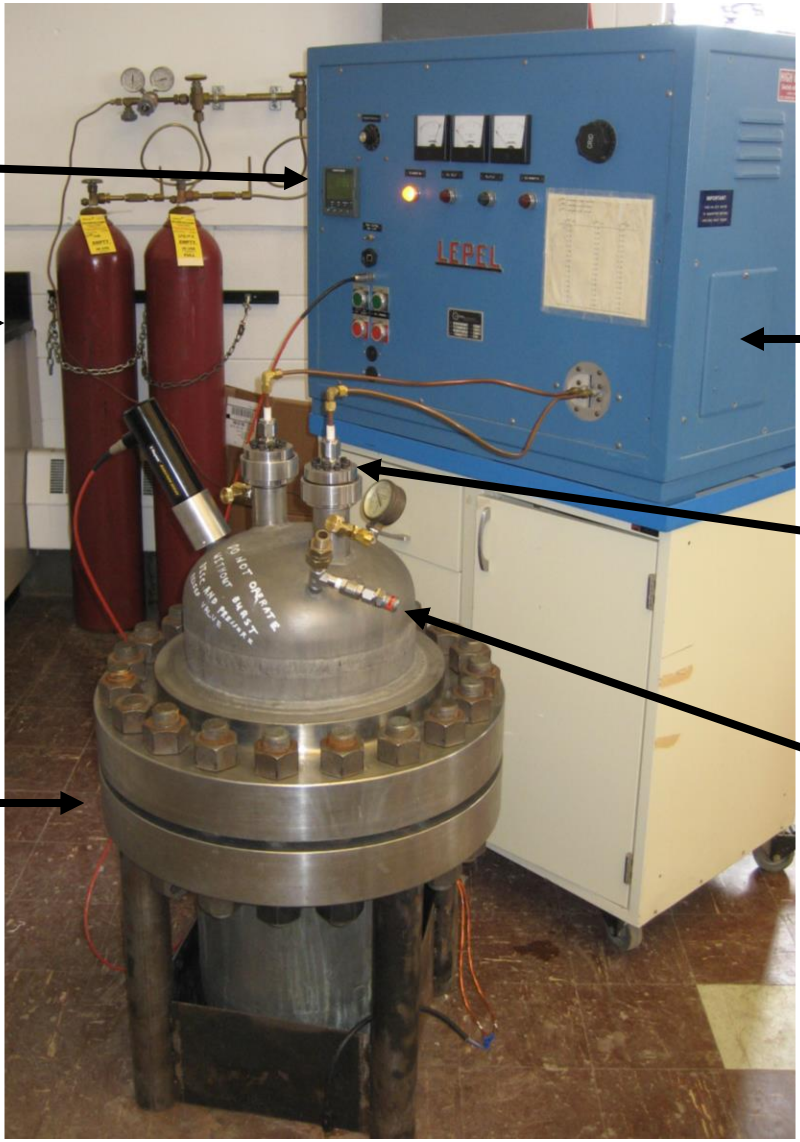
High Pressure and High Temperatures

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

Clausius-Clapeyron Equation: $dP/dT = L/(T\Delta V)$

1 bar	1090 ° C
10 bar	~1475 ° C
100 bar	~2200 ° C

High Temperature High Pressure Vessel



Eurotherm 3504 Temperature Controller

99.998% Argon

Type C thermocouples (W-Re)

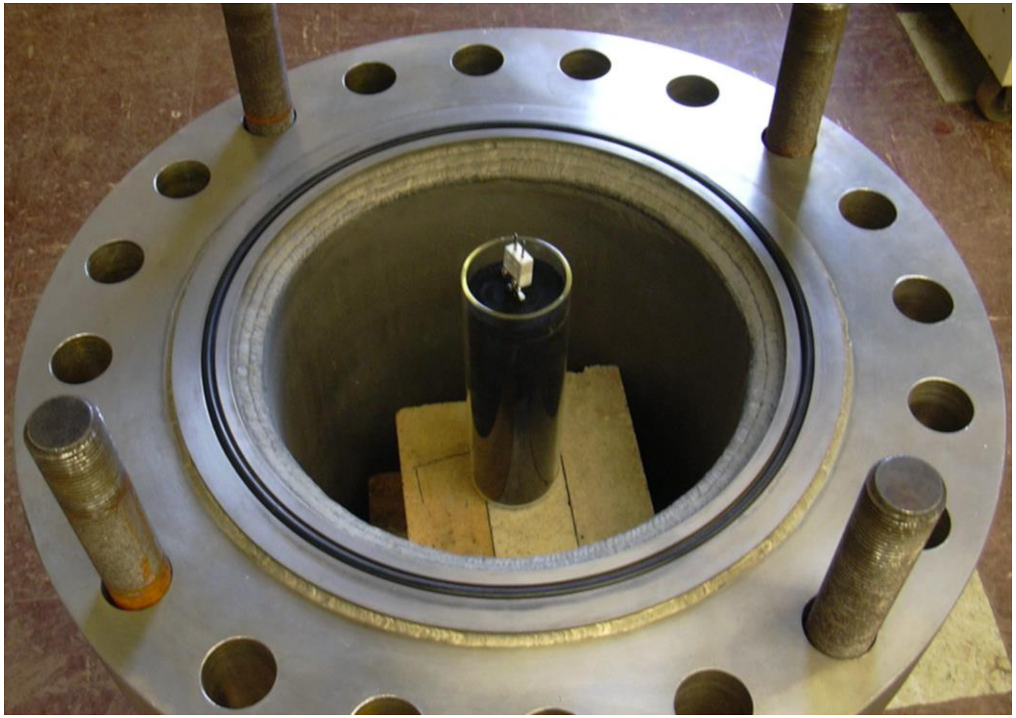
Monel Pressure Vessel (1500 psi maximum pressure)

Lepel 5 kW Induction Power Supply

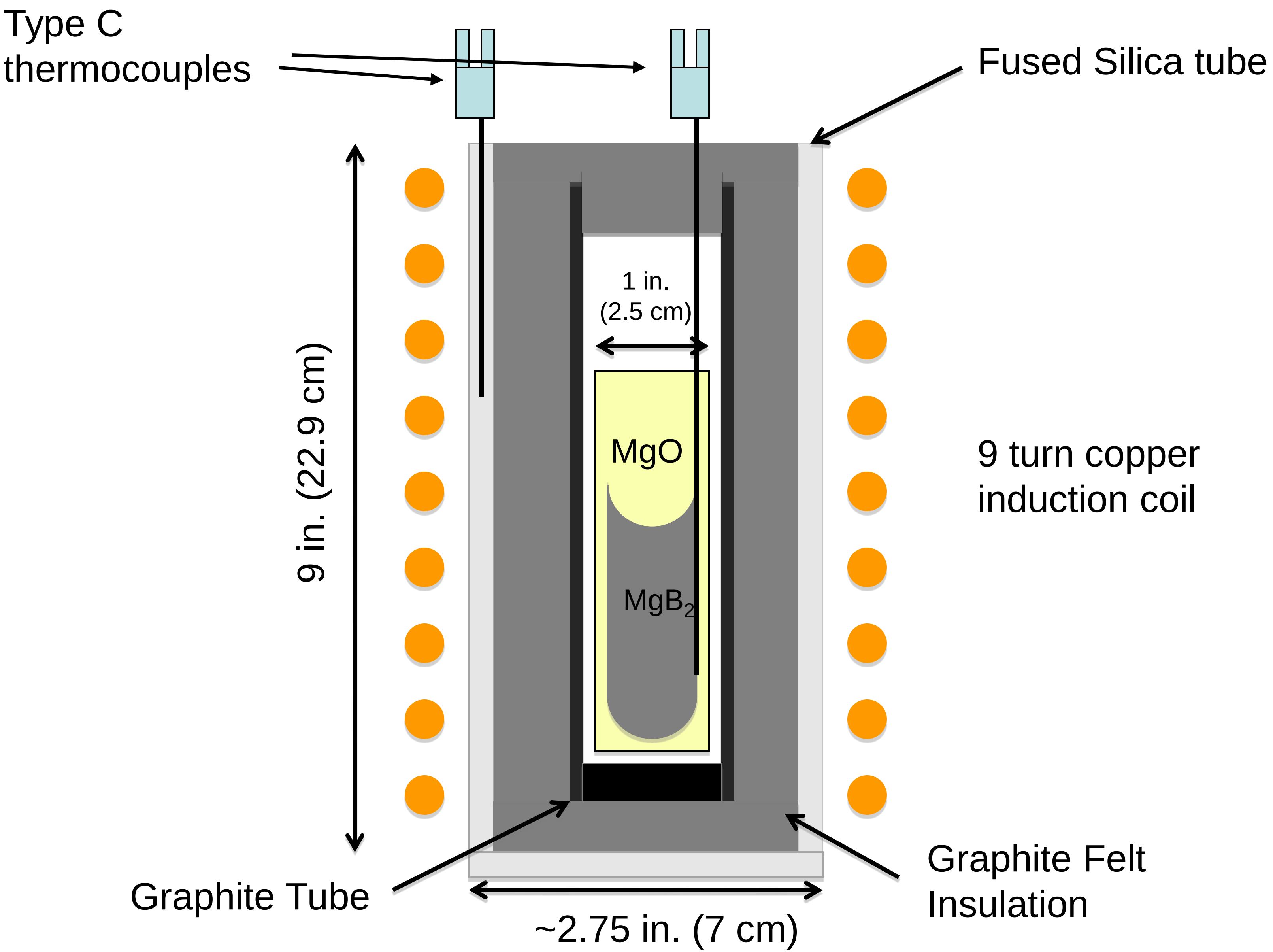
Conax High Pressure Feedthroughs

Burst Disc and Pressure Relief Valve

Induction Coil and Hot Zone



Hot Zone Design



Type C thermocouples

Fused Silica tube

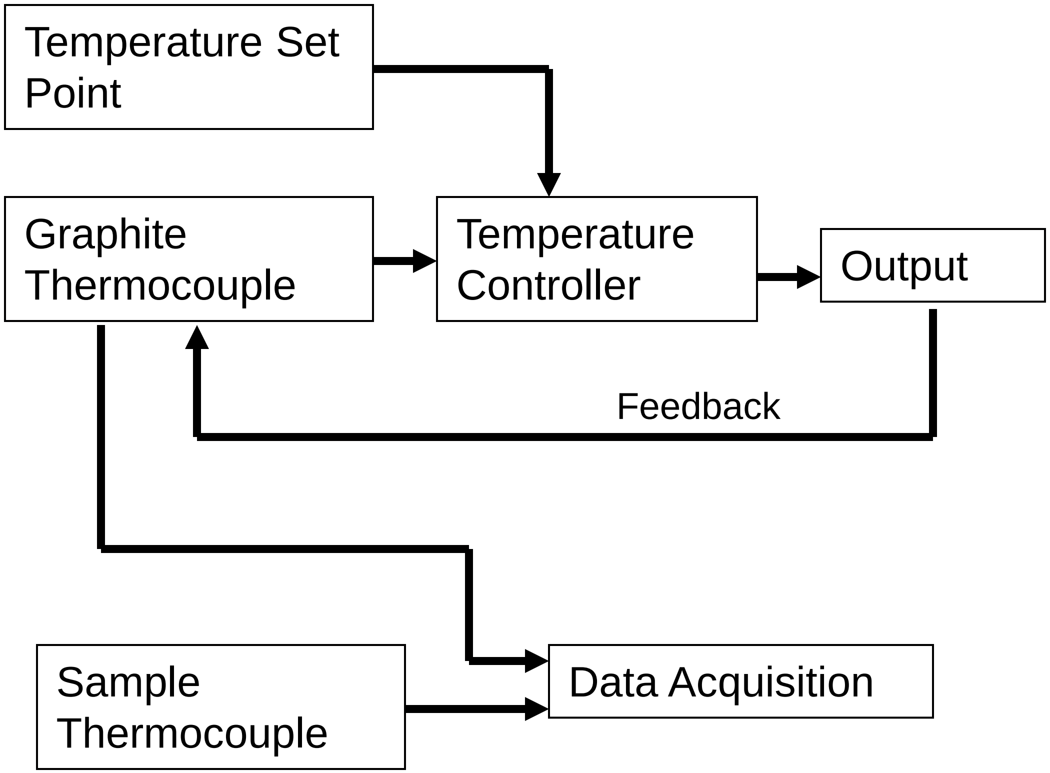
9 turn copper induction coil

Graphite Tube

Graphite Felt Insulation

~2.75 in. (7 cm)

