

SYNTHESIS OF MAGNESIUM DIBORIDE SUPERCONDUCTOR WITH CU DOPING

A Thesis

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Master of Science

by

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ABSTRACT

For this thesis, we are going to explore the method of fabricating Magnesium Diboride (MgB_2) superconductor using Magnesium and Boron powder with Copper doping. The composition and structural analysis of our products are examined by X-ray diffraction(XRD) and Scanning Electron Microscopy(SEM). Later, we also perform resistance vs. temperature measurements on our products to find out the critical temperature. Based on the results of XRD and SEM, we believe we have successfully fabricated MgB_2 with Cu doping. The successful products are fabricated using LabTemp furnace heated at 800°C and 900°C for 12 hours under argon environment. Also, the superconducting test suggests our products possess high quality, and the superconducting transition temperature is found at $T_c=39\text{K}$. In the end, we discuss briefly about the possibility of making superconducting cavity employing our method.

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Abbreviations

XRD	X Ray D iffraction
SEM	Scanning E lectron M icroscope
PPMS	P hysical P roperties M easurements S ystem
CCMR	C ornell C enter for M aterial R esearch

For my family and my bull terrier...

Chapter 1

Introduction

Currently, superconducting RF(SRF) cavities mainly use niobium as the superconducting material. The technology to fabricate and operate Nb SRF cavities is almost mature, and the achieved accelerating field gradient is approaching the theoretical limit. However, in order to improve the performance of SRF cavities, other superconductors have been proposed and explored in the past. Among all the superconductors that have been discovered so far, magnesium diboride (MgB_2) is a very promising material for the SRF cavity applications. MgB_2 has the highest critical temperature($T_c=39\text{K}$) among all the conventional BCS superconductors[1]. Besides the high critical temperature, MgB_2 also has simple crystal structure, large coherence lengths, and high critical current and fields[2]. Unlike other unconventional superconductors, such as YBCO cuprates and oxidized Nb and NbSn_3 , MgB_2 does not exhibit weak-link electromagnetic behavior at grain boundaries or fast flux creep, which limits the performances of the more "advanced" superconductors in cavity applications[2–4].

Therefore, we believe that MgB_2 has the potential to achieve lower RF loss and higher acceleration field. However, the fabrication of MgB_2 superconductor is rather difficult and the current synthesis methods can hard be applied to the SRF cavity. MgB_2 wires and thin films has been successfully fabricated for decades[5], but we still do not have any reported MgB_2 SRF cavity demonstrating superior properties comparing to the current Nb cavity.

In this thesis, we try to innovate new fabrication method of MgB_2 , and apply this method to the cavity. During our testing of Mg and B elements based on the available facilities. We have thought about several approaches towards a sound MgB_2 product. We have tried simple reaction of Mg and B powders, and also the compressed Mg-B mixture. The results are not satisfying, so we first use Cu as catalyst to lower the temperature and avoid Mg lost during experiment. We have certain number of trials

with Cu doping, and finally we fabricate MgB_2 product successfully with the method appearing to have no difficulty in the cavity application. The method we use is described as following. We compress Mg-Cu and B powders into discs first, then we combine the two discs and have the sample heated at 800°C and 900°C for 12 hours. Based on the X-ray diffraction(XRD) analysis and scanning electron microscope(SEM), we identify our product to be MgB_2 . Later, we also have superconducting test for our product, which is found to be superconducting at around 39K.

The thesis will be organized in the following method. In chapter 2, we discuss the properties of MgB_2 and explain why we interest in this material for the application of SRF cavity. In chapter 3, we describe some our earlier approach to MgB_2 , as well as some fabrication methods. In this chapter, we also discuss the theoretical fundamentals of our method in the end. In chapter 4, we describe the experimental equipment, procedures and analyzed result from XRD and SEM. In chapter 5, we discuss the result from superconducting test, some error analysis and our provisions of using our method to build a MgB_2 SRF cavity.

Chapter 2

Magnesium-diboride

2.1 Introduction

MgB₂ has been discovered in 1950's, but only until recently its superior properties as a conventional superconductor has been studied and explored. MgB₂ has a remarkably high critical temperature-39K, which is actually the highest discovered up to now among all inter-metallic compound. In this chapter, we will discuss some fundamental properties of MgB₂, including the crystal structure, origin of superconductivity, etc. This chapter will demonstrate the advantages of this material comparing to the commonly used superconductors.

2.2 Crystal and electronic structure of MgB₂

Comparing to other conventional superconductor(Nb, etc.), MgB₂ has great advantage in terms of critical temperature. However, the 39K transition temperature is still 3 times lower than the 130K attained mercury based high-T_c superconducting cuprates. Also, High-T_c copper oxide has been able to work under liquid nitrogen temperature [6]. The difficulty in fabrication and high residual resistance due to the weak link effect limit the application of these un-conventional superconductor to SRF cavity[3]. So we shall start with the crystal and electronic structure of MgB₂, and try to understand the attractive properties that make MgB₂ a promising material for superconductor industry.

MgB₂ has hexagonal AlB₂-type structure with space group P6/mmm. It contains graphite-type honeycomb Boron layers which are separated by alternating hexagonal close-packed layers of magnesium(Figure 2.1). The unit cell lattice parameter are a=3.08Å

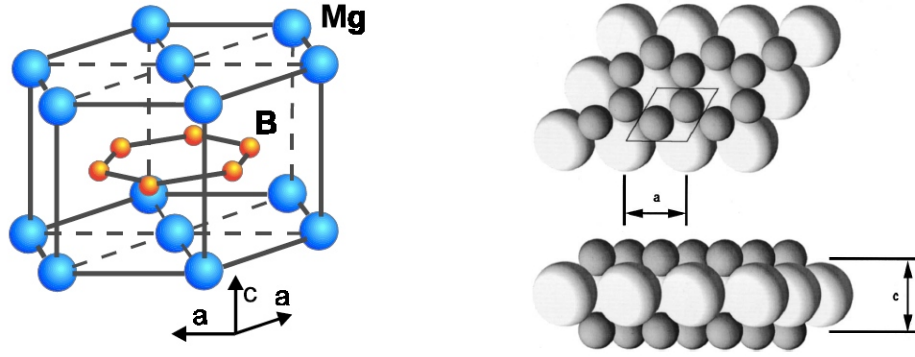


FIGURE 2.1: Crystal structure of MgB_2 . Lattice parameter are specified in the right image[6, 7].

and $c=3.52\text{\AA}$ [8]. Similar to graphite, the distance between Boron planes is a lot longer than the intra-planar B-B bond, which leads to strong anisotropy of the Boron bonding[6].

MgB_2 is a phonon-mediated BCS superconductor. The atomic structure of Mg and B are: $\text{Mg}(1s^2 2s^2 2p^6 3s^2)$ and $\text{B}(1s^2 2s^2 2p^1)$, and the electronic structure of MgB_2 is suggested in Figure 2.2. The σ bands are formed by the overlapping sp^2 hybrid orbitals of Boron atoms, and there are three σ bonds for each Boron atom. The π bonds are formed by the p_z orbitals of Boron and s orbitals of magnesium. Magnesium atom donates two electrons to the neighboring two Boron atoms and becomes fully ionized Mg^{2+} . As a result, the Mg^{2+} ions exert greater attractive potential to the electrons at p_z orbital than to those at electrons from σ bands, and electrons are transferred from σ bands to π bands. The hole doping at σ bands suggests strong covalent bonds localized in Boron layer, and the three strong σ bonds also manifest the honeycomb shape of each Boron layer. In three dimensions, electrons and holes in π bands form "metallic" type bonding that brings Boron layers together[8, 9].

2.3 Superconductivity in MgB_2

For BCS based or intermetallic compound superconductors, MgB_2 exhibits the highest critical temperature of $T_c=39\text{K}$. The high transition temperature brought people great interest in this material, and the superconductivity of MgB_2 has been extensively studied.

MgB_2 has each of its elements aligned in two-dimensional planes, and the material is therefore expected to have two-dimensional superconductivity as a result of its crystalline structure. In conventional superconductors, the electron-phonon interaction creates Cooper pairs of approximately equal pair strength, distributed evenly over the

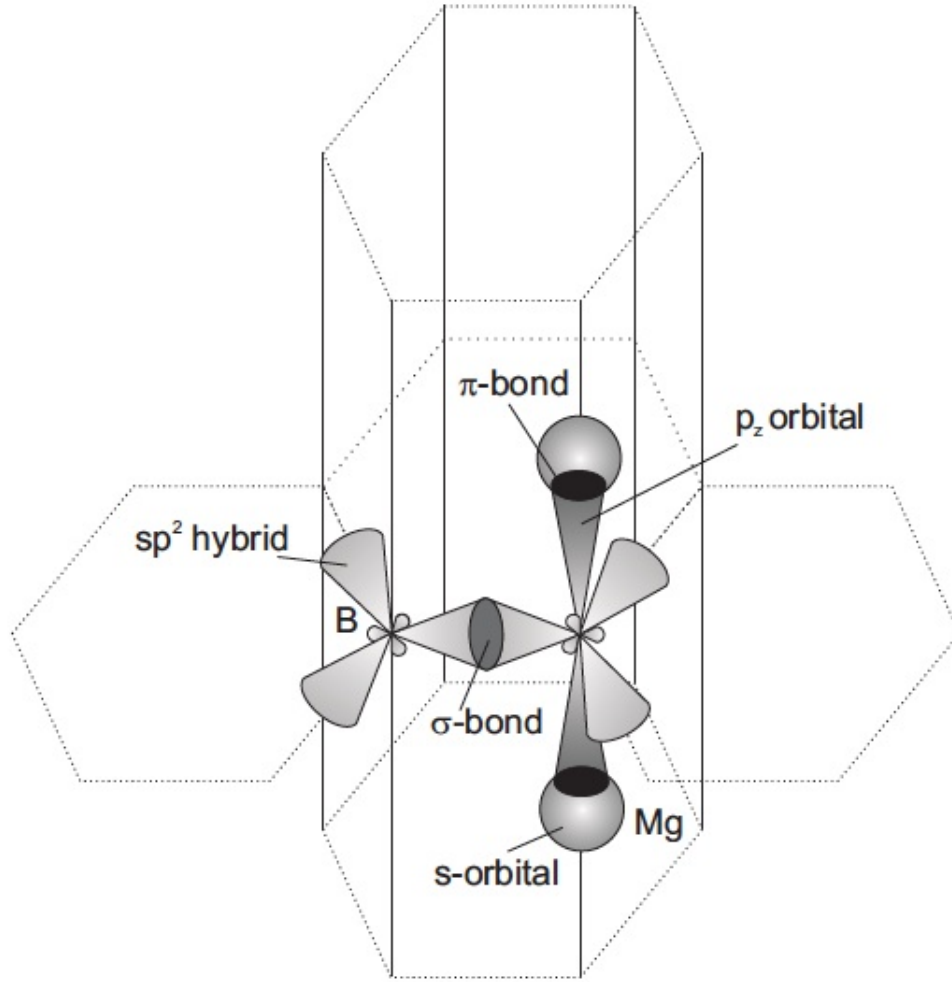


FIGURE 2.2: Electronic structure of MgB₂. σ bond is formed by Boron atoms have overlapping sp² orbitals, and π bond is formed by s orbital of magnesium atom and p_z orbital of Boron atom [8]

Fermi surface. In MgB₂, there is one high-energy optical phonon mode (E_{2g}), which couples very strongly to electrons in the 2D σ band. The strong coupling comes from the special covalent nature of the σ band. As stated before, the Boron layer of the MgB₂ forms honeycomb configuration that is similar to graphite. However, Boron atoms have less electrons than carbon atoms and not all the σ bands in MgB₂ are filled. As a result, lattice vibration in the Boron planes has a much stronger effect, and consequently, strong electron pairs are formed and confined to the planes of Boron. These σ bands form cylindrical Fermi surface and are 2D in character, and the 2D superconducting gap along the B-B axis is found to be $\Delta_{\sigma}=7\text{-}8\text{meV}$. On the other hand, MgB₂ also has weaker electron-phonon interaction in π bands, which are 3D in character and form tubular Fermi surface. The π bands have energy gap of $\Delta_{\pi}=2\text{-}3\text{meV}$, and both gaps

close at the same critical temperature $T_c=39\text{K}$ [8, 10, 11].