Standard Temperature Control



Temperature Set Point

Graphite Thermocouple

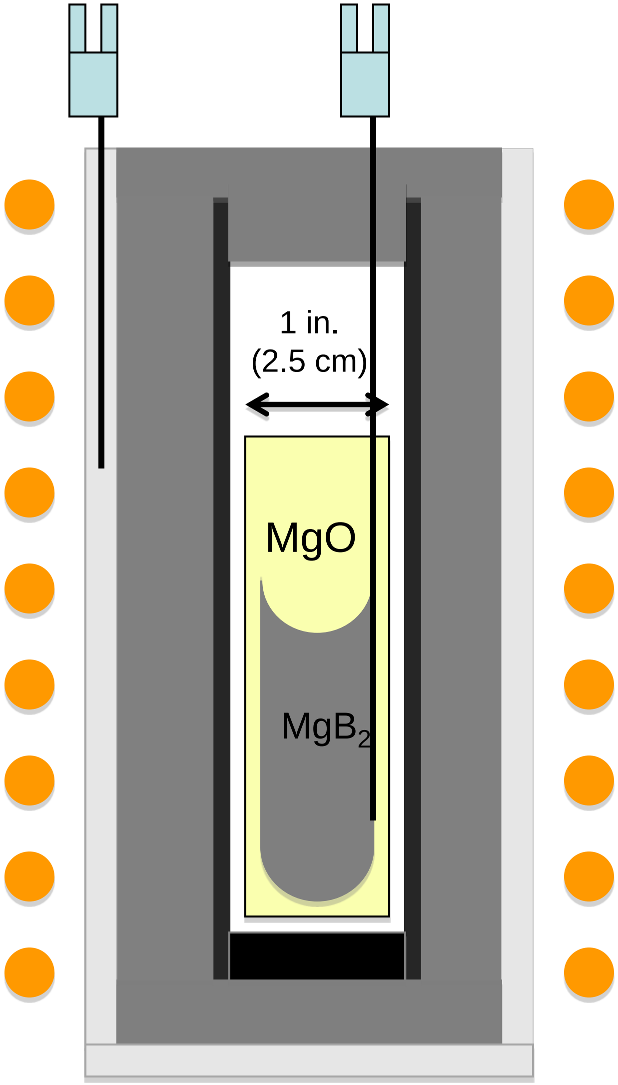
Temperature Controller

Output

Feedback

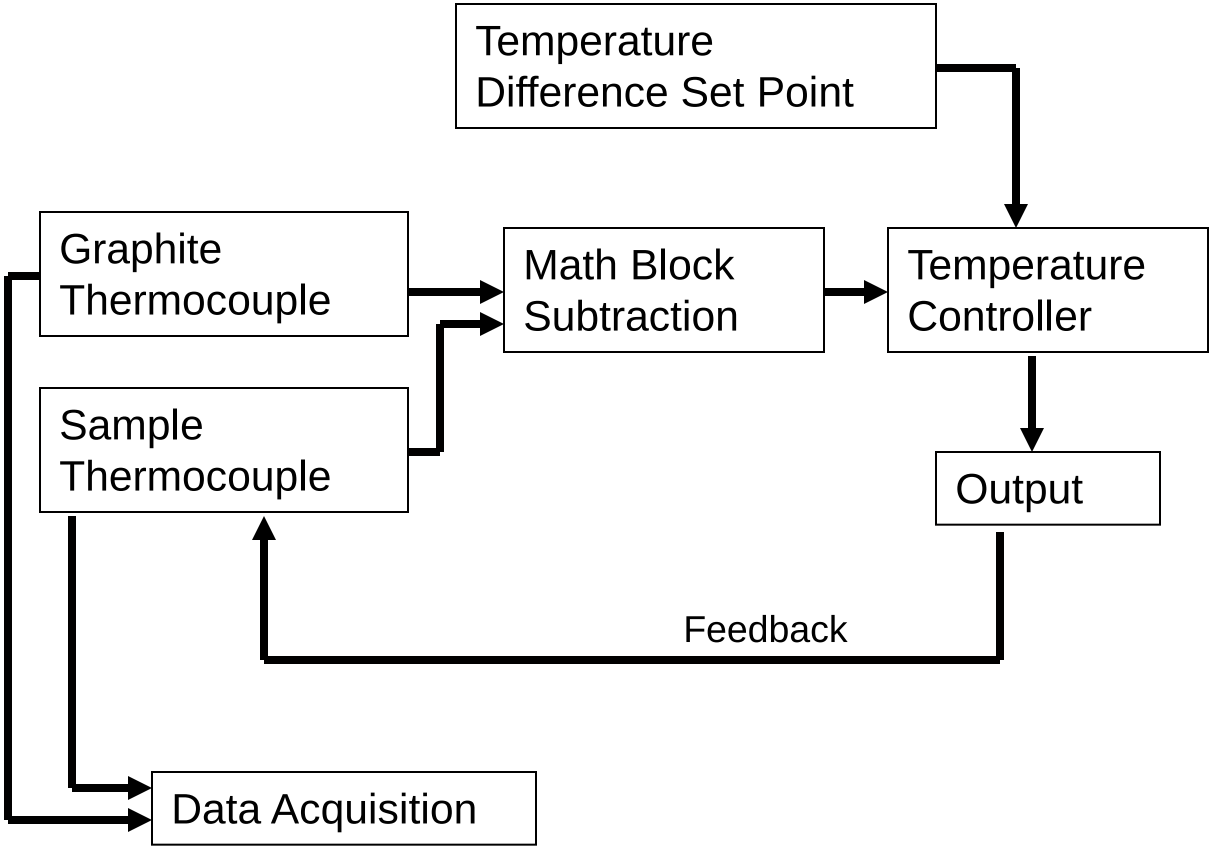
Sample Thermocouple

Data Acquisition



The sample thermocouple is passive and not part of the temperature control loop.

Smith Thermal Analysis Method



Temperature Difference Set Point

Graphite Thermocouple

Math Block Subtraction

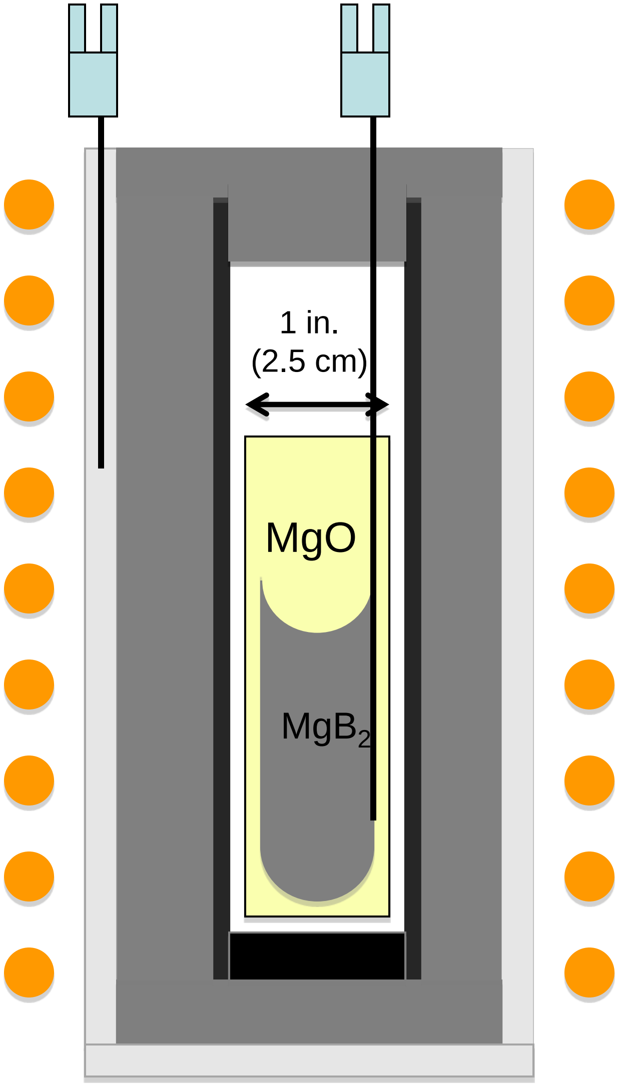
Temperature Controller

Sample Thermocouple

Output

Feedback

Data Acquisition

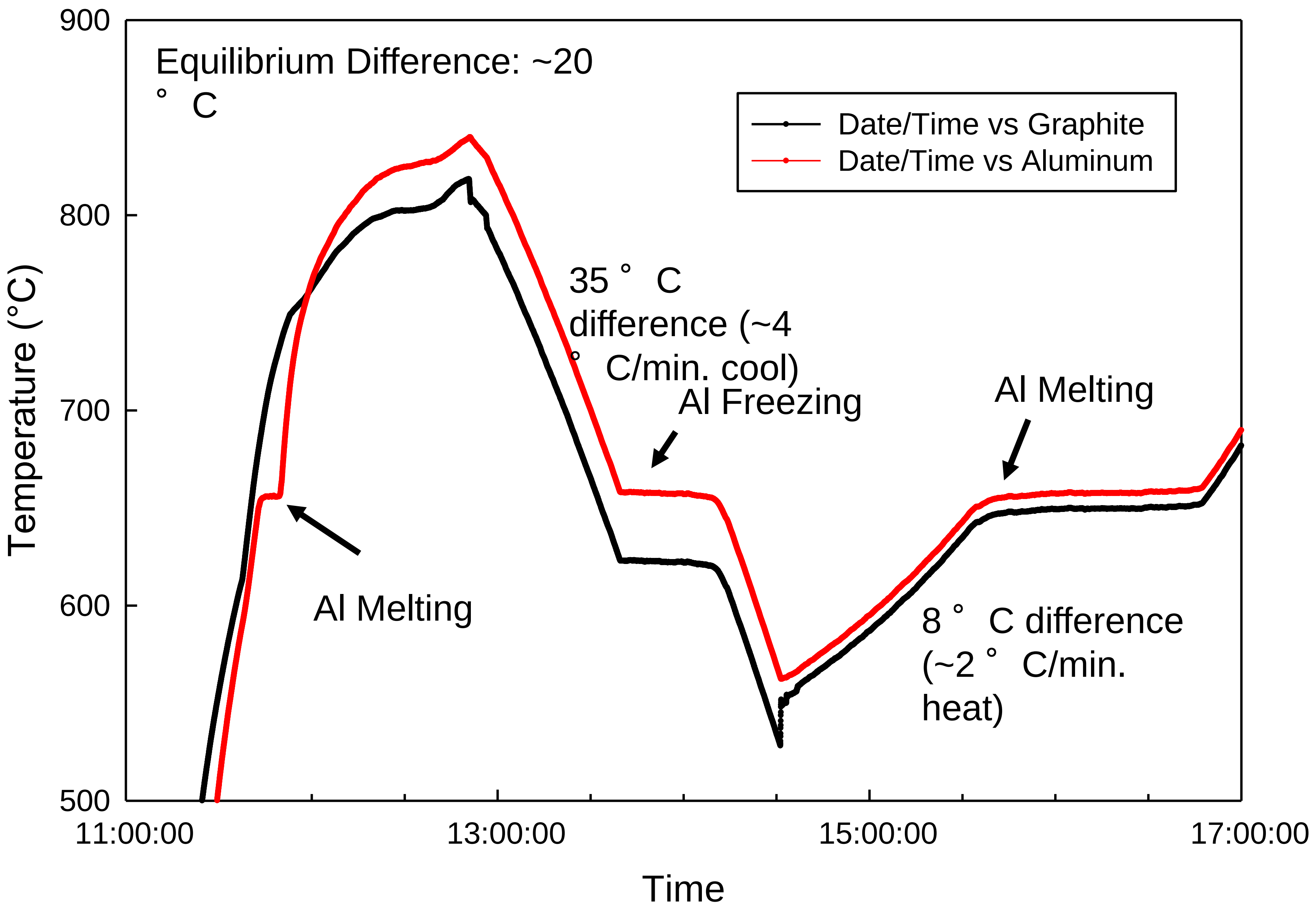


The sample and graphite thermocouples are part of the temperature control loop and a temperature difference is maintained.

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

35 ° C difference (~4 ° C/min. cool)

Al Freezing

Al Melting

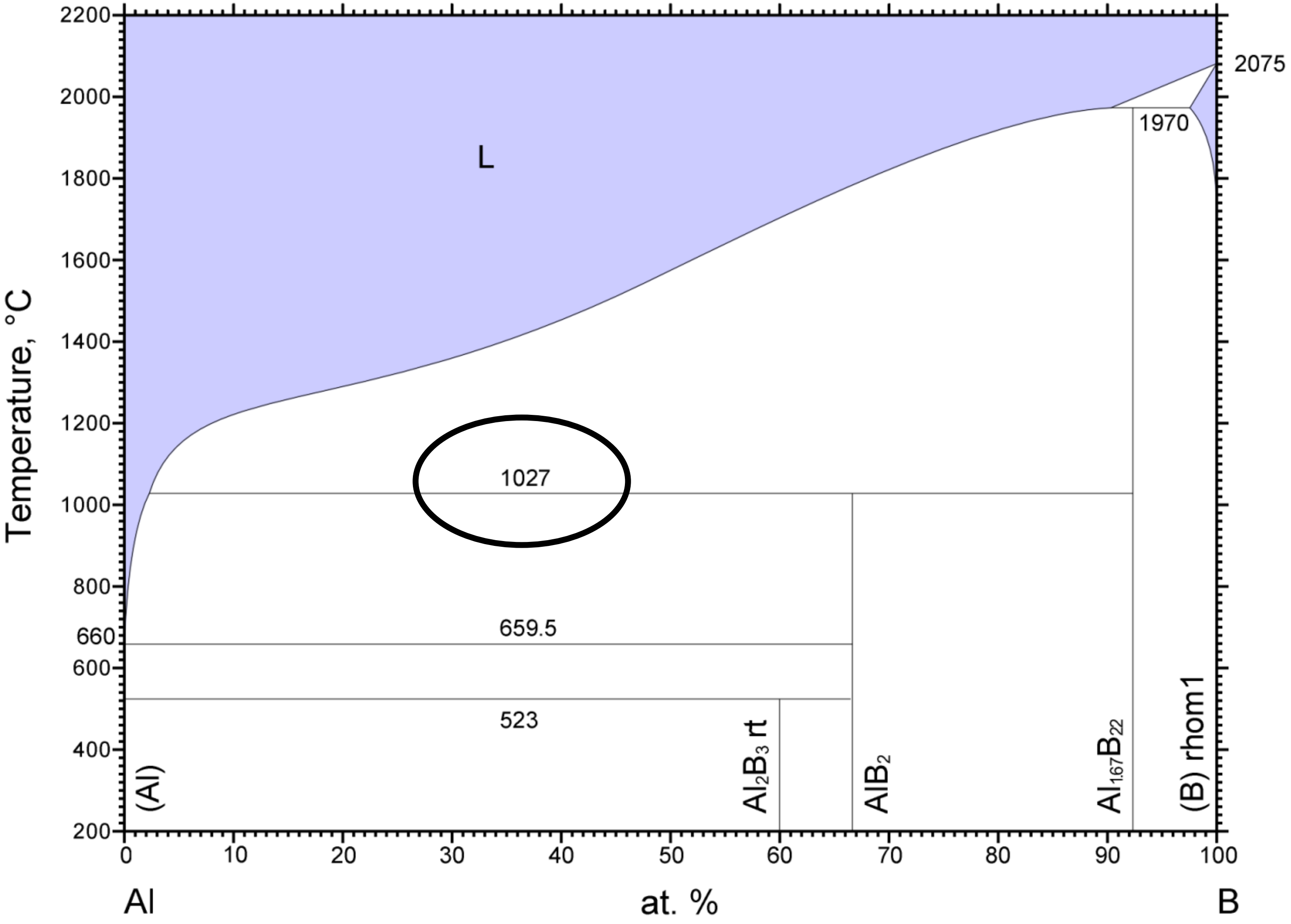
Al Melting

8 ° C difference (~2 ° C/min. heat)

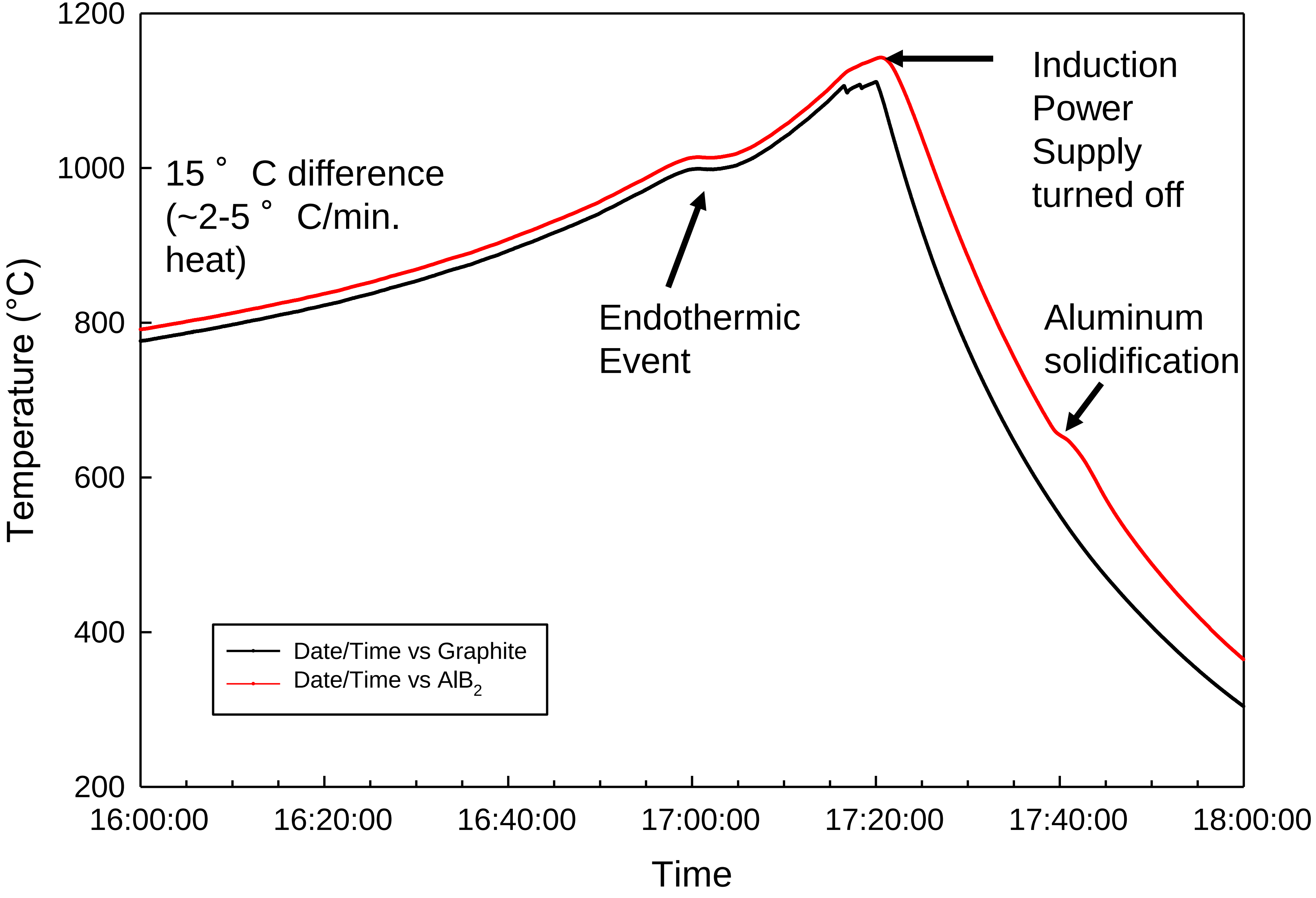
Advantages over DTA and DSC

- 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)

Al-B Phase Diagram



Smith Thermal Analysis Run on AlB_2

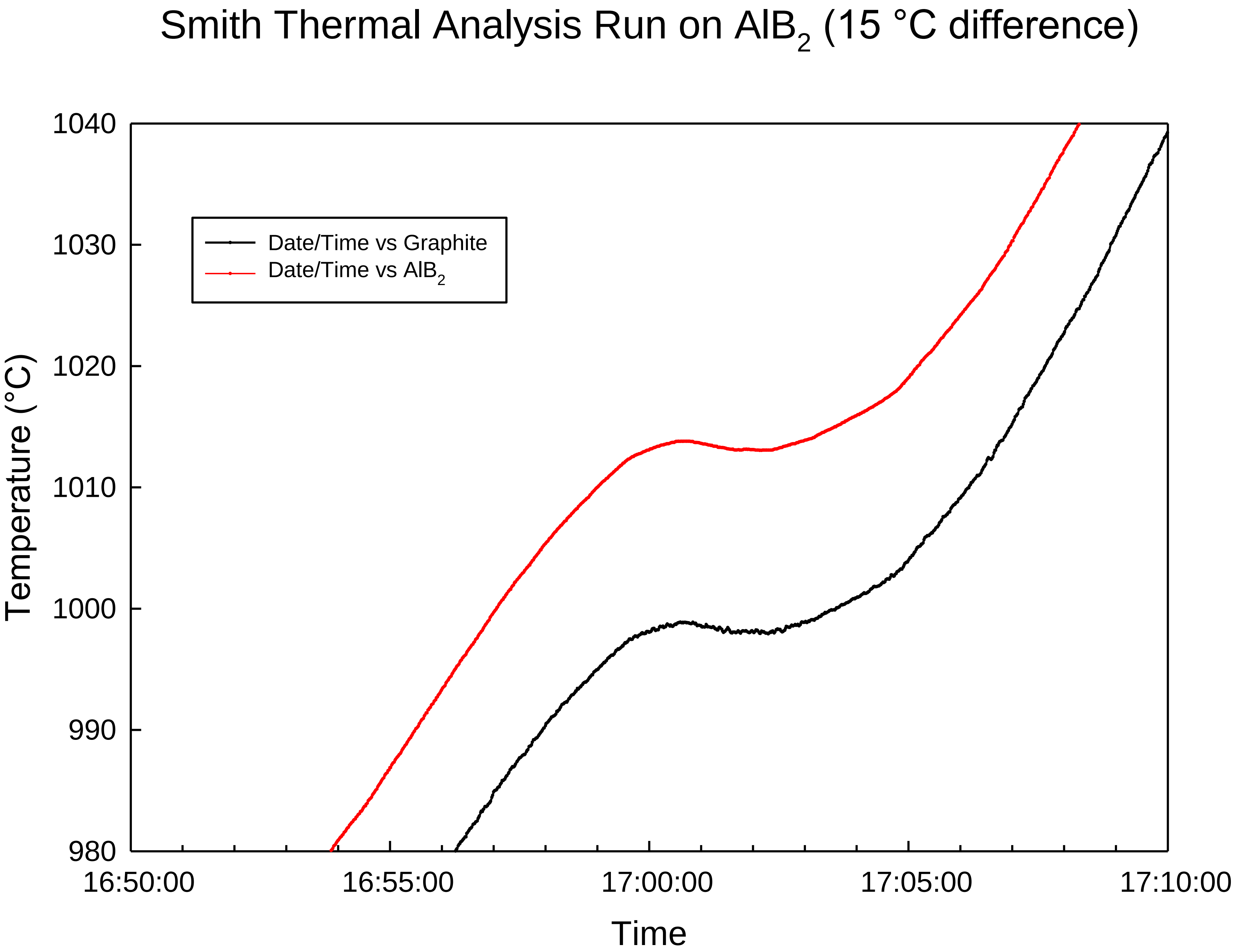


15 ° C difference (~2-5 ° C/min. heat)