2.4 Basic properties of MgB_2

TABLE 2.1: List of some superconducting parameters of MgB_2 [8]

Parameter	Experimental values	Theoretical values
Coherence length	$\xi_{ab}(0)=3.7\text{-}12\text{nm}$ $\xi_c(0)=1.6\text{-}3.6\text{nm}$	
Penetration depths	$\lambda(0)=85\text{-}180\text{nm}$	$\lambda_{ab}(0)=39.2\text{nm}$ $\lambda_{ab}(0)=39.2\text{nm}$
Energy gaps	$\Delta_\sigma(0)=5.5\text{-}8.2\text{meV}$ $\Delta_\sigma(0)=1.5\text{-}3.5\text{meV}$	$\Delta_\sigma(0)=7.09\text{meV}$ $\Delta_\sigma(0)=2.7\text{meV}$
Upper critical field	$H_{C2} \text{ab}(0)=14-39\text{ T}$ $H_{C2} \text{c}(0)=2-24\text{ T}$	
Lower critical field	$H_{C1}(0)=27-48\text{ T}$	

BCS type II superconductors are usually characterized by lower and upper critical magnetic field (H_{c1} and H_{c2}), and these values for MgB_2 are listed in Table 2.1. Other parameters, such as coherence length, penetration depths, are also listed for reference. The experimental values for these values vary mainly because of the different type of MgB_2 sample and different examination methods. Based on these basic properties, we shall compare MgB_2 and other current superconductors used for SRF cavities in the next section[8].

There are two other parameters that are worth mentioning here, resistivity and thermal conductivity. MgB_2 has fairly low resistivity even at room temperature. The resistivity of MgB_2 is approximately $5\text{-}6\text{m}\Omega\text{-cm}$, which can be compared with Cu of $2\text{m}\Omega\text{-cm}$ Nb of $15\text{m}\Omega\text{-cm}$, and Nb_3Sn of $80\text{m}\Omega\text{-cm}$ [12, 13]. At 40K , MgB_2 has thermal conductivity of 170mW/cmK , while Cu has 10^4mW/cmK and Nb has 20mW/cmK [14, 15]. So MgB_2 does not possess high thermal conductivity and other materials may be needed to remove the excessive heat during usage.

2.5 Comparison with other superconductors

In this section, we briefly compare MgB_2 with Nb and Nb_3Sn to demonstrate why MgB_2 has the potential to success in the industry of superconducting RF cavity.

2.5.1 Critical fields and acceleration gradient

Besides the lower and upper critical magnetic field (H_{c1} and H_{c2}), we need to introduce thermodynamic critical magnetic field (H_c) and superheating critical magnetic field (H_{sh}). These parameters are related as following.

$$H_{c1}H_{c2} = H_c^2 \ln(K_{GL}) \quad (2.1)$$

where $K_{GL} = \lambda/\xi_0$. λ is the penetration length and ξ is the coherence length[16]. Based on different K_{GL} , H_{sh} is determined as $H_{sh} \approx 1.2H_c$ for Nb or $H_{sh} \approx 0.75H_c$ for Nb₃Sn and MgB₂. Assuming the ratio between field intensity and acceleration gradient is $H_{peak}/E_{acc}=40\text{Oe}/(\text{MV}/\text{m})$. The acceleration field gradient can be calculated using the equation,

$$H_{sh}(T) = H_{sh}(0)(1 - (T/T_c)^2) \quad (2.2)$$

where T is the operation temperature[16]. The results are shown in Table 2.2.

TABLE 2.2: Theoretical acceleration field limit and BCS resistance of Nb, Nb₃Sn and MgB₂[3]

Material	Operation Temperature(K)	Theoretical Limit Eacc(MV/m)	$\frac{1}{T} \exp(\frac{-\Delta}{k_b T})$
Nb	4	49	1
Nb ₃ Sn	4	95	0.0195
MgB ₂	4	80	0.00000217
MgB ₂	20	52	0.369

From the table, we can see that MgB₂ has greater theoretical acceleration field than Nb, and the limit is close to Nb even at 20K

2.5.2 Surface resistance

The quality factor of a cavity depends on the geometrical factor and cryogen heat load which comes from the surface resistance. It is necessary to reduce the surface resistance to avoid the excessive cooling cost.

The surface resistance(R_s) includes the BSC resistance(R_{BCS}) and residual resistance (R_{res}). The BSC resistance is determined by the following,

$$R_{BCS} = A \frac{f^2}{T} \exp(-\frac{\Delta}{k_b T}) \quad (2.3)$$

where A is a constant depending on the superconducting parameters of a material and f is the frequency[16]. The effect of operating temperature on the BCS resistance can be found in Table 2.2. At 4K, the resistance is dramatically reduced comparing to Nb and Nb₃Sn. Therefore, MgB₂ is able to increase the Q factor of a cavity and reduce the operational cost if successfully built.

From previous discussion, we can see that Nb₃Sn is also a good candidate for building superconducting RF cavity. However, Nb₃Sn has a drawback when referring to the residual resistance. It has been found that R_{res} of coated surfaces of Nb₃Sn cavities increases steeply at high H_{rf} as compared to bulk Nb cavities[17, 18]. This increase in residual resistance is because of the weak links at the grain boundaries, i.e., weak coupling across grain boundaries that limits SC current flow and makes the surface sensitive to H_{rf} and H_{ext} . Unlike Nb₃Sn, MgB₂ does not show signs of weak links and resulting high residual resistance[3].

Chapter 3

Discussion of MgB_2 fabrication techniques

3.1 Introduction

There are numerous approaches of fabricating MgB_2 that have been explored since its discovery, and high purity MgB_2 product has been synthesized for many years. Traditionally, there are three common ways of fabricating MgB_2 : pulsed laser deposition, co-deposition and Mg diffusion[19–21]. However, in this chapter, we shall briefly introduce some innovative ways of making MgB_2 superconductor. We believe these methods are applicable in constructing superconducting cavity. In the end, we will discuss more about the method we use for the fabrication of MgB_2 .

3.2 Direct Mg diffusion with B

We start the discussion with the most straight forward approach, and we shall see the obstacles of making large-scale MgB_2 product using this method. Also, from various reports, MgB_2 product fabricated by Mg diffusion method has the highest T_c and sharpest transition[6, 22]. Ideally, when the temperature and pressure are well defined, one can have Mg element and B element fully reacted to have MgB_2 product. The phase diagram of Mg and B element can be found in Figure 3.1. For our purpose, we mainly focus on the 1 atm figure and where liquid Mg and MgB_2 is found. The temperature range at 1 atm is found to be approximately from 650°C to 1100°C. These temperatures are reasonable if comparing to the melting and boiling temperature of Mg element(650°C and 1091°C).

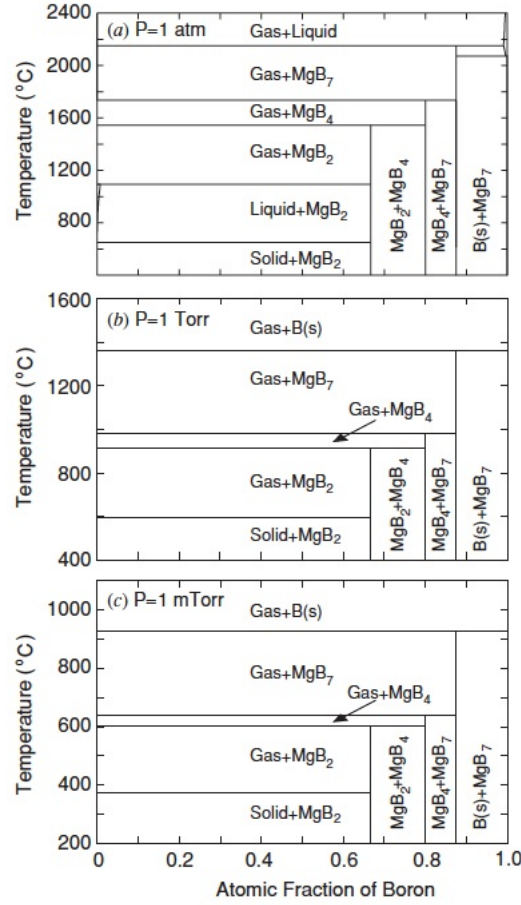


FIGURE 3.1: Phase diagram of Mg and B mixture reacting at different atomic ratio, temperature and pressure. We mainly focus on the region where MgB_2 and liquid Mg is found at 1 atm. It suggests that between 650°C and 1100°C we should be able to find the mixture of liquid Mg and MgB_2 . The phase diagram is adapted from [23].

As the phase diagram suggested, if we mix Mg and Boron elements with Boron less than 70% at 1 atm, and we heat the mixture at around 900°C, we should be able to find the desired MgB_2 . We have employed this method as the first approach toward MgB_2 product, and we begin the test without using Boron to see the capability of the available equipment. We start using 99.8% pure Mg powder with grain size of 250 micron. The Mg powder has been placed into a Carbon crucible and heated to different temperatures. The results are shown in Table 3.1. As we can see from the table, the Mg powder disappears when the temperature goes up, especially a lot higher than the melting point of Mg. Even though the boiling point of Mg is not reached during the heating, we still observe the "evaporation" of Mg powder. We can attribute some of the Mg loss to the constant inert gas flow, but the results definitely indicate the possible Mg loss during the reaction of Mg and B at high temperatures. The volatility of Mg mainly result in the loss, and we have seen the loss of Mg during MgB_2 during many reports[6, 24, 25].

TABLE 3.1: Mg powder melting using carbon crucible: this table shows the experimental results of Mg powder melting at 1 atm under Argon environment. The Mg powder is placed in a carbon crucible inside a furnace with constant Ar flowing. The ramp rate for the furnace is set to be 300°C per hour, and the sample is heated for 4 hours. The total mass includes both the Mg powder and crucible, and the percent missing is based on the loss of Mg.

Melting Temperature(°C)	Mg mass(g)	Total Mass Before(g)	Total Mass After(g)	Mass Change(g)	Percent Missing
500	0.243	9.083	9.08	0.003	1.2%
600	0.221	9.237	9.22	0.017	7.7%
650	0.371	9.391	9.38	0.021	5.6%
675	0.333	9.356	9.289	0.067	20.1%
700	0.05	8.91	8.865	0.045	90%
900	0.423	9.449	9.036	0.413	97.6%

The loss of Mg proposes a critical drawback for the method of direct melting Mg with B because it can be very likely Mg evaporates before reacting with B. Also, since Mg is a highly reactive element, the evaporation can lead to severe contamination to the equipment. Therefore, we would like to find alternative methods or improvements to synthesis MgB₂ without such issue. Also, there will be less economical cost and less contamination from other elements when we use a lower reacting temperature. The possible improvements for this method are discussed as following. First, the melting temperature of Mg can be lowered by doping, such as copper and lead, and the reaction temperature between Mg and B is lowered with the presence of the other metals. This is especially interesting if we can use superconducting material, such as Pb, as to avoid the problems associated with non-superconductor. In the end, we have decided to work on this approach with Cu doping based on the funding and equipment, and we will discuss this approach in detail in the last section of this chapter. Second, we can use Mg and B disc rather than powder for the application. It is possible to use a non-reacting substrate, and we place the Mg disc on top of it. Then we press another B disc onto the Mg disc. So the Mg element is confined in the region between B and substrate. We also follow this idea to avoid the volatility of Mg, and our experiment later on use discs for reaction rather than powder.

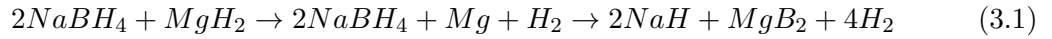
In the end, as the phase diagram suggests, it is possible to use gaseous Mg under low pressure to acquire the MgB₂ as well. Pulsed laser deposition has been discovered to be very effective in achieving high purity MgB₂ thin film, but this method is not effective enough as for our superconducting cavity application.

3.3 Reactions using borohydrides

We have thought about other methods of synthesizing MgB₂ in large scale. In spite of the fact that many different techniques have been discovered and proved to be successful

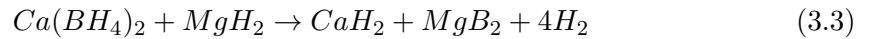
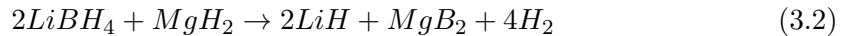
in creating high purity MgB_2 , we were trying to find innovative approaches that are both economical and applicable to the industrial demand. For this section and the next, we are going to discuss two techniques that are not as well studied as other common synthesis methods, and these two techniques can be very promising if their disadvantages can be avoided.

The inspiration for the first approach comes from the chemical reactions used for hydrogen storage. The materials for hydrogen storage should possess high hydrogen content, low heats of dehydrogenation, low operation pressures and low economical cost[26]. Solid metal borohydrides are proposed as promising materials for the purpose of storing hydrogen for industrial use. There are several borohydrides will have their product containing MgB_2 after releasing hydrogen, and we start with the discussion of $NaBH_4$. The chemical reactions for $NaBH_4$ are shown as following.