Endothermic Event

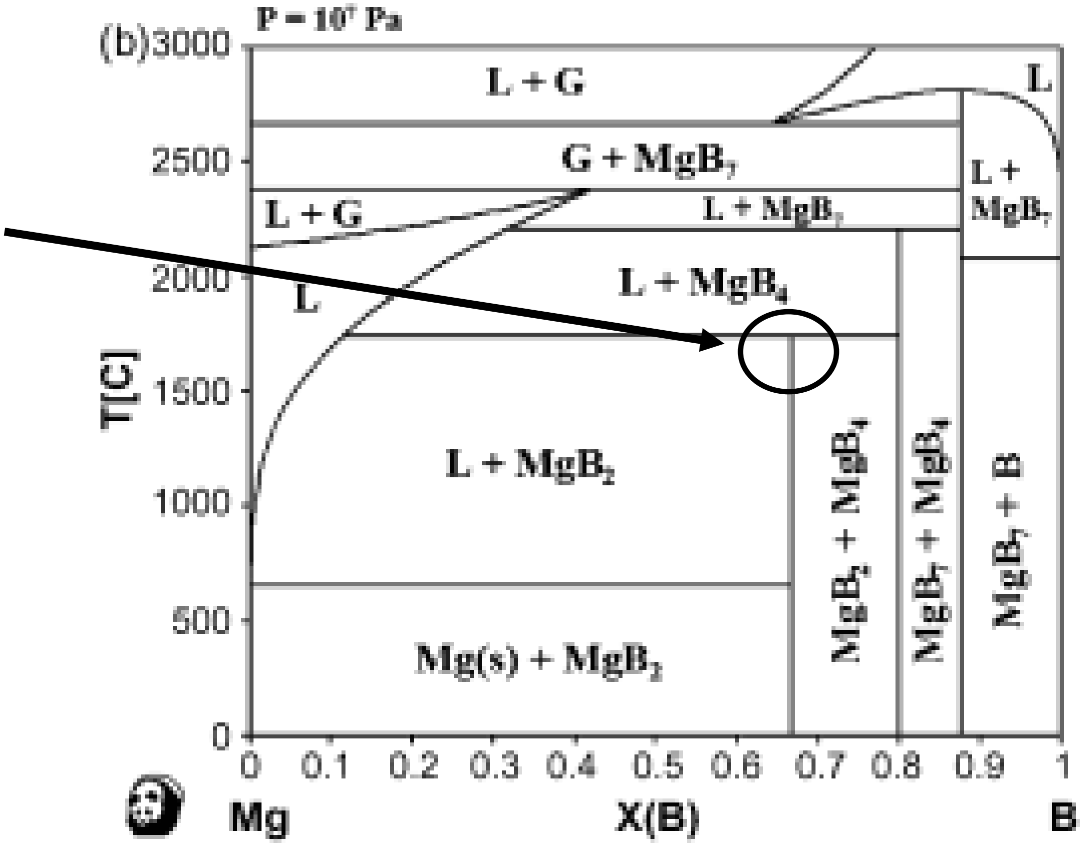
Induction Power Supply turned off

Aluminum solidification


Smith Thermal Analysis Run on AlB_2 (15 °C difference)
Date/Time vs Graphite
Date/Time vs AlB_2
Temperature (°C)
1040
1030
1020
1010
1000
990
980
16:50:00
16:55:00
17:00:00
17:05:00
17:10:00
Time

Predicted Mg-B Phase Diagram (CALPHAD)

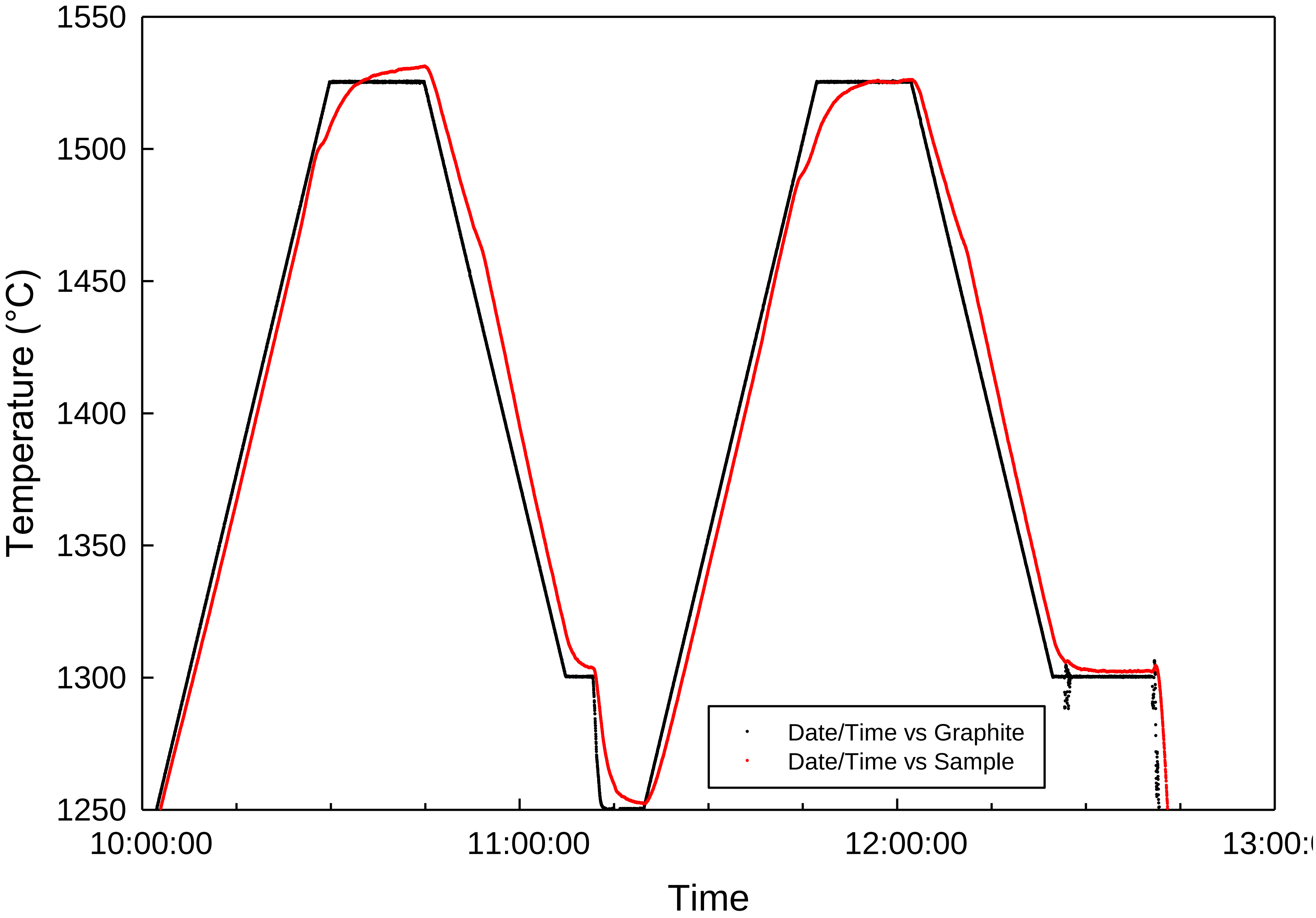
$MgB_2 \xleftrightarrow{1740\ ^\circ C} Mg_L + MgB_4$



Peritectic: $\beta \leftrightarrow$ Liquid + α

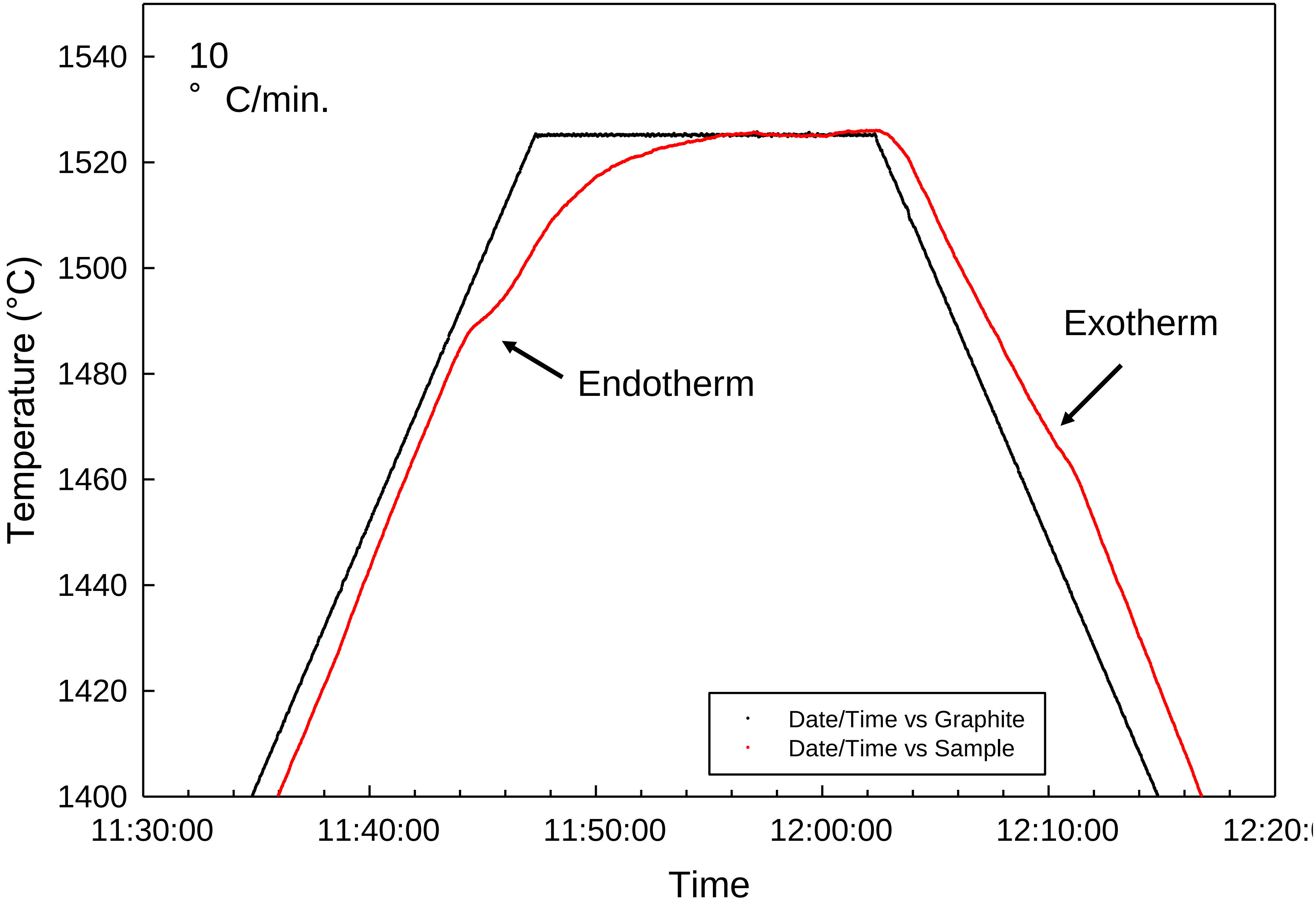
Pressure: 10^7 MPa (~1450 psi or 98 bar)

S. Kim et al., *Journal of Alloys and Compounds* **470** (2009) 85-89

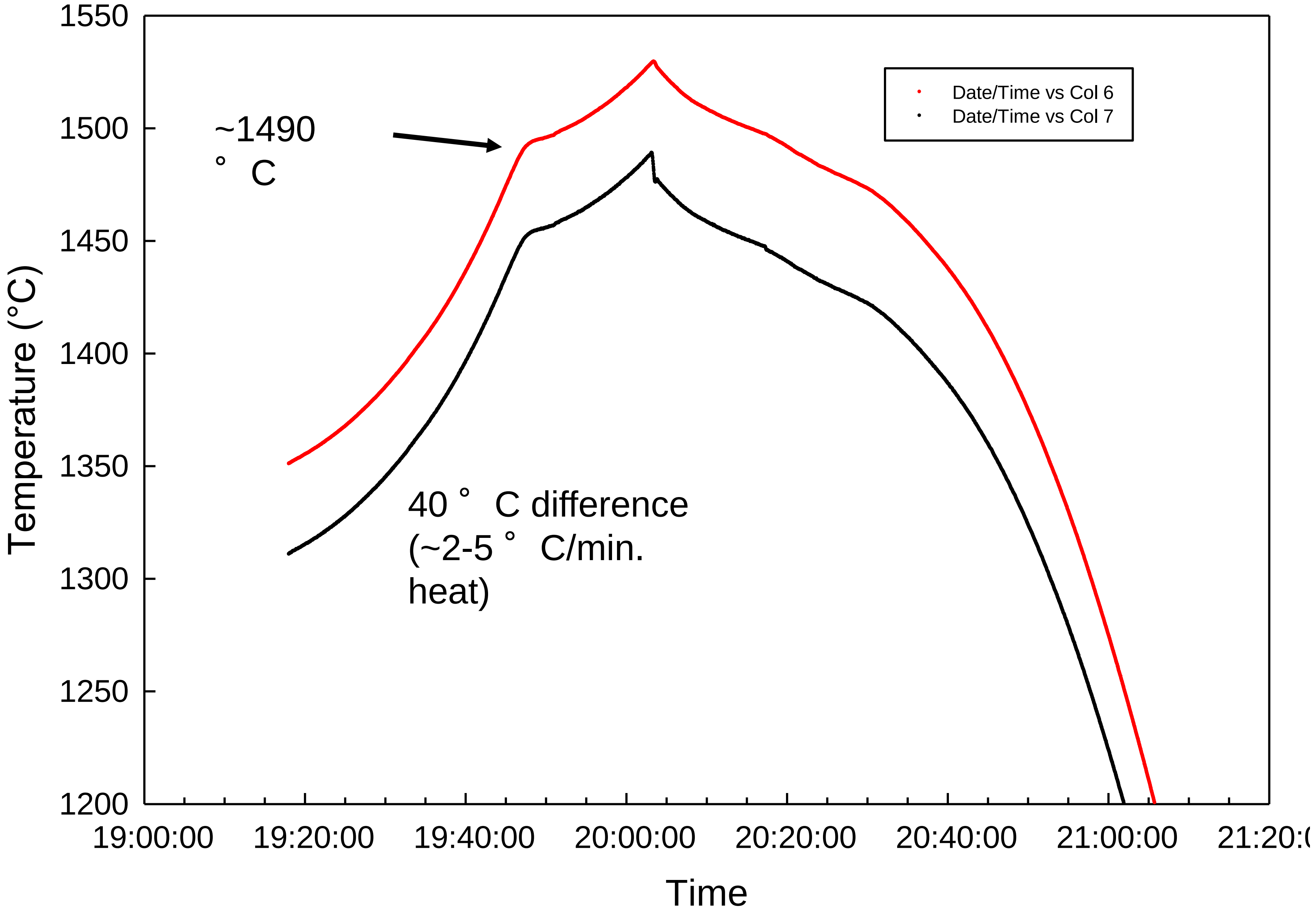


Ramp/Dwell/Cool Runs in Mg-B Mixture

Second Ramp/Dwell/Cool in Mg-B Mixture

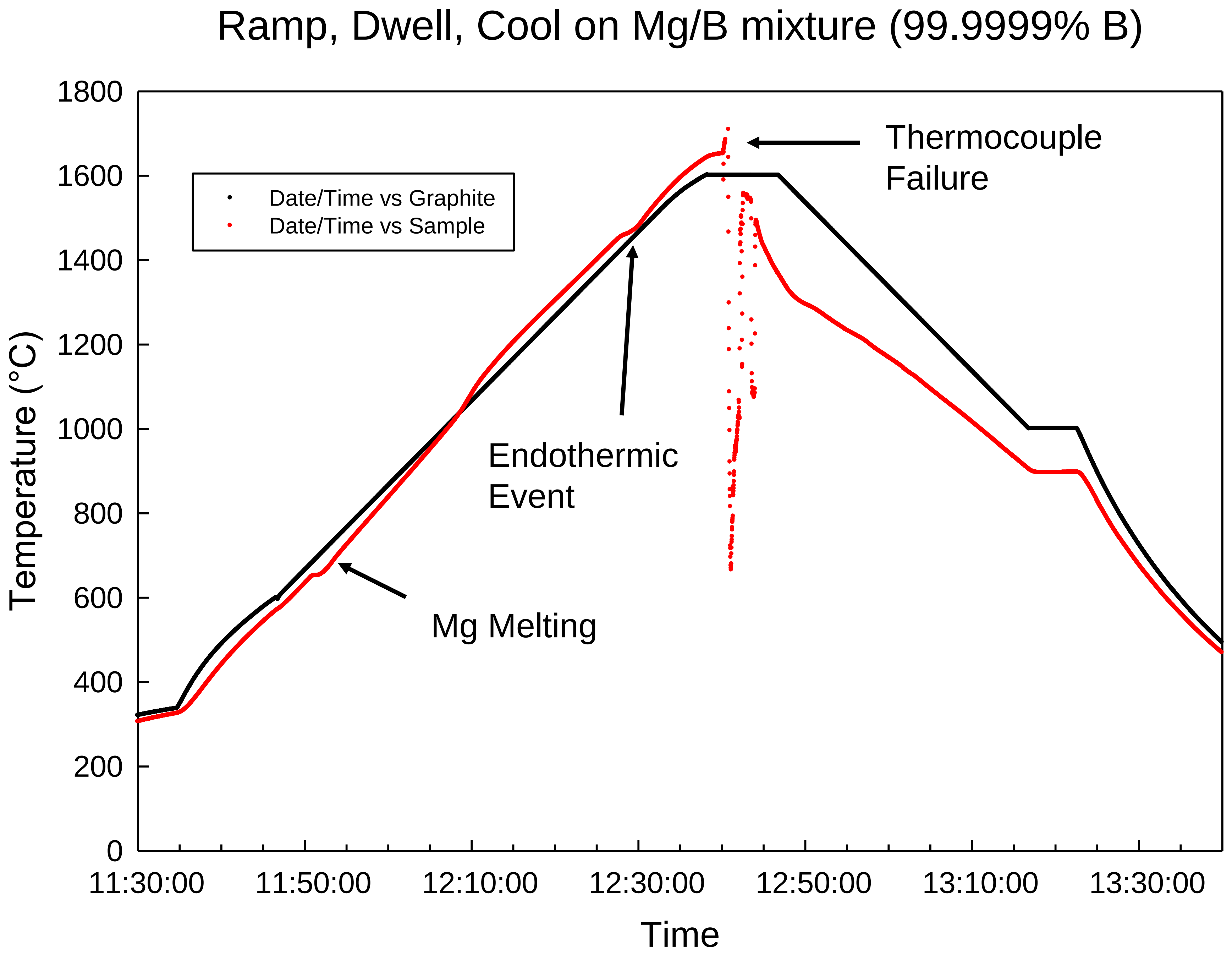


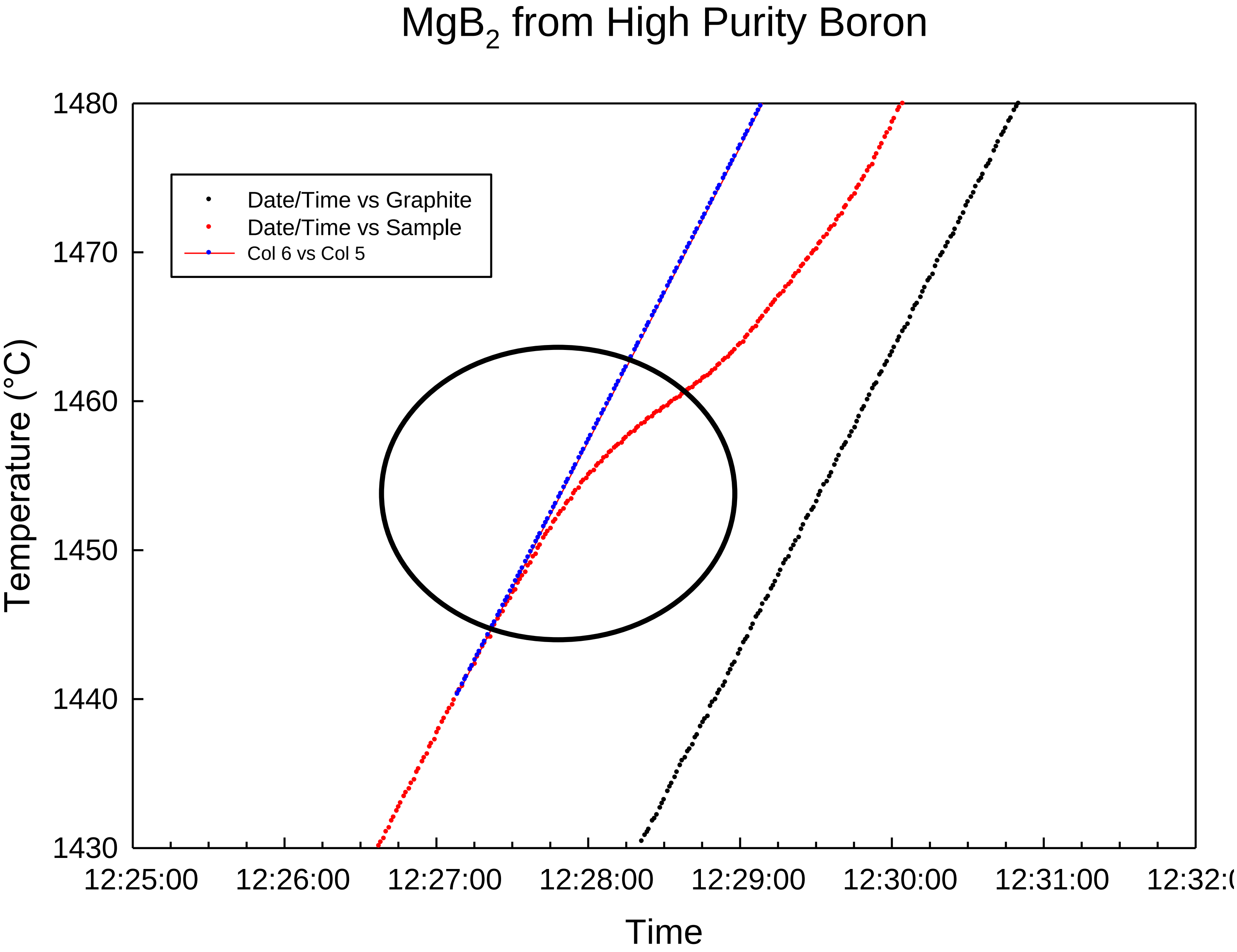
Smith Thermal Analysis Run on Mg-B Mixture