The desorption of hydrogen occurs in the two step chemical reactions, where MgH_2 decomposes into Mg and H_2 first, and $NaBH_4$ reacts with Mg and producing MgB_2 and H_2 . The decomposition temperature is found to be at $351^\circ C$ and the total decomposition happens at $600^\circ C$ [27]. After the total decomposition, hydrogen will be removed and only product of MgB_2 and NaH remain. Then theoretically, the two compounds should form two different layers when liquidized because of the density difference($NaH:1.40g/cm^3$, $MgB_2:2.57g/cm^3$). However, there are several issues may happen when heating the product to the melting point of these compounds($NaH:800^\circ C$, $MgB_2:830^\circ C$), such as the decomposition of MgB_2 into MgB_4 , reactions of contamination at high temperature. So far no one has ever claimed of achieving high purity MgB_2 using this method, even though from XRD analysis that MgB_2 is successfully discovered with NaH (Figure 3.2).

There are several other borohydrides can be considered for the MgB_2 production, such as $LiBH_4$ and $Ca(BH_4)_2$.



These borohydrides works similarly as $NaBH_4$ [28]. They react at low temperatures and have products of metal hydride with MgB_2 . The criteria for choosing the borohydrides are the availability of separating reaction products and the cost for reactants. Also, for some of these borohydrides, catalyst are needed for the reactants to be completely decomposed. For instance, $NaBH_4$ will have better performance when adding aluminum[29].

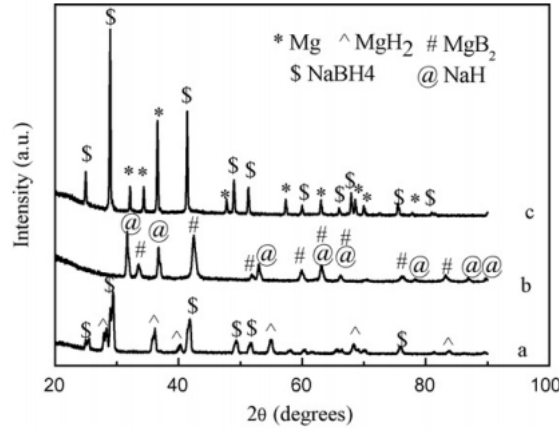


FIGURE 3.2: X-ray diffraction patterns of $NaBH_4$ / MgH_2 mixture: (a) after 1 h ball milling under argon; (b) after dehydrogenation at $600^\circ C$; (c) after dehydro-genation at $380^\circ C$ [27]. We mainly focus on the pattern b, which includes the peaks for MgB_2 and NaH[27].

At last, there has not been many research into the possibility of using borohydrides as a way to synthesize MgB_2 . But from the current result of hydrogen storage material, it is very promising to extrapolate MgB_2 from the products if properly handled. Since hydrogen storage material has been used extensively in industry, MgB_2 can be acquired in an inexpensive way as a side-product of dehydrogenation. More research into this method are required, and we only present the possibility of this innovative method of synthesizing MgB_2 .

3.4 Electroplating MgB_2 from molten salt

Another economical and interesting method to synthesize MgB_2 is to electroplate it from molten salt. Electroplating is one of the most popular techniques to fabricate conductive films and has been applied to various kinds of materials. The process of electroplating can be used to fabricate uniform films and also films on irregularly shaped surfaces[30]. Such virtue makes electroplating a very promising method on the application of accelerating cavity. Molten salt is served as electrolysis, and it is a mixture of $MgCl_2$, MgB_2O_4 , $NaCl$, KCl , etc. The setup for the electrochemical synthesis of MgB_2 is simple and economical, and DC power supply and tubular furnace are required for the process. The reported critical temperature of MgB_2 bulk sample prepared by this method is $37K$ [31], which is very close to the intrinsic T_c of $39K$. The reported transition temperature of MgB_2 bulk suggests this method can be possibly applied for superconducting cavity construction.

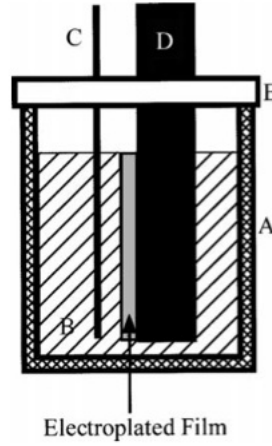


FIGURE 3.3: Schematic picture of an electrolysis cell[30].

The process of electroplating MgB_2 from molten salt will be briefly discussed as following. An alumina crucible is used as the electrolyte container. The crucible is filled with an electrolyte composed of $MgCl_2$, MgB_2O_4 , KCl , and $NaCl$ with a molar ratio of 10:2:5:5. This ratio is the optimum composition to form MgB_2 [32]. A graphite rod (C) and a semicylindrical graphite substrate (D) are inserted in parallel into the electrolyte powder. There is an interspace between the axis of the graphite rod C and the flat face of the substrate D. The graphite rod C and the graphite substrate D work as the anode and cathode respectively, and they are insulated by an insulating ceramic plate (E). The graphite anode C and the substrate D are connected to Pt leads. The electrolysis cell is placed in a tubular furnace with an insertion quartz tube. One end of the insertion tube is connected to Ar gas, and the other end is connected to an exhaust. The Pt leads are led out of the insertion tube via a hermetic connector to a DC electric power supply outside. Then the electrolysis is dried by heating at $400^\circ C$ for 1 hour, and then the temperature is raised to $600^\circ C$, at which the electrolyte fuses completely. The electrolysis process is started by applying a constant DC voltage between electrodes. The process is kept for one hour to allow the electroplate to complete. The product has to be polished before analysis due to the nature of the molten salt[30].

The electroplated layer on the substrate is identified to contain MgB_2 with a volume fraction higher than 90%. Since molten salt has a lot of unwanted elements, such as K, Cl, Na, etc, the product coming from this method can not be guaranteed to be purely MgB_2 . However, the critical temperature for the electroplated layer is found to be 37K, which is not far from the intrinsic value of 39K. This makes such process very interesting in producing large bulk of MgB_2 in an economical way.

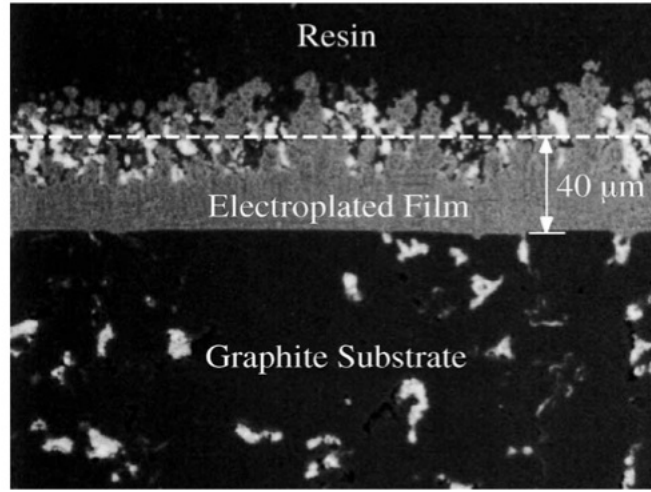


FIGURE 3.4: Cross-sectional image of the film electroplated on the graphite substrate[30].

3.5 MgB_2 synthesis using Cu doping

Having thought about the different possible fabrication techniques, we finally decide to add Cu doping to our tested method of direct melting Mg with B. The intuition comes from the fact that adding small amount of Cu to Mg will lower the melting point of Mg (see Figure 3.5). As a result, we can avoid the volatility of Mg and maintain the reaction in a liquid environment.

Moreover, there are other advantages of using Cu doping with MgB_2 sample. Originally, despite the fact that MgB_2 has the highest $T_c=39K$ among all the conventional superconductors, the critical current of MgB_2 is still smaller than expected for an ideal material[34]. So various chemical doping method has been tested in order to increase current density in MgB_2 sample. There are generally two approaches of increasing the critical current in MgB_2 : enhance pinning and increase grain connectivity[35]. Since weak pinning in pure MgB_2 can result in rapid degradation of critical current J_c as a function of magnetic field, it is necessary to enhance the pinning effects, which include increasing pinning of grain boundaries, eliminating nanoimpurities, avoiding lattice defects, etc.. On the other hand, it is possible to increase J_c by increasing the connectivity of MgB_2 grain[35, 36]. To increase the connectivity of MgB_2 grain, one can void porosity by high pressure sintering, or it is possible to use highly purified B and Mg elements for reaction[37, 38]. More importantly, one can change the morphology and crystal structure of MgB_2 grains. Therefore, Cu is considered as a good doping material for MgB_2 to increase the connectivity and therefore achieving higher critical current.

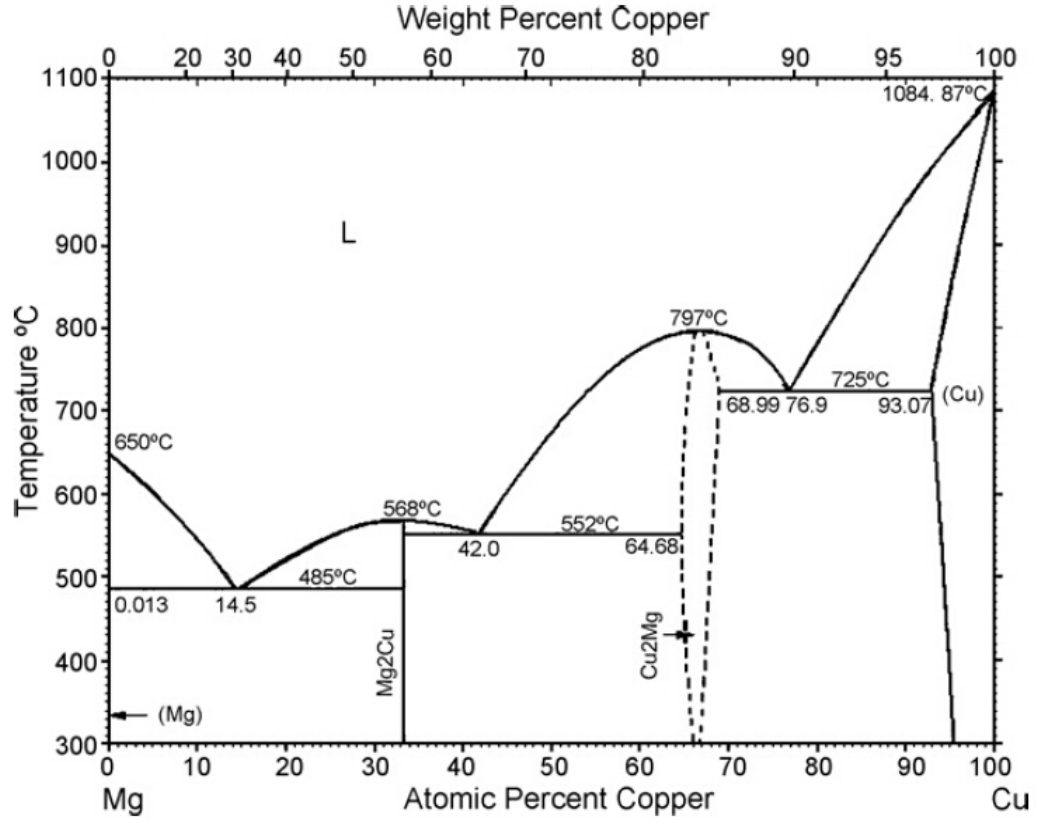


FIGURE 3.5: Phase diagram of Mg-Cu mixture. We can see that Mg becomes liquid at 475°C when adding 15% Cu in molar ratio. Also, adding small amount of Cu generally lowers the melting point of Mg[33].