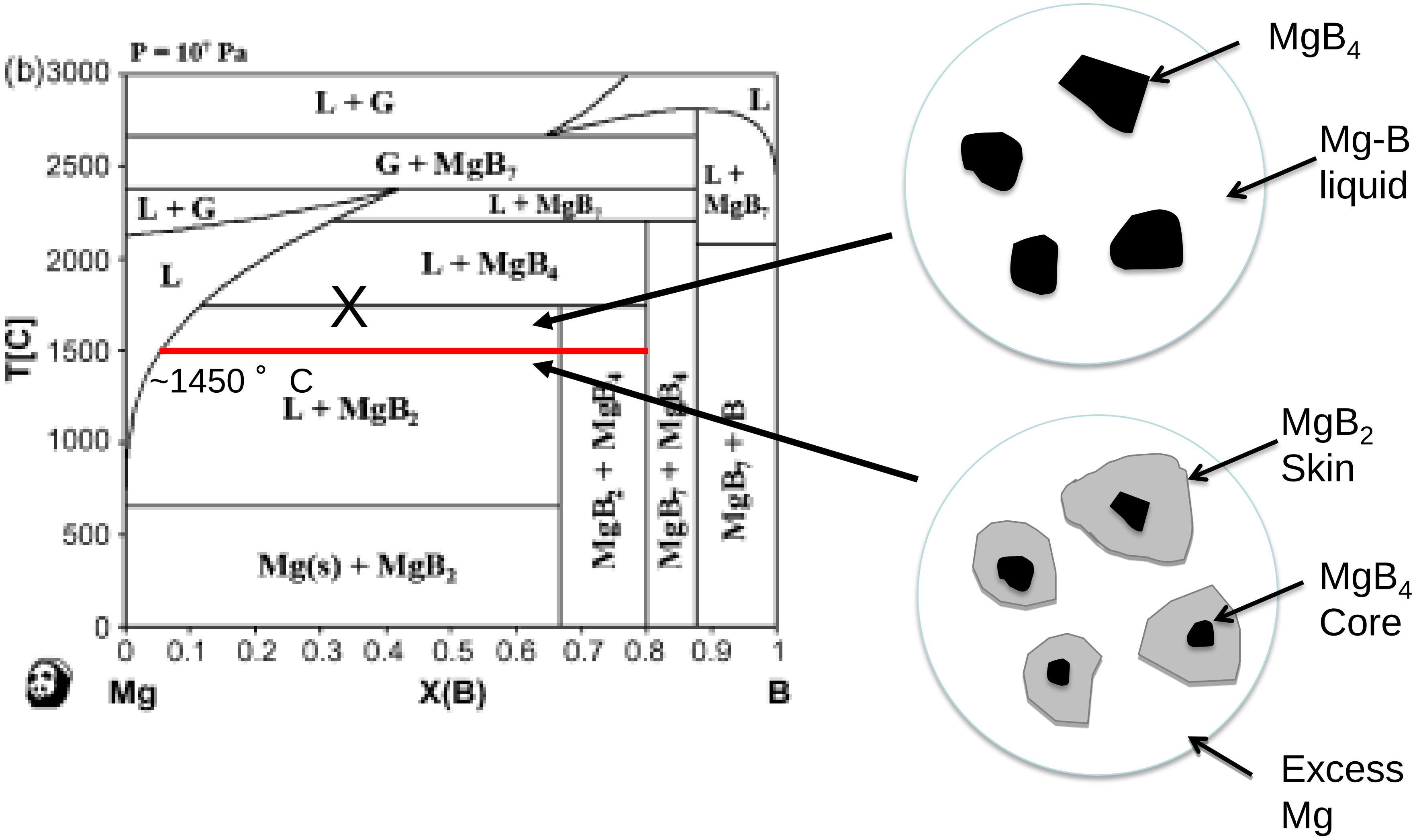
~1490 °C

40 °C difference (~2-5 °C/min. heat)

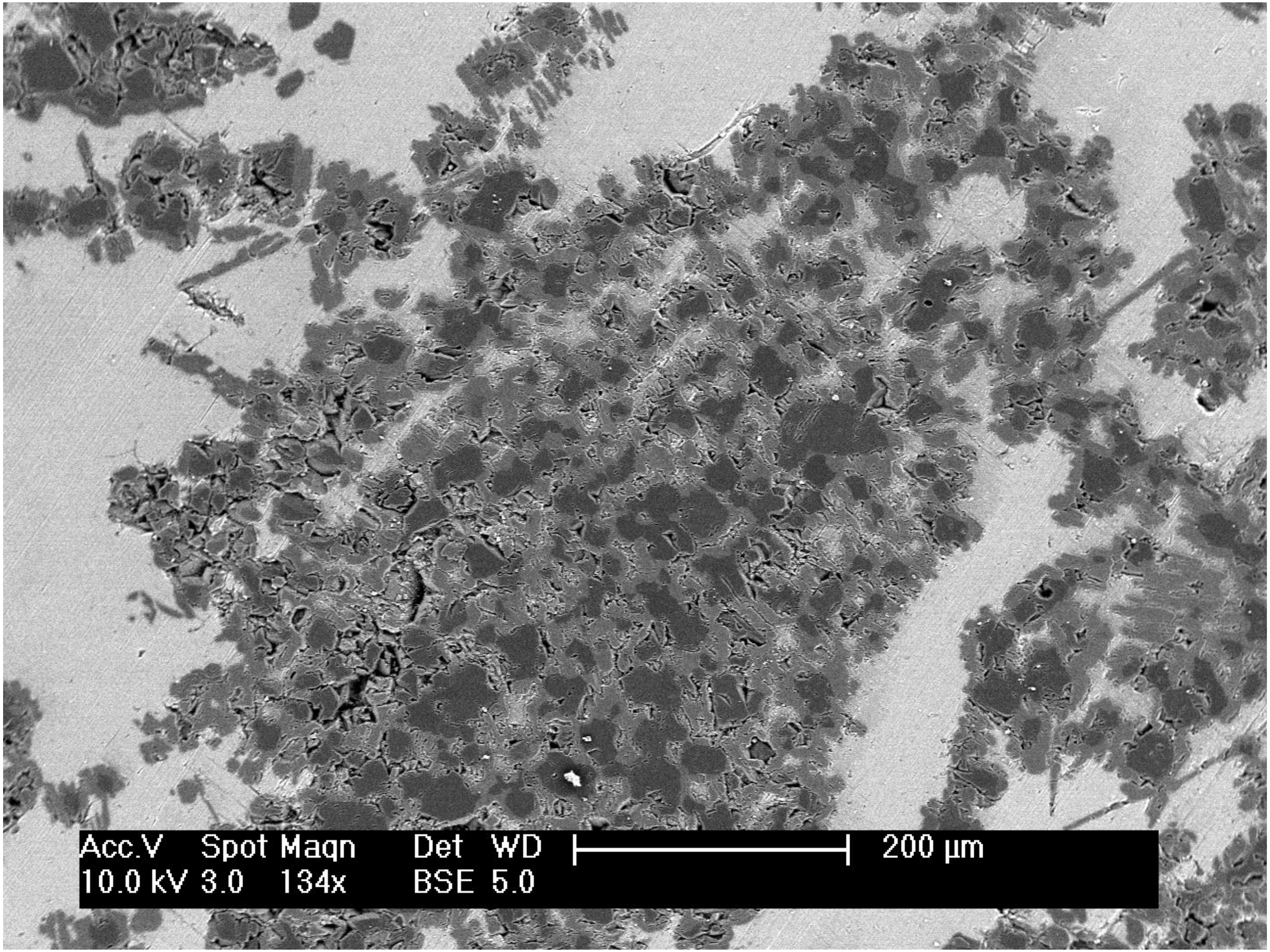

Ramp, Dwell, Cool on Mg/B mixture (99.9999% B)
● Date/Time vs Graphite
● Date/Time vs Sample
Thermocouple Failure
Endothermic Event
Mg Melting
Temperature (°C)
Time
0
200
400
600
800
1000
1200
1400
1600
1800
11:30:00
11:50:00
12:10:00
12:30:00
12:50:00
13:10:00
13:30:00


MgB$_2$ from High Purity Boron
Temperature (°C)
1480
1470
1460
1450
1440
1430
12:25:00
12:26:00
12:27:00
12:28:00
12:29:00
12:30:00
12:31:00
12:32:(
Time
Date/Time vs Graphite
Date/Time vs Sample
Col 6 vs Col 5

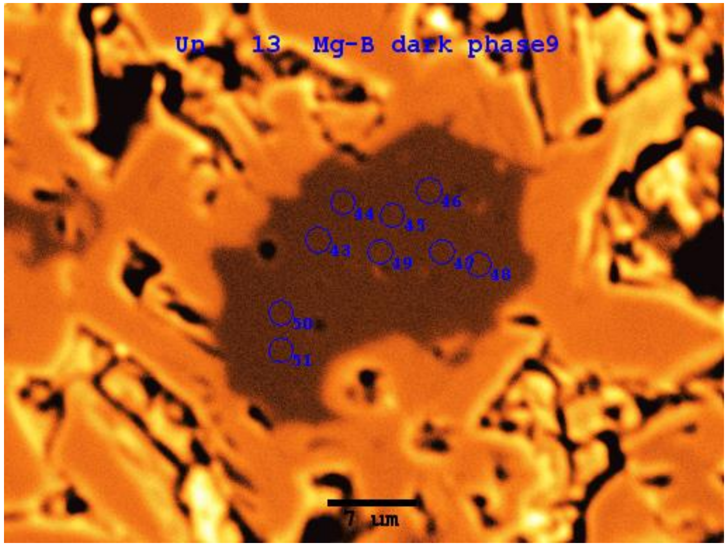
Expected Microstructure for Peritectic



Mg/B Microstructure – 99.9999% B

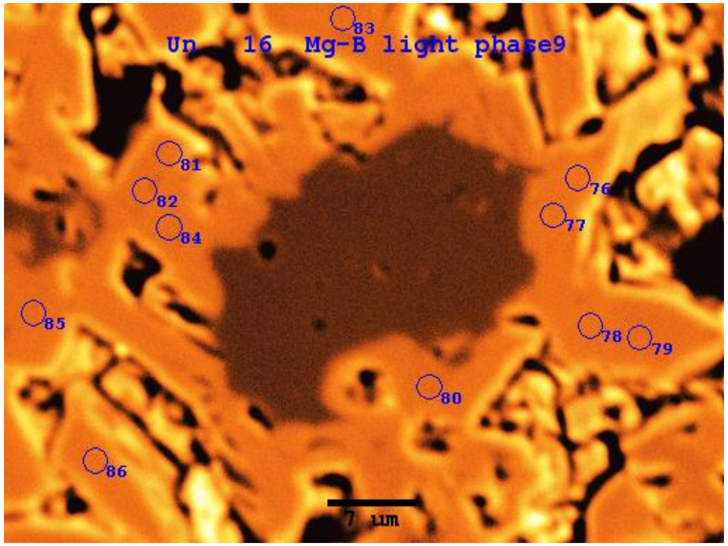


EMPA Measurements by John Donovan



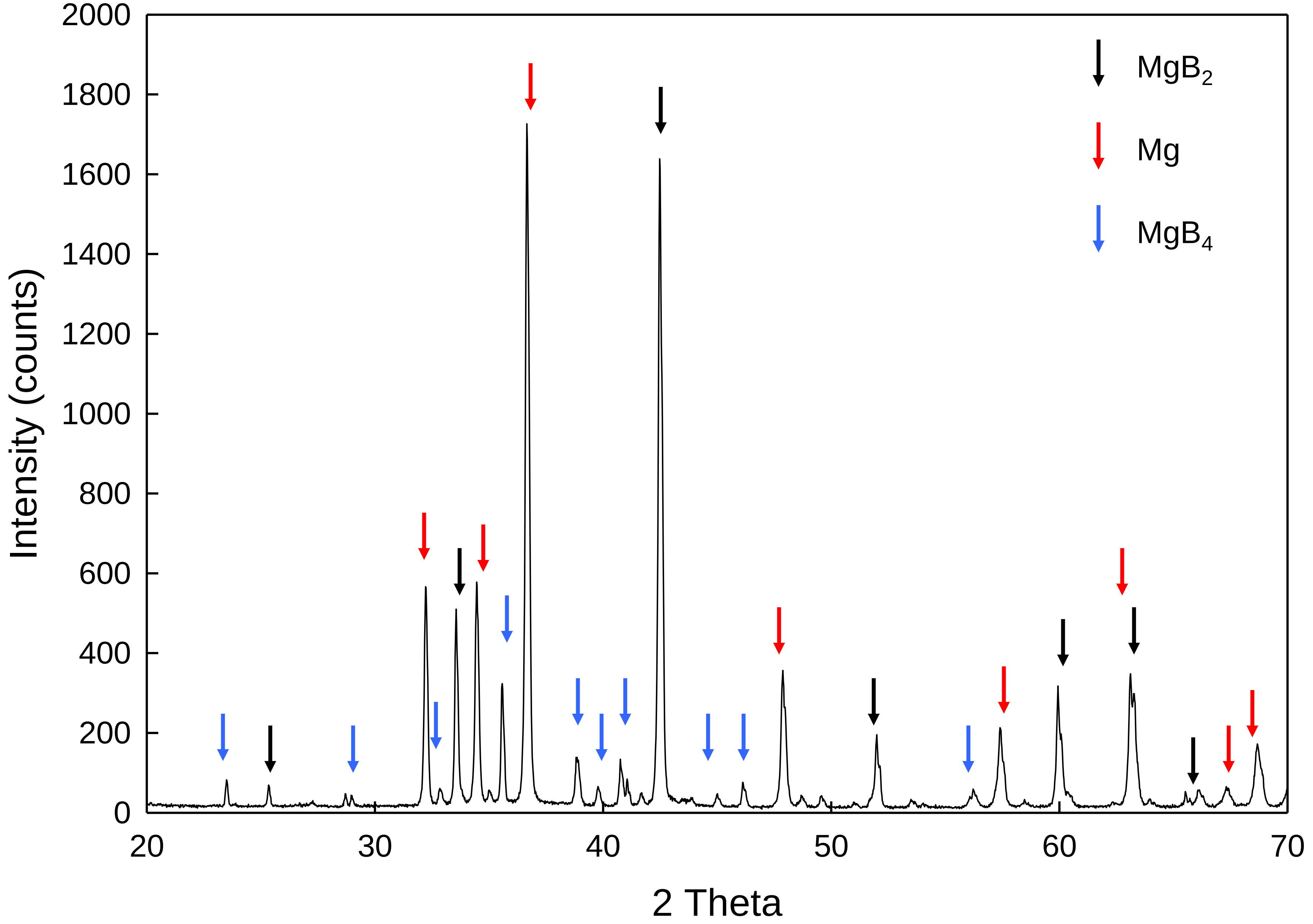
Dark Phase – MgB_4

Element	Measured	Theoretical
Mg	20.9%	20%
B	78.7%	80%
O	0.4%	0%



Golden Phase – MgB_2

Element	Measured	Theoretical
Mg	32.6%	33.3%
B	66.9%	66.6%
O	0.5%	0%

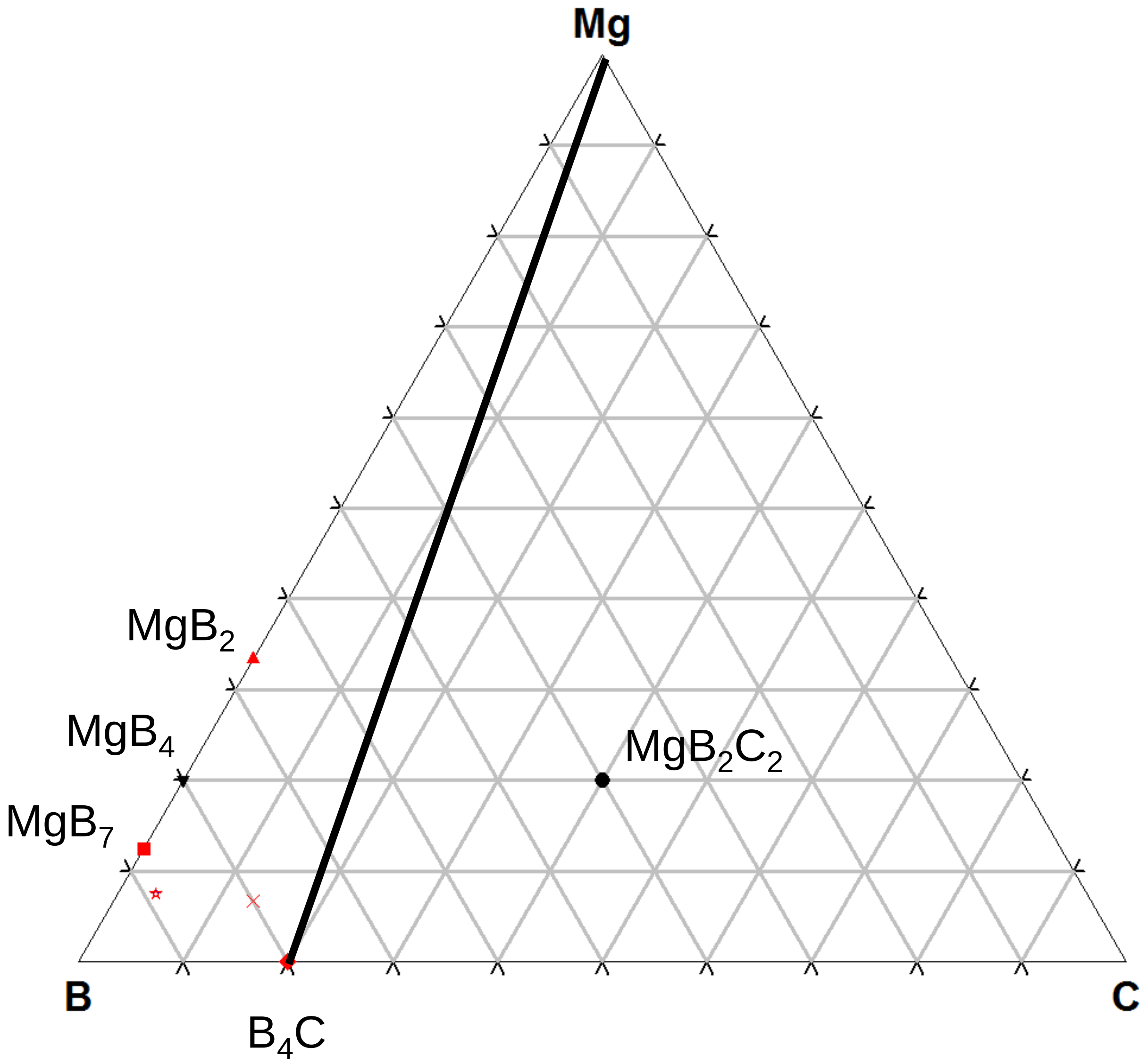


XRD on Mg-B High Purity Ingot

Remaining work on Mg-B binary

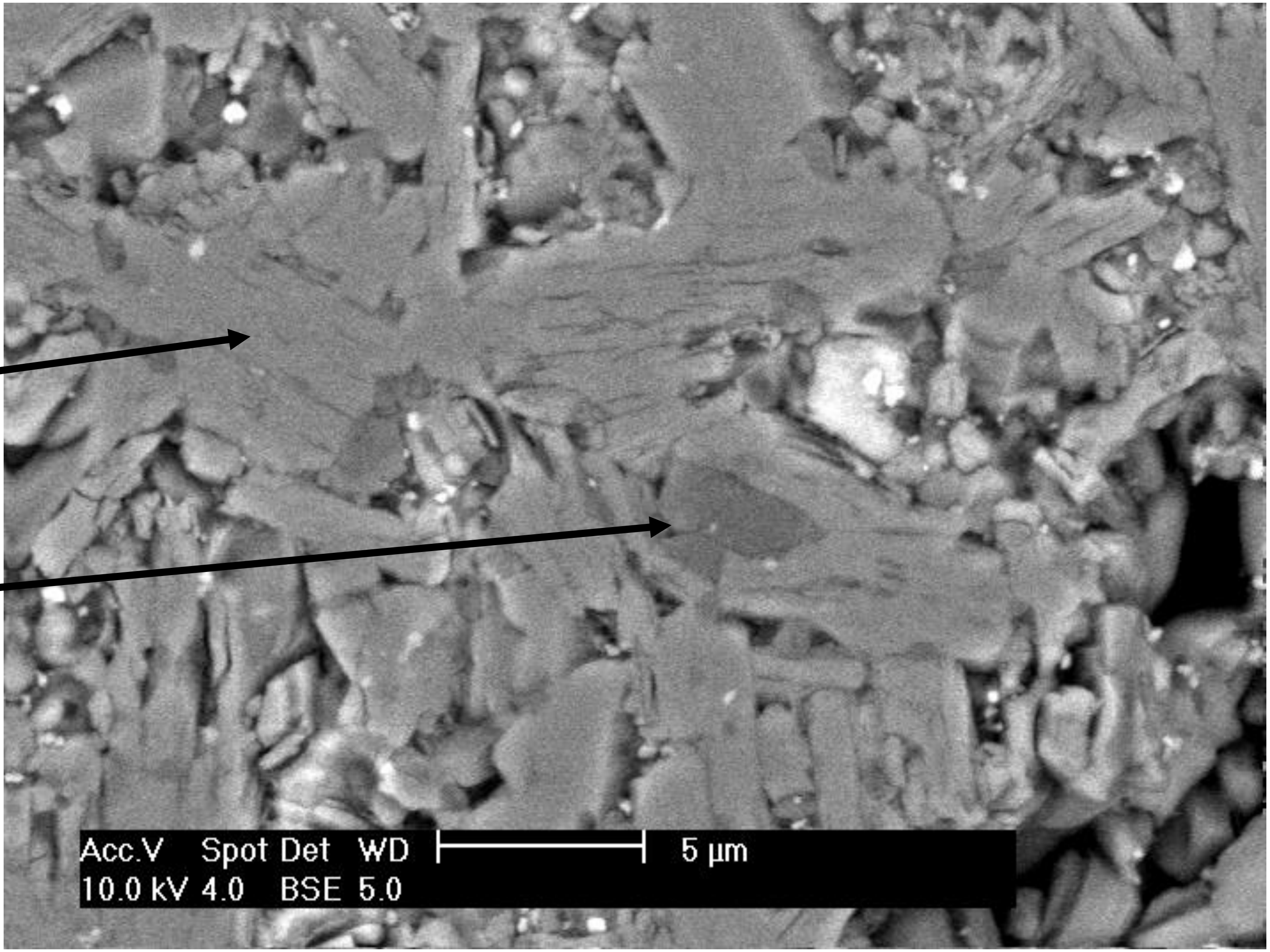
- Redo Smith Method with the high purity boron (99.9999%) and magnesium and obtain the peritectic temperature
- Characterize the sample
- ??