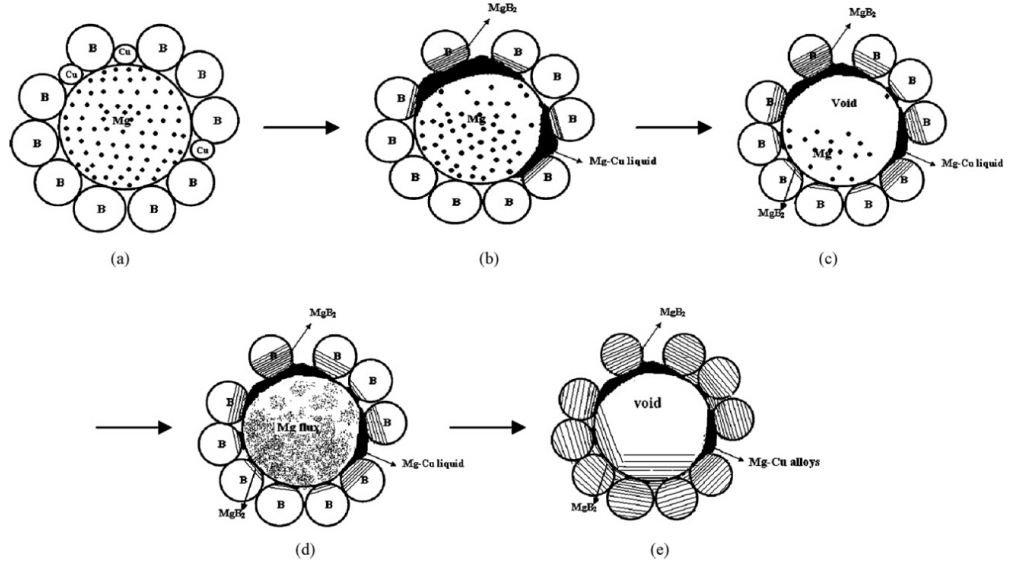


FIGURE 3.6: The sintering model of Cu-doped Mg powder reacting with B powder. (a) starting stage, (b) eutectic reaction stage, (c) solid-solid reaction stage, (d) Mg melting stage, (e) solid-liquid reaction stage[39].

The mechanism of Cu-doped Mg powder reacting with B powder is illustrated in Figure 3.6. Since Cu has smaller powder size than Mg and B, Cu powder will be mainly distributed in the interspaces between Mg particles and B particles at the starting stage(Figure 3.6(a)). When the temperature reaches the eutectic point of MgCu system, Mg melts with the presence of Cu and starting penetrate into B powder. Afterwards, the Mg atoms next to the liquid will diffuse into the B particles and react with B to form a small amount of the MgB_2 . The MgCu liquid serves as the high transport for the diffusion of the Mg atoms(Figure 3.6(b)). If we keep increasing the temperature, the reaction $Mg(S) + 2B = MgB_2$ starts between Mg atoms and B atoms far away from the MgCu liquid region and the reaction $2Mg_2Cu(L) + 6B = 3MgB_2 + MgCu_2$ also begins next to the MgCu liquid region. These reactions will cause voids produced at the former location of the Mg atoms.(Figure 3.6(c)). Then the residual Mg melts and spreads to the former place of Mg and ensures the reaction continuing without interruption(Figure 3.6(d)). As a result, the Mg flux mixed with MgCu liquid continues to react with the residual B rapidly. The voids where are formerly Mg atom will appear again in the end(Figure 3.6(e))[39]. We adapt this method, complete mixing of Mg, Cu and B, as our initial approach toward MgB_2 product. However, as the picture suggests, the product is very porous and inhomogeneous. Therefore, we have to think about other mechanism for fabricating MgB_2 .

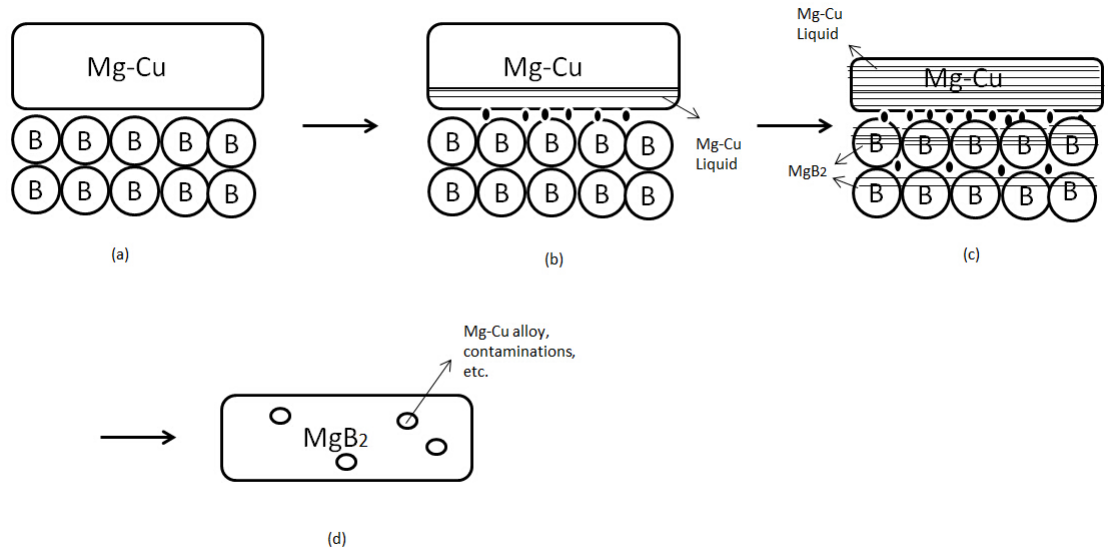


FIGURE 3.7: The sintering model of compressed Cu-doped Mg disc reacting with B disc. (a) starting stage, (b) eutectic reaction stage, (c) Mg melting and liquid-solid reaction stage, (d) final stage.

The method we use to fabricate MgB_2 is to have Mg-Cu mixture and B powders compressed separately into cylindrical discs, and then compress these two disc together.

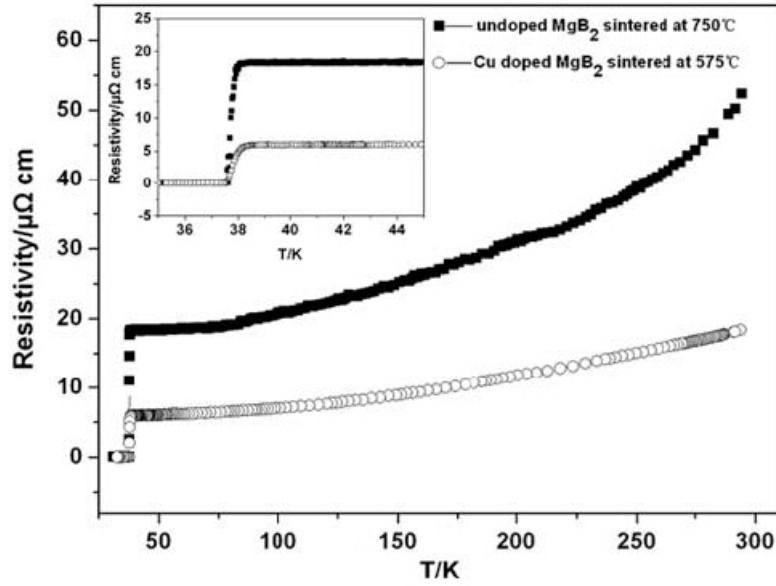


FIGURE 3.8: The temperature dependence of resistivity of the Cu-doped sample and undoped sample[39].

Therefore, we first eliminate the empty spaces between powders before reaction, and we also reduce the effect of different powder size. The mechanism is illustrated in Figure 3.7. For our method, the main difference is that we compress the Mg-Cu mixture into disc to avoid the problem of large Mg powder size. We also compressed B powders, B is very difficult to compress and it remains in powder form at the starting stage(Figure 3.7(a)). Then the eutectic point of Mg-Cu system is reached, and liquid Mg-Cu is formed. At this stage, the liquid Mg-Cu is able to diffuse into the interspaces between B particles(Figure 3.7(b)). When increasing temperature, more Mg-Cu liquid diffuse into B powders and the reaction of $\text{Mg(L)} + 2\text{B} = \text{MgB}_2$ starts to taking place. The Mg-Cu disc starts to reduce in size and the reaction starts from top to bottom(Figure 3.7(c)). Finally, a homogeneous MgB_2 is formed, assuming no decomposition occurs(Figure 3.7(d)). The issue associated with our method is that the after the synthesis of MgB_2 , the formally created MgB_2 will decompose into MgB_4 or Mg_2B_{25} because of the excessive heating, and MgB_2 can be only found at the bottom of the product.

There are several reports about fabrication MgB_2 with Cu doping, and they have achieved doped MgB_2 sample with greater critical current[34, 36–38](Figure 3.8). The experiment process is to have powders with molar ratio of $(\text{Mg}_{1.1}\text{B}_2)_{0.92}\text{Cu}_{0.08}$ pressed into pellet, and then heated at 575°C for 5 hours. The results appears to be successful

and inspiring. So we renovated this approach by using a two-disc melting system, and the experimental procedure and result will be discussed in the next section.

In the end, it is possible for the Cu element to bring issues with cooling the temperature to superconducting region. Since Cu is not a superconductor, the performance of the MgB₂ superconductor may be undermined. Fortunately, Cu can be replaced with Pb, which has transition temperature at $T_c=9.26\text{K}$. Similar experiment of fabricating MgB₂ with Pb doping has been reported successful, and the comparison of products made with different doper can be done in the future to determine which one is more suitable for superconducting RF cavity application[40].

Chapter 4

MgB₂ fabrication with Cu doping

4.1 Experimental tools and techniques

For this section, we discuss the facilities used in the MgB₂ fabrication with Cu doping, as well as the routine of preparing each sample. We will introduce the equipment being used and go through the process of one complete test, meanwhile possible issues will be discussed.

4.1.1 Powder

We start with the powders being used for the experiment. We have ordered magnesium, copper and boron powder with different specifications and from different vendors. As the experiment went on, we realized that the specifications of powders made dramatic influence on the result, and the major specifications are listed in Table 4.1.

TABLE 4.1: Powder Specifications of Mg, B and Cu

Element	Vendor	Size(μm)	Purity	Density(g/ml)
Mg	Sigma-Aldrich	300	99%	1.74
B(crystalline)	Sigma-Aldrich	250	99%(trace metal)	2.56
Cu	GoodFellow	5	99.8%	8.96

Ideally, we would like to have the three powders have similar particle size and then completely mix them before heating, so we could have a homogeneous product of MgB₂. However, the nature of Mg makes it impossible to have its particle size get close to micron level. The minimum particle size for Mg we found is approximately 45 micron from American Element. We tried to reduce the 300 micron Mg powder using the

available pulverizing machine but failed. Mg is known for its malleability, which makes it extremely difficult to reduce its powder size while maintaining high purity.

There are two types of boron powder available on market: amorphous and crystalline. Amorphous boron powder has been reported to be very effective in synthesizing MgB₂ from various literature. For our experiment, we tried boron in crystal form mainly because of its lower cost comparing to amorphous form. The other issue when ordering boron powder is that the purity in most vendors is labeled as trace metal basis. We did XRD analysis for the boron powder and found peaks for carbon and other elements. Also, even though the boron particle is said to have 250 micron particle, the actual particle is a lot smaller than the labeled size. From the electron microscope, we found the largest grain of Boron is around 40 micron, and most of the powder is at micron level.

Unlike B and Mg, Cu is used as catalysis for the experiment. So we would like to have copper powder as tiny as possible. The Cu powder we order accomplish this requirement, because of its small size. However, Cu powder for less than 1 micron(50 nm as the smallest found) is available on market, and that may give better result.

4.1.2 Substrate

Initially, we assume the Mg melts at high temperature first and then reacts with B, and the MgB₂ crystal grows on the substrate as a result. Many methods of fabricating MgB₂ thin film have mentioned such routine[8], even some of them used vaporized Mg for pulsed laser deposition instead[19]. For the best product quality, we would like the MgB₂ to have epitaxial growth on the substrate. MgB₂ has a hexagonal structure, and therefore substrate with a hexagonal lattice at the surface would give better result. For substrate with hexagonal structure, we would like their lattice structure as similar to MgB₂ as possible. Based on the lattice parameter, one can calculate the lattice misfit on planar level(a-a), which is perpendicular to the direction of crystal growth. As the Table 4.2 suggested, AlN and SiC would be very suitable material for the substrate.

Further, besides lattice matching, the reactivity between substrate and thin film also has to be considered. Common oxidized substrates, such as SiO₂ and Al₂O₃, react with Mg at high temperature starting at 600°C with product of MgO, MgB₄ and Mg₂Si. Fortunately, non-oxidized substrates usually do not react with Mg at high temperature, and AlN and SiC are also included as well. Therefore, we conclude that AlN and SiC can be used for our experiment, and we finally choose AlN only based on the cost, even though SiC has the least lattice misfit.

TABLE 4.2: Lists of some substrates with hexagonal structure. The lattice misfit is calculated from a-a parameter comparing to MgB₂[8].

Material	Lattice Parameters(Å)	Lattice misfit to MgB ₂
MgB ₂	a=3.086 c=3.524	0%
Al ₂ O ₃	a=4.770 c=13.04	-23%
TaN	a=5.170 c=2.890	-6.50%
GaN	a=3.190 c=5.198	-3.30%
AlN	a=3.110 c=4.980	-0.80%
Si	a=3.800 c=6.269	-23%
TiB ₂	a=3.028 c=3.228	-1.80%
SiC(4H)	a=3.073 c=10.53	0.42%
SiC(6H)	a=3.081 c=15.12	0.16%

We used AlN substrate provided by MTI corporation. The substrate has square shape and has 50.8mm length and 0.5mm thickness. The substrate has both side polished, and we then cut the substrate into 1cm×1cm small square for further use.

Except the AlN substrate, we also use a BN bar to place the substrate and the sample inside the furnace, since the dimensions of our sample is extremely small comparing to the size of the furnace tube. We use a 12cm×3cm×3cm BN bar to serve as the boat. In the center of the BN bar, we drill a pocket to place the substrate and the sample. There are several advantages of using BN instead of other materials. First, BN does not introduce any other element to the reaction (we have Mg, B, Cu as reactants and Al, N as substrate). Second, BN is easily machinable. After reactions, there are inevitably some contamination attached to the BN boat. However, BN is "chalk" like ceramic and one easily peel off the surface to remove the contamination.

4.1.3 Furnace

We mainly used two types of furnaces provided by Cornell Center for Material Research (CCMR). The two furnaces are LabTemp Tube furnace and Lindberg Tube furnace, and they work almost in the same way except the difference in maximum temperature. Figure 4.1 illustrates the complete setup for LabTemp furnace.

The furnace uses a Al₂O₃ tube with dimensions of 5.08cm diameter and 91.4cm length. Un-reacted sample is first placed at the center of the tube, and then both ends of the tube are connected to gas input and exhaust tank. When heating, there is a constant inert gas flow through the tube to avoid air during reaction. The settings, such as ramp rate, final temperature, heating duration, etc., are programmable and easy to adjust. The furnace is very simple to use, but it does not have any logger for the temperature profile during heating.

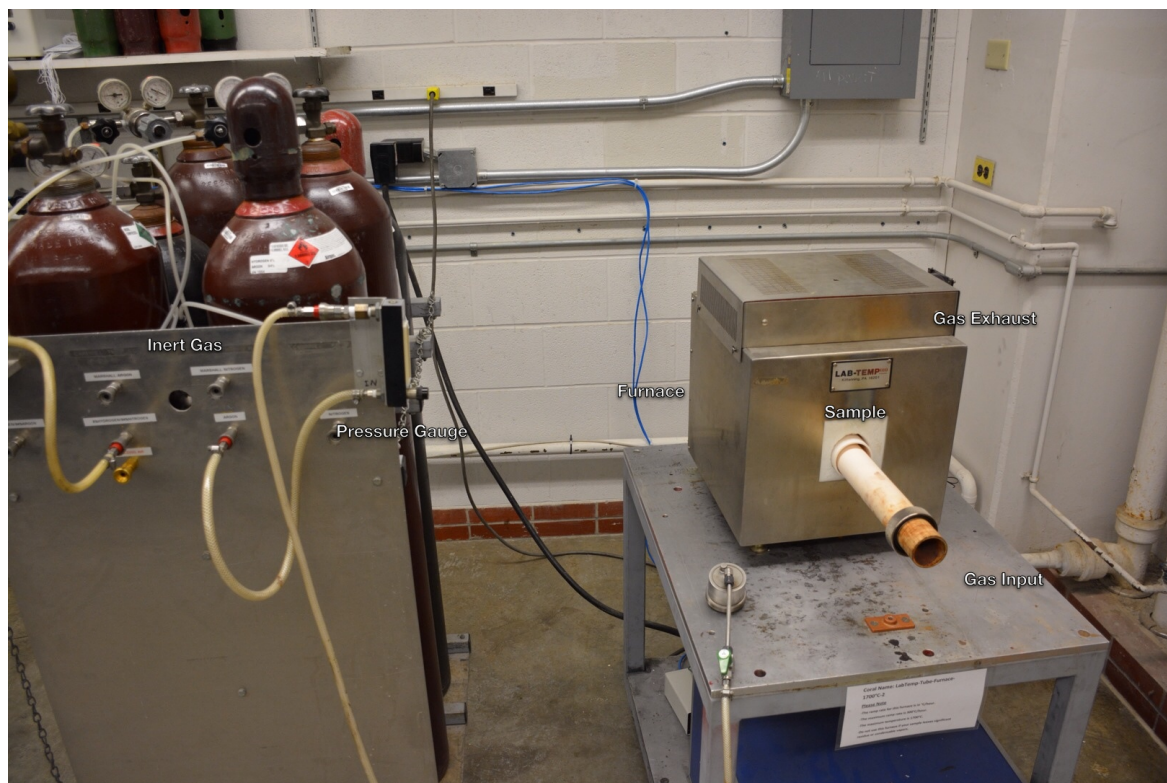


FIGURE 4.1: Complete setup for LabTemp Tube furnace. On the left side there are multiple gas input choices, The furnace has a heating tube with dimensions of 5.08cm diameter and 91.4cm length. The tube used in the experiment is made of Al_2O_3 .

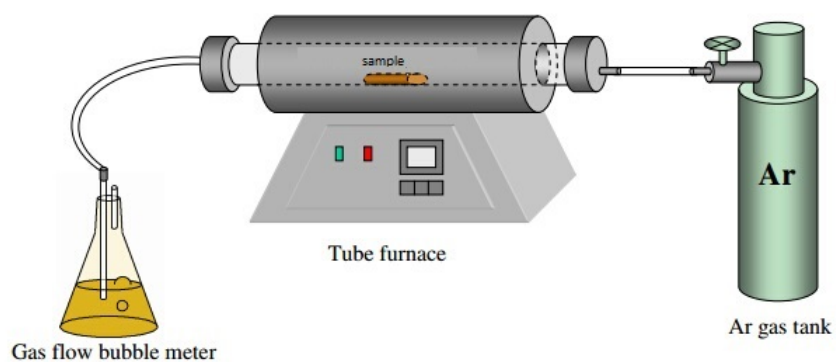


FIGURE 4.2: Schematics of the entire furnace system.

There are several major issues related to this type of furnace. First, it is difficult to tell if the tube is completely air free. Based on the product after heating, there are signs of oxidization and SEM find oxygen during the later analysis. Second, after several experiments, there are some residues inside the furnace, and it is difficult to remove them. Third, there is no external thermal-couple so the readings of the furnace is not completely trustworthy. At last, AlN is theoretically the best material for furnace tube. We use Al₂O₃ mainly for the economical reason, but it is possible that a small amount of oxygen will be released at high temperatures.

4.1.4 Techniques for identifying MgB₂

4.1.4.1 X-ray diffraction

For the sample identification, we mainly use the method of X-ray diffraction(XRD). XRD is used for identifying the atomic or molecular structure of crystal by using X-ray. The incident X-ray beam hit the atoms in the sample and then diffract into many specific directions. By measuring the angle and intensity of the diffracted beam, the crystal structure, chemical bonds and other information can be acquired. The theory of XRD is mainly based on Bragg's law.

$$2d\sin\theta = n\lambda \quad (4.1)$$

The constructive interference determined by Bragg's law results in some high intensities that corresponds to certain incident angles. So the diffraction pattern is a intensity vs. incident angle graph, and the element identification is based on the peaks from the graph. For real application, each crystal produces one unique XRD pattern, and we compare our pattern from the sample to the one from established database to verify the composition of product.

For our sample identification, we use Sintag 2- θ diffractor provided by CCMR. For this type of X-ray diffractor, the sample stays stationary in horizontal direction. The X-ray tube and detector moves simultaneously over an angle of θ . Therefore, the angle between the incident beam and detector becomes 2θ instead. The Sintag diffractor uses copper radiation of characteristic wavelength of $\lambda = 1.5418\text{\AA}$. The X-ray is produced at 40kV voltage and the beam current is 40mA.

4.1.4.2 Scanning electron microscope

For our sample analysis, we have used standard optical microscope as an elementary approach to examine the reaction between Mg and B. But the images from the optical microscope only suggests very little knowledge about the product after reaction, and therefore advanced tools to study the properties of the product are required as the next step. As a result, Scanning electron microscope(SEM) has been used to examine the structural properties and element composition of the sample. SEM is a type of electron microscope that produces images by scanning the sample with focused electron beam. The electron beam can be focused in an extremely narrow region, and producing images with fine resolution($\sim 1\text{nm}$).

SEM can have its signal being produced in multiple ways, which includes secondary electrons, transmitted and back-scattered electrons, characteristic X-rays, etc.. But secondary electron detectors are standard in all SEM, and we will discuss it further. In a SEM, an electron beam is thermionically emitted from a tungsten filament cathode(electron gun) under vacuum. The electron beam, usually carries energy up to 40keV, then passes through a certain number of condenser lens(focusing the beam)and deflection coils(make the beam onto a rectangular area). When the electron beam interacts with the sample, the electrons lose energy by scattering and absorption. The electrons will interact with the atoms in sample within a teardrop-shaped volume which is known as the interaction volume[41]. Within the interaction volume, the energy from the electron beam exchanges with the sample, and it results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. These are the signals coming from the sample, and they can be detected by specialized detectors. The most common way of acquiring image is to process the secondary electrons originated from the sample. These electrons are ejected from k-shell of the specimen atoms and possess low energy comparing to the reflected electrons. The detector receives the secondary electrons and then converts the intensity distribution of electrons into digital image at μm to nm scale[42].

The specific SEM equipment we have used is called LEO 1550 Scanning Electron Microscope. LEO 1550 is capable of resolving $5 - 10\text{nm}$ features, and using X-ray to determine element composition of the sample. The utilities and images captured by LEO 1550 will be demonstrated in the next section.

4.1.5 Sample Preparation

We used several ways of preparing the sample, and the products comes out with dramatic differences. For this section, we will introduce these different methods. For the first method, complete mixing of Mg, Cu and B, we shall discuss its result immediately since the results are not desired. For the next two methods, we shall discuss the results later in detail.

4.1.5.1 Complete mixing of Mg, Cu and B

First, we try to mix Mg, Cu and B together according to the atomic ratio of these elements to have $Mg_1B_2-Cu_{0.05}$. Then the mixture is compressed into a 0.5cm radius 1mm thickness pellet under 10k psi. The pellet is placed in the furnace and conditioned for different temperature and duration(Figure 4.3).

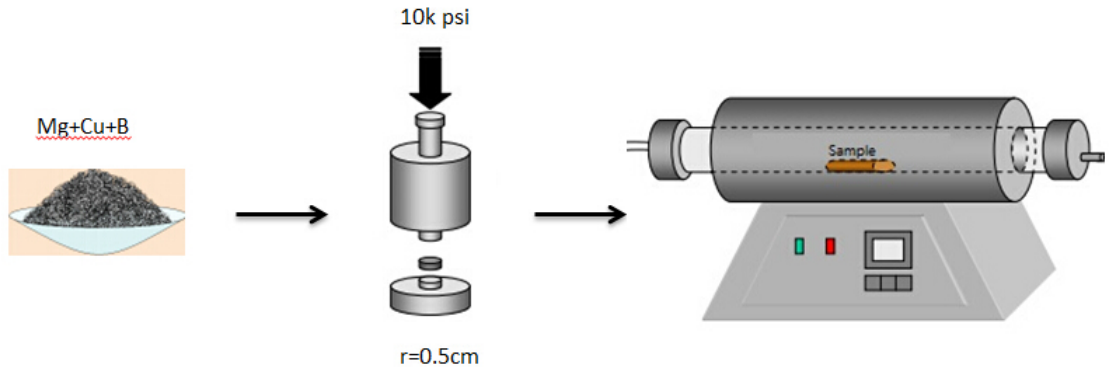


FIGURE 4.3: Steps of complete mixing of Mg, Cu and B for MgB_2 production.

The results using this approach are rather interesting. Initially, the mixture is black due to the tiny particle size of B. After conditioning, the sample shows metallic color in the center of the disc, and as the heating time goes up, the disc becomes completely metallic and no dark area is left. The difference is suggested in Figure 4.4. When the temperature is increased, similar patterns occur as well.