Synthesis of Mg-B-C Alloys



Ternary Ingot from B_4C Powder

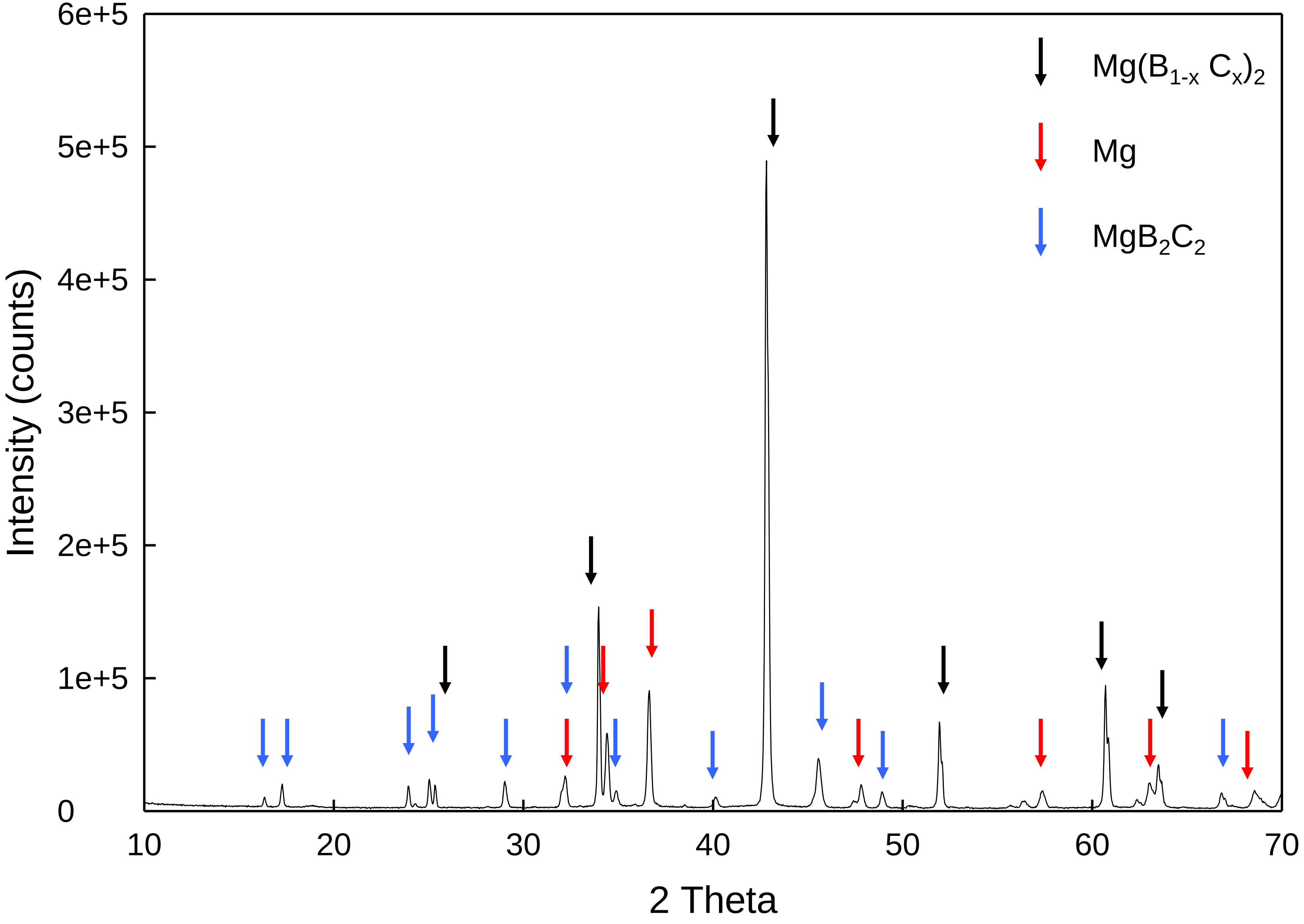
1500 ° C for 10
min., 2 ° C/min.
cool



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

MgB_2C_2

XRD on Mg-B_4C Ingot

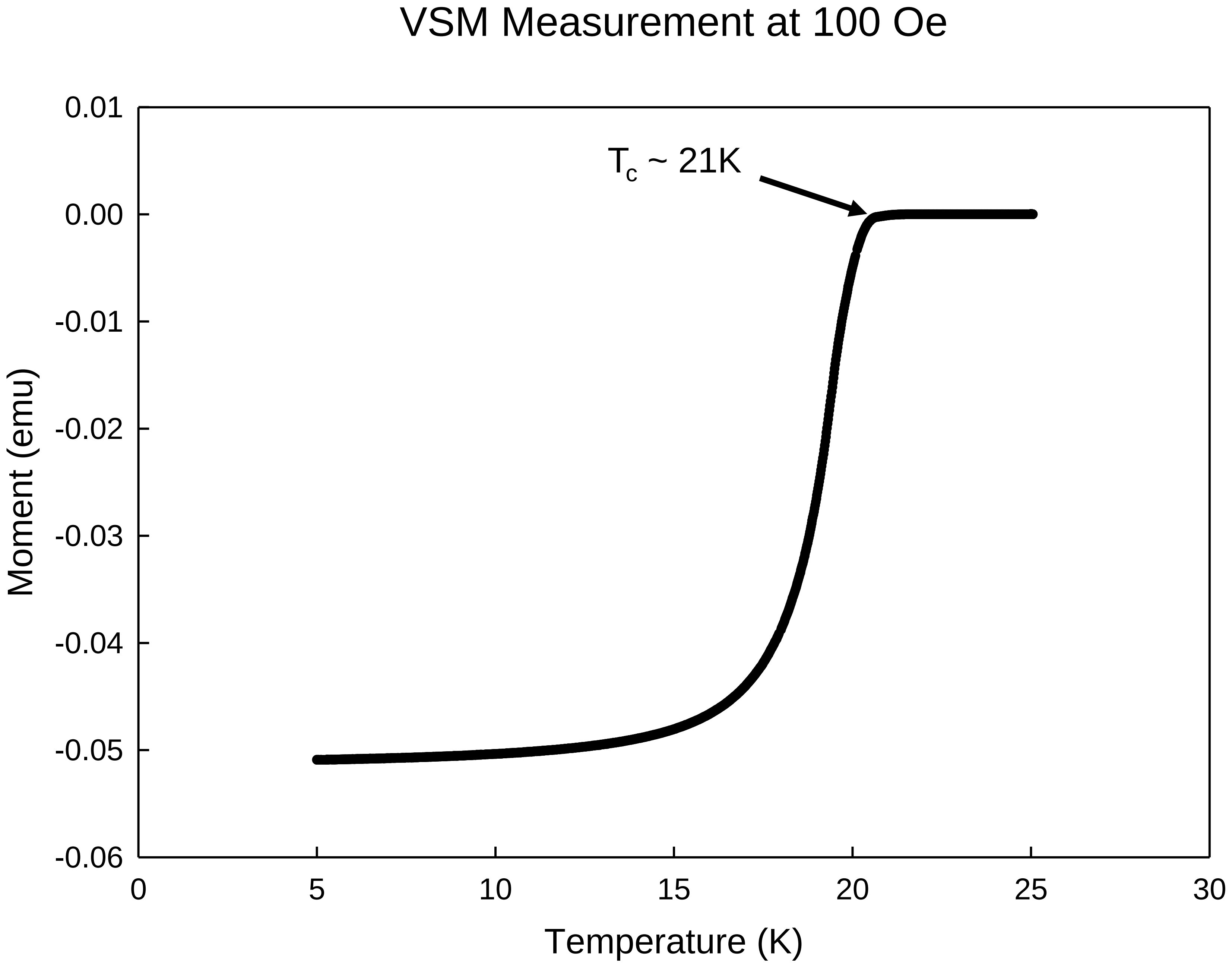


Peak Shift in XRD

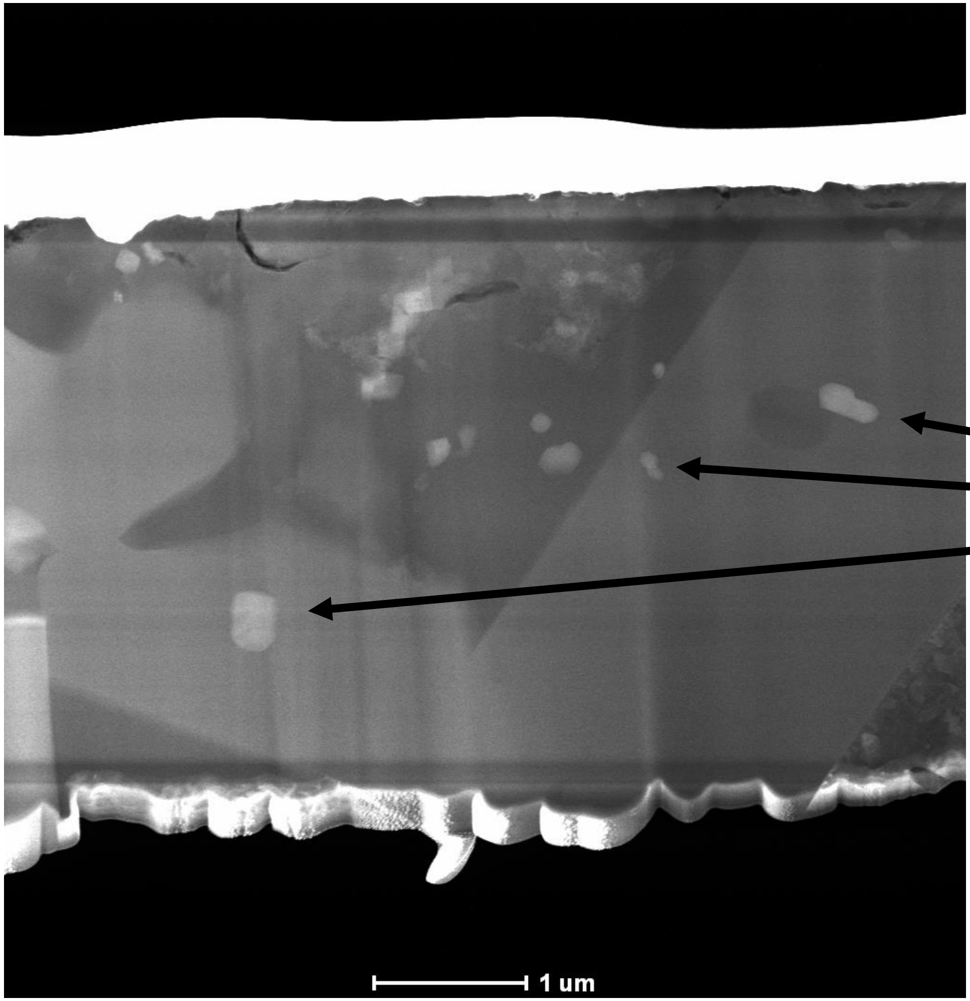
HKL	2θ Pure MgB_2*	2θ $Mg(B_{1-x}C_x)_2$	Difference
(001)	25.266 (3.5221 Å)	25.332 (3.5131 Å)	+0.066
(100)	33.483 (2.6742 Å)	33.962 (2.6375 Å)	+0.479
(101)	42.412 (2.1295 Å)	42.796 (2.1113 Å)	+0.384
(002)	51.885 (1.7608 Å)	51.941 (1.7590 Å)	+0.056
(110)	59.886 (1.5433 Å)	60.697 (1.5246 Å)	+0.811
(102)	63.173 (1.4706 Å)	63.487 (1.4641 Å)	+0.314
(111)	66.044 (1.4135 Å)	66.817 (1.3990 Å)	+0.773
(200)	70.403 (1.3363 Å)	71.375 (1.3204 Å)	+0.972
(201)	76.125 (1.2494 Å)	77.051 (1.2367 Å)	+0.926
(112)	83.191 (1.1603 Å)	83.861 (1.1527 Å)	+0.670

← (00x) peaks do not shift very much indicating c lattice parameter has little change

*Pure MgB_2 based on PDF #00-038-1369 and Cu $K_{\alpha1}$=1.5405982 Å

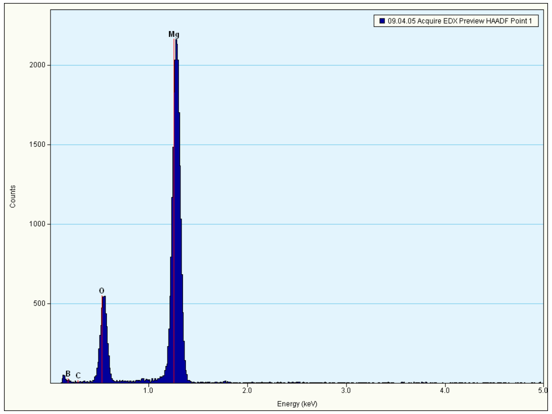

VSM Measurement at 100 Oe
T_c ~ 21K
Moment (emu)
0.01
0.00
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
0
5
10
15
20
25
30
Temperature (K)

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.
- ??