From the XRD analysis for the product, we found Mg, MgB_2 and $CuMg_2$ peaks on the metallic region and B peaks on the outer ring. However, from the SEM, we observe images similar to Figure 4.10, in which there are bulk of untreated B grain and diffusing Mg. So what happens in the furnace is that, the Mg at center is heated to the reacting time first, then the reaction slowly goes out. The diffusing Mg from large Mg powder gradually spread out and changes the color of the disc. So we observe a larger outer

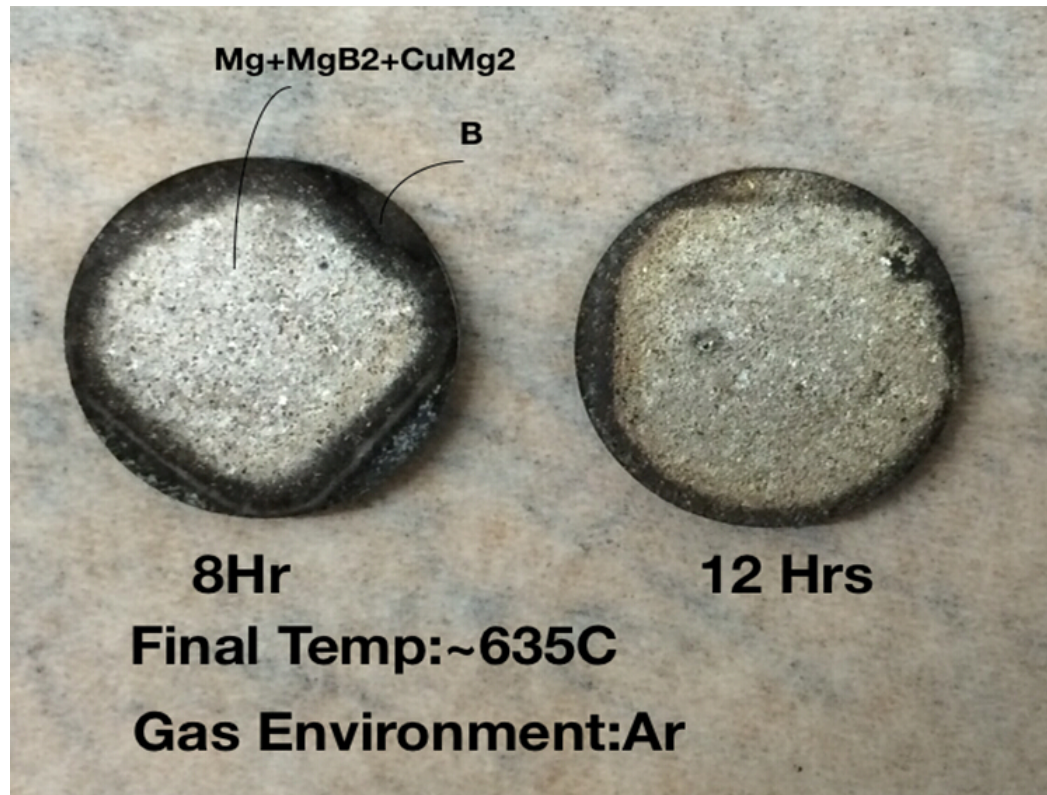


FIGURE 4.4: These are the products using complete mixing heated at 635°C for 8 hours and 12 hours. The dark region is composed of boron, while the metallic part is mainly Mg, MgB_2 and $CuMg_2$. As the heating time goes up, the area of the metallic region increases.

ring on the 8 hour sample, and a thinner one on the 12 hour sample. Also, the product is very inhomogeneous and the reaction is not completely finished even after 12 hours. Moreover, when polishing the product using this method, we found the product is very porous: there are cavities in the product that makes it low quality and can hardly be used for other applications. This is mainly because Mg and B has huge difference in terms of particle size, and the schematic is explained in chapter 3. To avoid such issue, we have to find a way to escape from the limits of Mg grain size, and therefore fabricating high quality MgB_2 .

4.1.5.2 Mg-Cu and B two disc system

Besides the complete mixing of Mg, B and Cu, we also tried to mix Mg with Cu first and compress into disc, and then compress B separately. During the compressing, the mixture of Mg-Cu can be easily formed into a smooth disc. However, B is very difficult to compress and the powders do not bound together. So the result of compressing B powders is a very loose disc. Afterwards, we put the B disc on top of the substrate, the

Mg-Cu mixture is placed on the B disc in the end(Figure 4.5). So from the bottom to top, we have AlN, B and Mg-Cu. Theoretically, the Mg-Cu mixture would melt first, and then react with the B on the bottom. We successfully observed such phenomenon, and found MgB_2 from the product. However, the product has four layers and only a extremely thin layer is our desired product(details in next section).

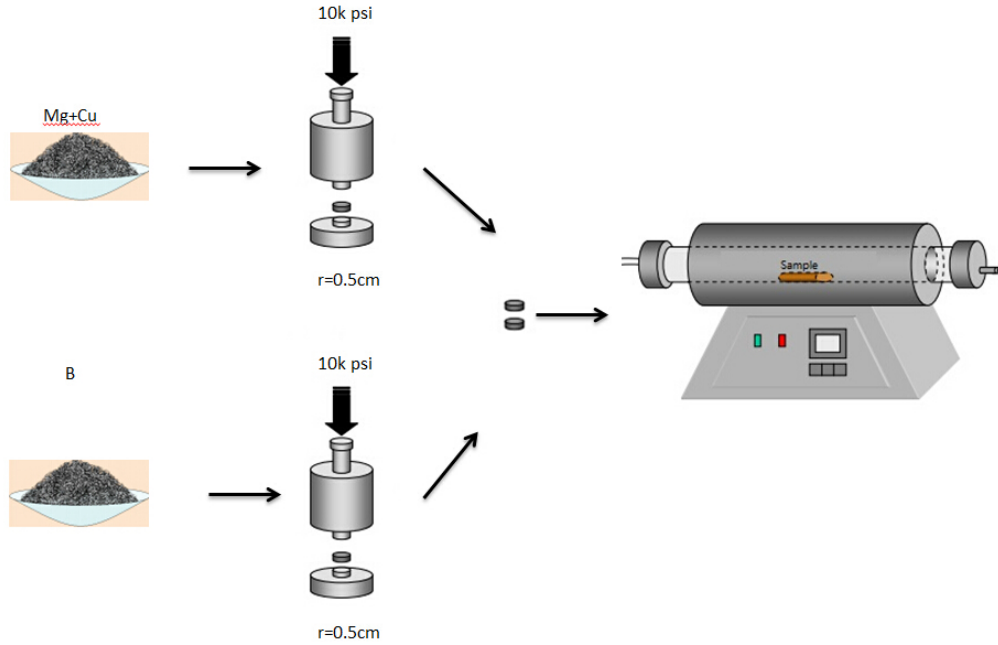


FIGURE 4.5: Steps of preparing Mg-Cu and B two discs for MgB_2 production.

Since the Mg transforms into liquid phase when temperature is above 650°C and this occurs before the reaction happens(or simultaneously), the particle size of Mg will hardly influence the reaction. However, we found the grain size of B also plays a dramatic role during reaction. From SEM, we found large areas of unreacted B grain so the major part of the product is rather similar to the one we found earlier using the method of complete mixing. The improvement for this method is that we find homogeneous MgB_2 layer next to the substrate.

4.1.5.3 Compressed Mg-Cu and B disc

The only difference between this approach and the previous one is that we compress the Mg-Cu and B disc again after the powders are compressed into disc. Unlike the previous compressing, the B powders attach to the Mg and the result is one connected disc even though B powders can still be easily rub off.

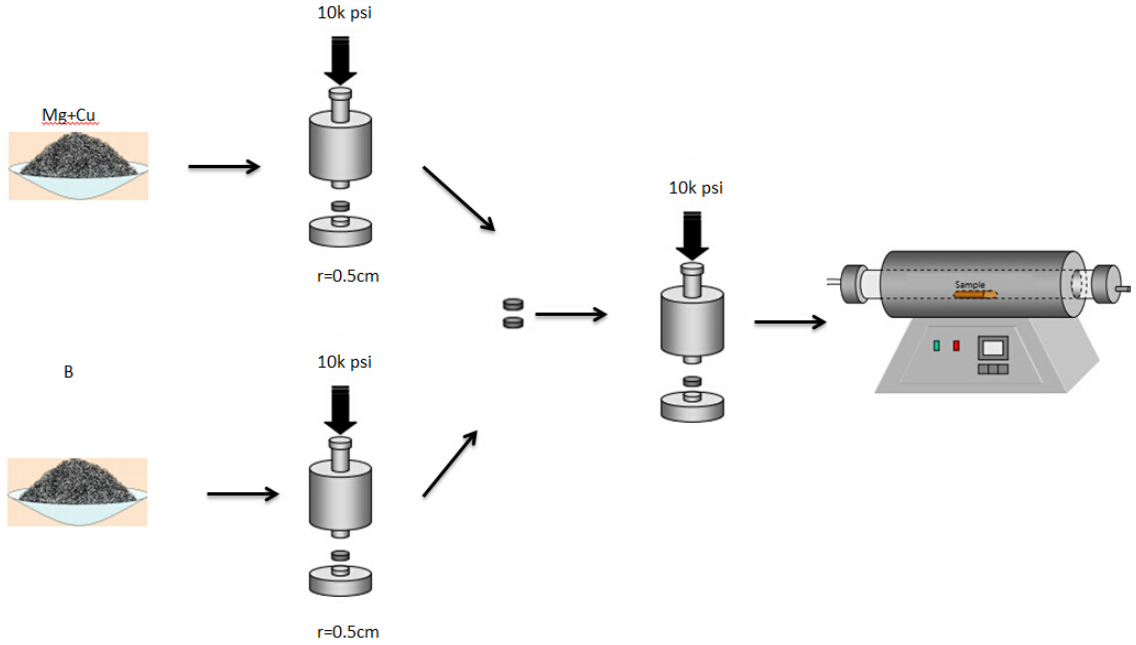


FIGURE 4.6: Steps of sample preparation of compressed $Mg-Cu$ and B disc for MgB_2 production.

From the XRD and SEM analysis, we find that the extra compressing greatly improved the quality of the product. First, we observe crystal structures of the Mg and B compound, even though some MgB_4 and other $Mg-B$ compounds form during the reaction. Second, we observe very high quality and purity MgB_2 during XRD analysis. The details, including XRD and SEM results, will be discussed in the next section.

4.2 Result discussion

4.2.1 $Mg-Cu$ and B two disc system heated at $730^\circ C$ for 12 hours

Using the $Mg-Cu$ and B two disc system, we acquire a product with 4 layers including the substrate AlN . As a summary, this 4-layer sample is prepared using a $Mg-Cu$ mixed disc put onto Boron powder. The two layers are not compressed together. Then this combined sample is placed on a AlN substrate and being heated for 12 hours at $730^\circ C$ in Argon atmosphere. After the sample is taken out from the furnace, the product is tightly bound to the substrate. Then the product, along with the substrate, is cracked into pieces and we can identify four layers using an ordinary optical microscope.

Then XRD has been performed on the top layer of the product. The other layers can hardly be X-ray diffracted because of the thickness. For the XRD test of the product,

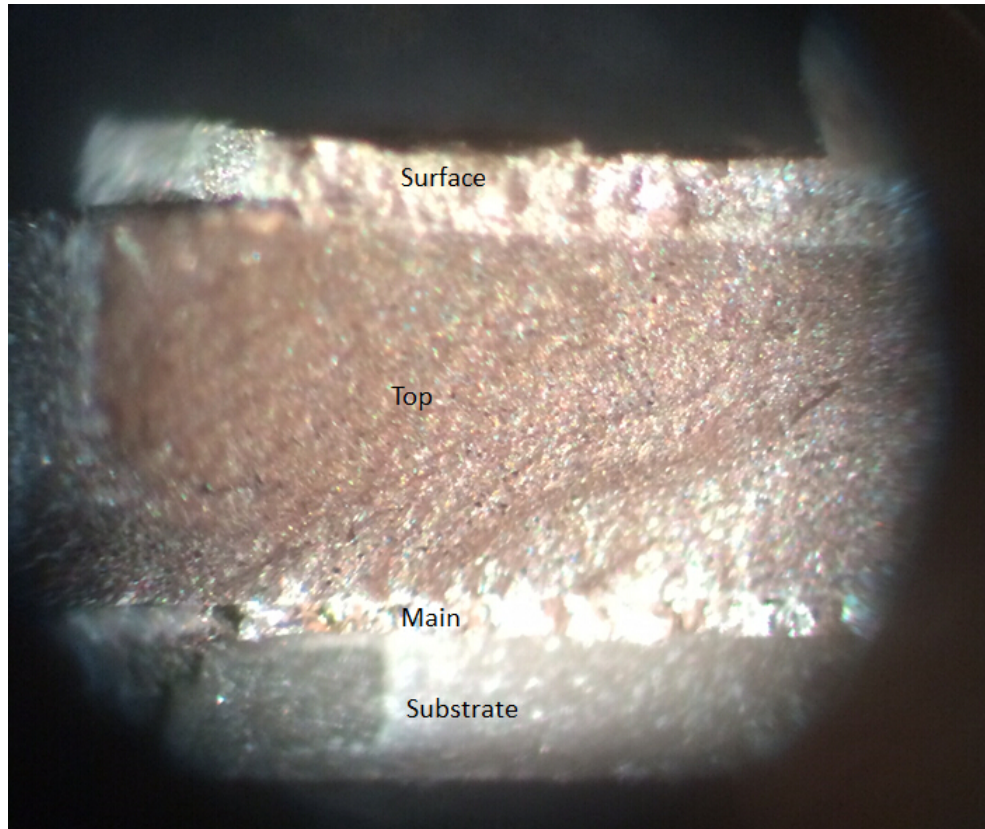


FIGURE 4.7: Optical microscopy of the 4-layer sample. The layers are named as surface, top, main and substrate based on their locations. The substrate is made of AlN.

we try to let the X-ray being focused on the top layer and examine the composition from the result. However, multiple tests have been done using XRD but we can hardly get convincing peaks for MgB_2 or any other chemicals. As shown from the XRD result, we can see that there is a high peak at 42 degrees corresponding to MgB_2 compound. But the intensity of counts is very low(45 counts) comparing to the diffraction result of other specimen(~ 1000 counts or more). As a result, we observe a lot of random peaks coming from the noise into the detector, and the result does not suggest the product contains high percentage of MgB_2 .

The failure to identify the specific composition of the sample lead to the pursuit of more advanced analyzing equipment. We used SEM then to look more closely at the different layers from the product. The overall view of the SEM image is shown in Figure 4.9. The SEM image clearly suggests the differences between the layers and the element composition of each layer can be identified as a function of the SEM setup as well.

Then, we examine the composition of each layer to try to understand the mechanism of reaction between Mg and B. From the surface layer, we observed a majority of magnesium along with a large amount of carbon and oxygen. Since the surface layer is in direct

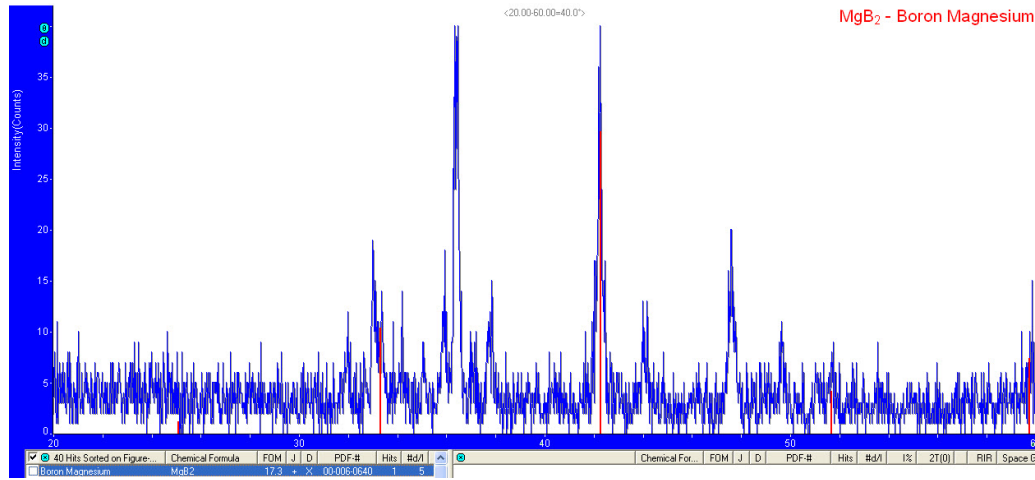


FIGURE 4.8: XRD result for the sample heated at 730°C for 12 hours. The vertical and horizontal axes represent the intensity and two-theta angle respectively. There is a high peak at around 42 degrees, which matches the observed value from other references. The other peaks with lower intensity can be magnesium and copper magnesium. The XRD only scanned angles from 20 to 60 degrees, which is mainly the range for Mg, MgB_2 and Mg_2Cu .

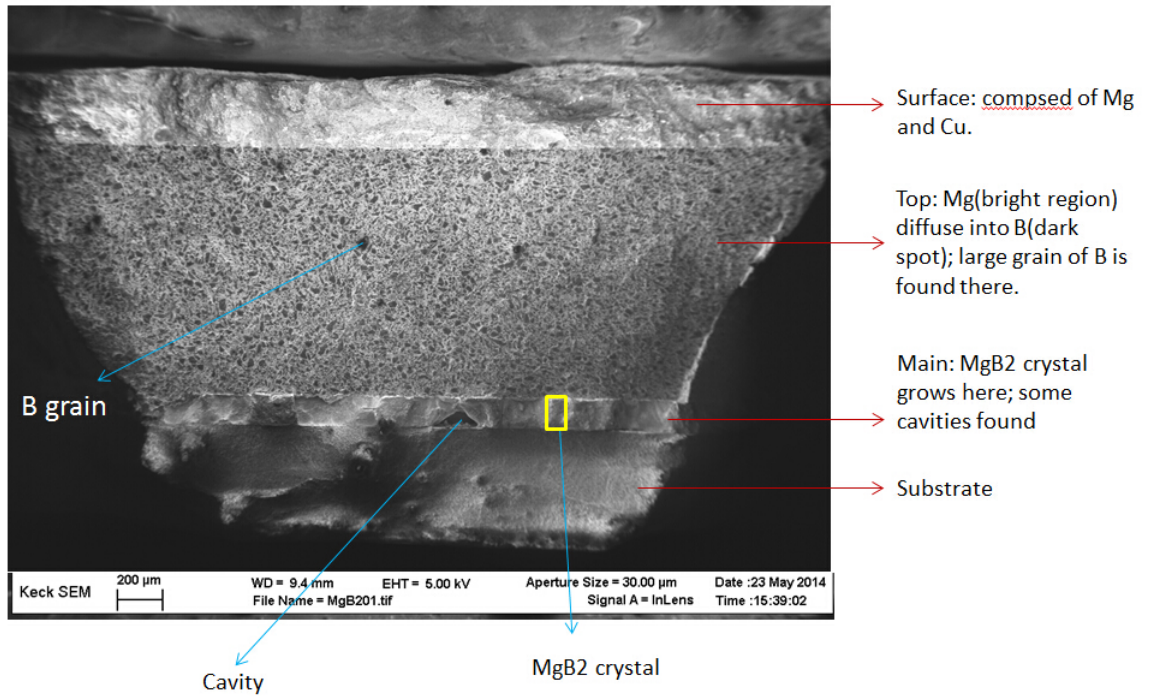


FIGURE 4.9: Overall SEM view of the 4-layer sample. The four layers use the same notations as in Figure 4.7. From the image, we see several large boron grains at the top layer, and some cavities at main layer. The details of each layer will be discussed then. This image is taken using electron voltage at 5keV and aperture size of $30\mu\text{m}$.

contact with argon gas flow and the surrounding, we expect there is a large amount of impurities at this layer. However, it is hard to tell why we have seen a lot of carbon here as we do not use any reactants containing carbon. We believe that these carbon coming from the impurities of the boron powder, and they coming out on the surface during the melting of magnesium. Moreover, the surface layer results from the excessive Mg that does not penetrate through the B disc. During the reaction, Mg diffuses and gradually react with B beneath. There is a certain small amount of Mg does not have enough time to react with B before cooling. Therefore, we observe a surface layer mainly made of Mg.

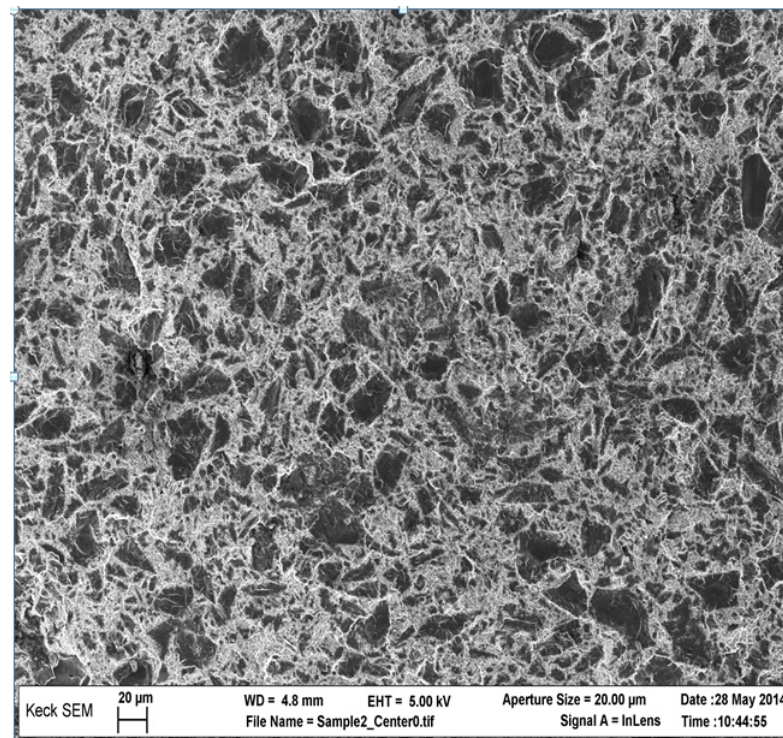


FIGURE 4.10: This is a zoom-in version of top layer comparing to Figure 4.9. The large black area are un-reacted Boron grain, and the light area corresponds to diffused Mg into the Boron powders. We believe that the detected MgB_2 originates from the boundary of the Boron grain and Mg. However, this layer is completely not uniform and we want to have the B and Mg fully react.

It is more interesting to discuss about the top layer, where we found MgB_2 from XRD, and main layer, where MgB_2 is theoretically to be found. The top layer looks like a snapshot of how the Mg diffuses and reacts with B. The SEM image of top layer is shown in Figure: 4.10. Since we detected MgB_2 using XRD at this layer, we hold great enthusiasm while performing SEM on it. However, we see many random large dark grain coming from the SEM image of this layer and we do not observe any crystal structure. Then, we performed the X-ray analysis to this layer and the result suggests this layer is mainly made of boron with a small percent of Mg, C, O and Cu. The X-ray identification

of each element is given in Figure 4.11. Several X-ray tests has been performed coming out with very similar results: there is a large amount of boron at this layer and it does not completely react with the magnesium diffused at this layer.

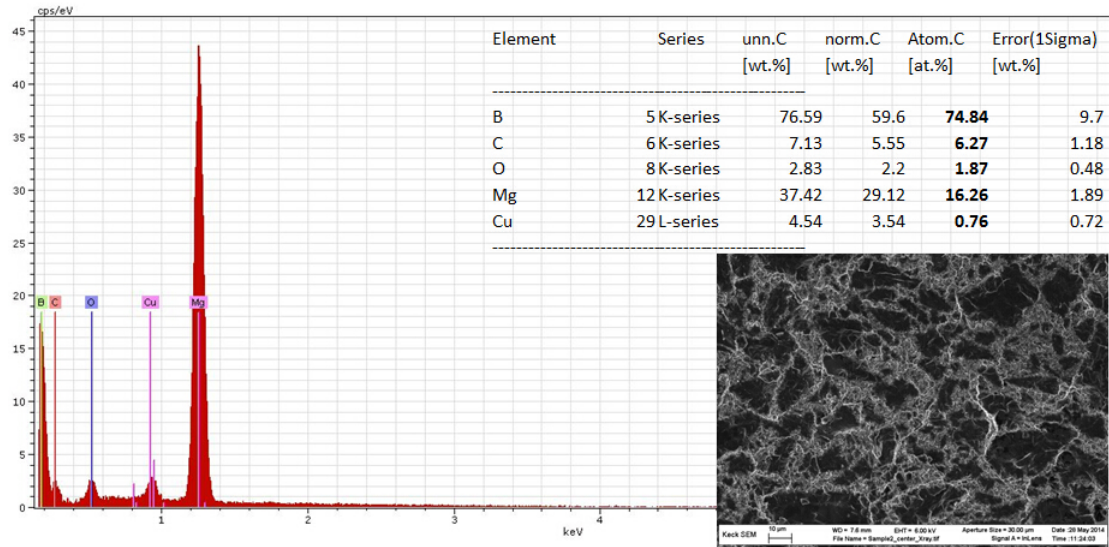


FIGURE 4.11: X-ray identification of each element in top layer. The peaks are identified elements from the software, and the atomic percentage of each element is highlighted in the table at column 5. The image at right-bottom corner is the area being examined using X-ray. The large black area in the image can well explain the large percent of Boron from the sample.

Furthermore, one X-ray mapping has been performed, and it validates the idea that the large dark grain observed by SEM is indeed boron. The result of X-ray mapping is shown in Figure 4.12. The image after X-ray mapping clearly indicates the composition of different regions as seen from the SEM. Therefore, it is very reasonable if we look back at the XRD result for this layer. Since the XRD result is the integration of a large area, the MgB_2 detected could be the reacted Mg with B at the border of the large B grain. The random peaks can be Mg, B and C at this layer since there are many peaks for these elements in XRD. From the discussion above, we can see that it is ideal to reduce the grain size of Boron powder and get the Mg fully reacted. The result from the main layer further supports this way of improvement.

Finally, we need to discuss about the main layer from the product. Initially, we do expect to see this layer because MgB_2 shall grow on AlN substrate because of their similar atomic structure, but we can not analyze the composition of it using XRD because of the limitation of the equipment. However, SEM enables us to look directly at this very thin layer and analyze its structure(see Figure 4.13). This layer is significantly different from the top layer we talked earlier. We do not observe any large bulk of boron grain

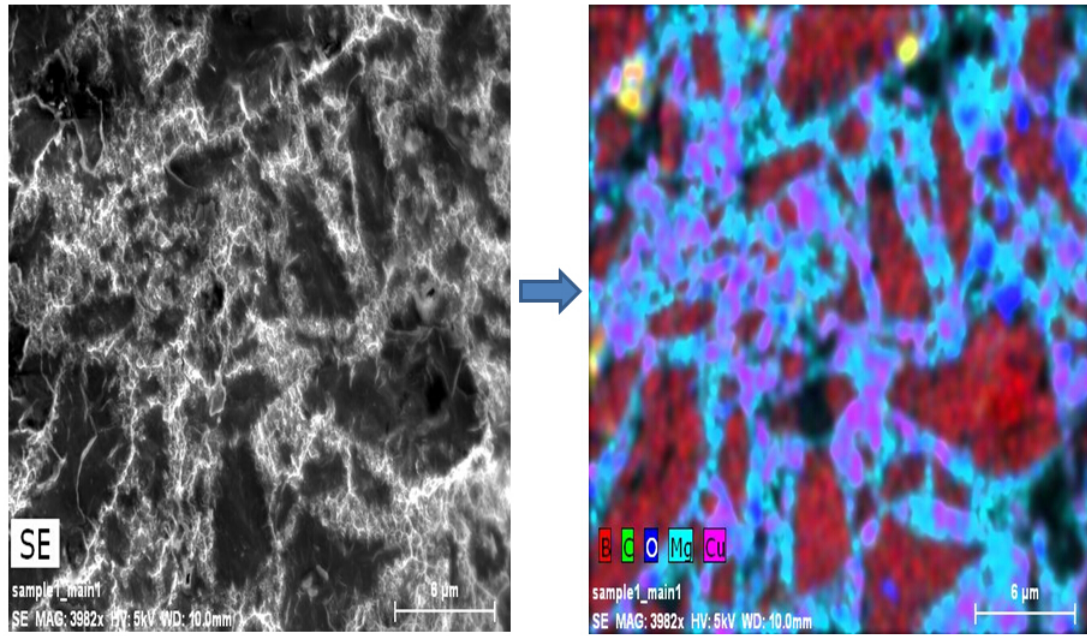


FIGURE 4.12: X-ray mapping of one area of the top layer. The left image is the original one taken from SEM, and the right one is the result after X-ray mapping. The different colors suggest each elements. The large red area in right are indeed boron, and the cyan and pink region are Mg and Cu.

or diffused metal. As what we have expected, we see the layer actually possesses crystal structures.

Then we repeat the same procedure as what we have done for the top layer. The X-ray identification is shown in Figure 4.14, and we find that this layer is mainly composed of Mg and B. More importantly, we observe the atomic ratio between B and Mg to be 1.5 to 1, which is very close to the theoretical value of 2 to 1. From the percentage of these elements, we believe that the Boron powder with small grain size falls to the bottom more easily during the melting of magnesium. Then melted magnesium reacts with boron with suited grain size and forms crystal on AlN substrate. At the same time, for the boron powder with large grain size, they stay on the top layer and let the melted Mg flow through.

We used the X-ray mapping for the main layer as well. The result is showing a uniform distribution of all elements at the examined location. The X-ray mapping of the main layer is shown in Figure 4.15, and the mapping of each individual element is shown in Figure 4.16. From the image, we conclude that compound of Mg and B is created at this layer. Since the ratio of B to Mg is 1.5 to 1, there should not be a significant amount of MgB_4 or other compounds being created. However, comparing to the top layer, the main layer is extremely thin. We would like to increase the thickness of this layer, so

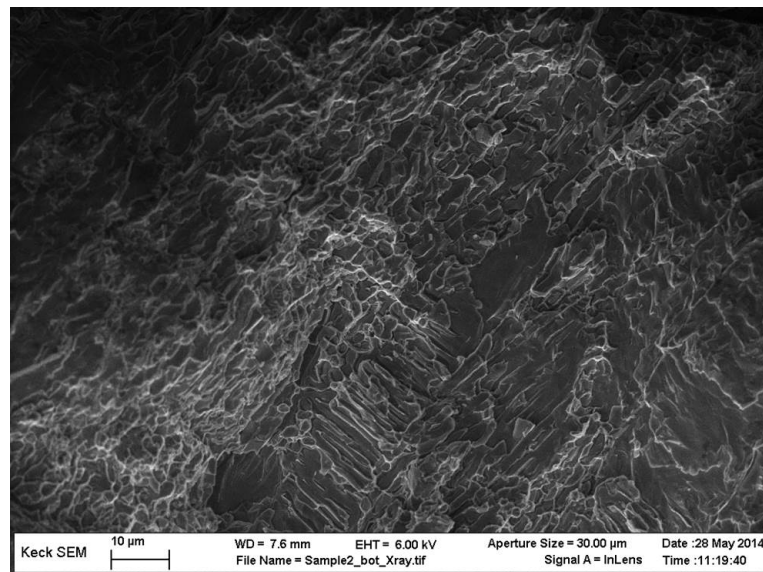


FIGURE 4.13: SEM image of the main layer of the product. From the image, we do not see any large grain of the boron, and we observe some crystal structure formed at this layer.

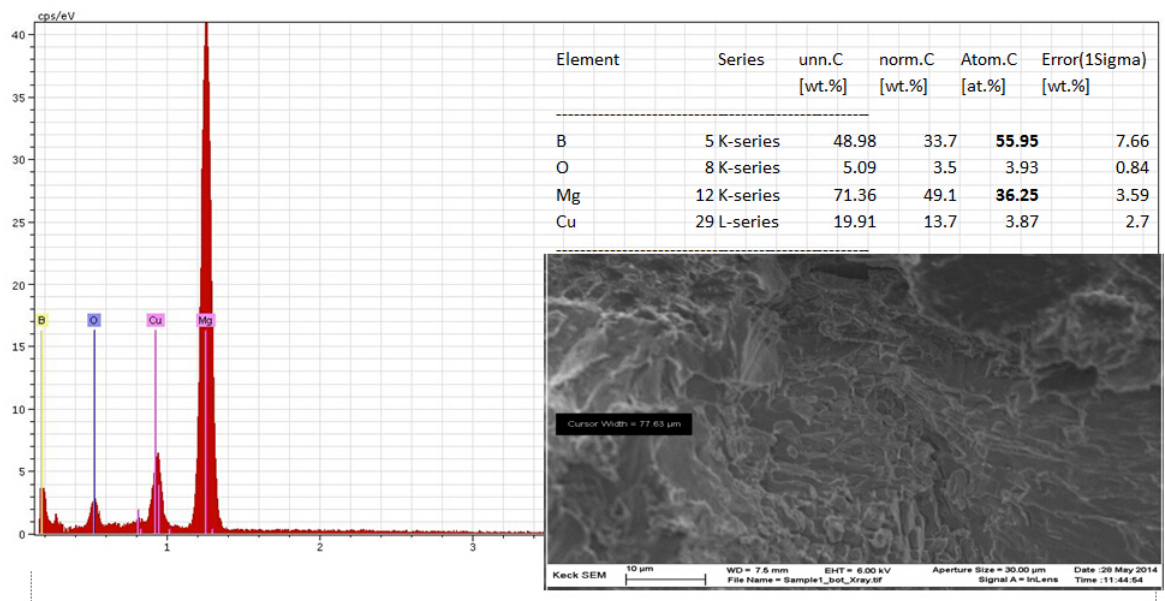


FIGURE 4.14: X-ray identification of each element in main layer. We see the majority of this layer is composed of B and Mg, and they have a B to Mg atomic ratio of 1.5:1. We believe there are some Mg diffused to the bottom but not enough B to react with. The theoretical ratio of these two elements should be 2:1. There is a small amount of oxygen and copper found here as well.

it can be used in real applications. As stated before, we believe the grain size of boron limits the reaction of these two elements based on the temperature and reacting time. In the end, we observe some small cavities at this layer, and the element surrounding the cavities are mainly magnesium. We think at some locations, there are not enough small-grain size boron to react, so that the magnesium will simply flow through the boron and forms teardrop shapes connecting to the substrate. Therefore the cavities are created, and we need to remove them in order to have an applicable MgB_2 crystal layer.

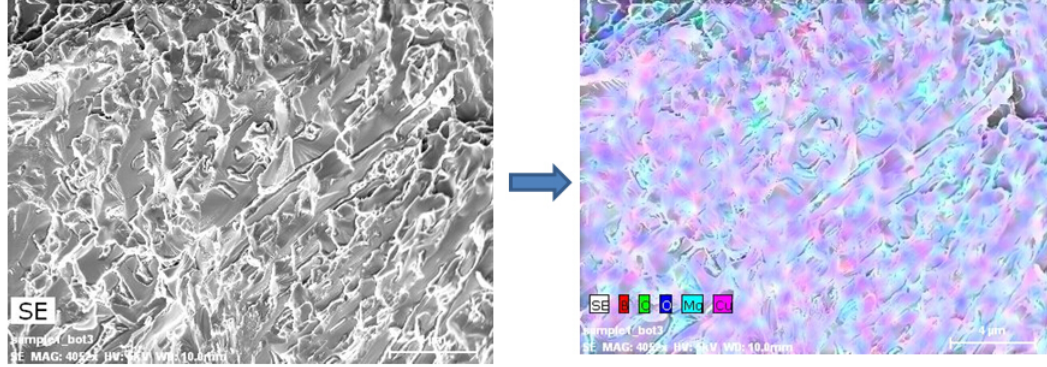


FIGURE 4.15: X-ray mapping of one area of the main layer. From the right image, we can see a uniform distribution of elements at this layer.

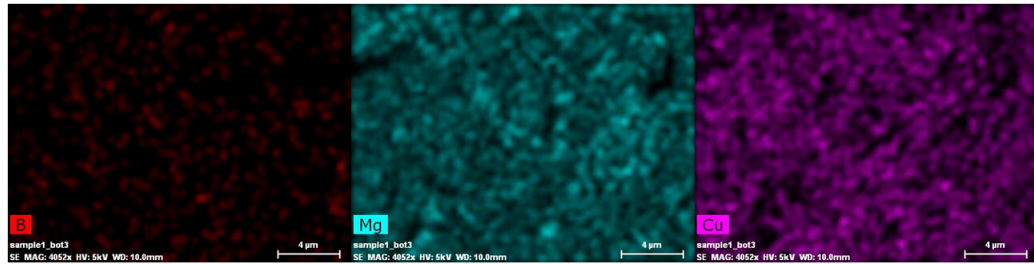


FIGURE 4.16: These are the images for boron, magnesium and copper element separately. We see the elements are spread evenly across the image.

In conclusion, the 4-layer sample shows what we expect before the experiment. From the surface layer, we see part of the Mg-Cu mixture diffuses into B while some unreacted and remain at top. From the top layer, we observe the pattern of diffusion. Since the B powder can hardly be compressed, there are many interspaces for the Mg-Cu to penetrate. Meanwhile, on the edge of Mg diffusion, B reacts with Mg forming MgB_2 . At last, we see MgB_2 crystal growth on the substrate. We believe when Mg reaches the substrate, they react with the B on top and having MgB_2 crystal forming on the substrate.

4.2.2 Compressed Mg-Cu and B disc

From previous experimental result, we would like remove the top layer or reduce its size at least. One thing that we can not do while preparing the sample for the previous test is to make an extra compressing of the two discs, because the unbounded B powders would fell off and damage the facility. Alternative approach is found afterwards and the two discs could be compressed again under 10k psi. After the extra compressing, most of the B powders attach to the Mg disc and the final disc has a solid shape(B powders does not go away easily). Then the product is placed in the furnace at different final temperatures(800°C, 900°C, 1000°C and 1100°C) for 12 hours. The results suggest that the product at 800°C and 900°C demonstrate the best quality of MgB₂ product. However, we believe that 800°C is still too high and the MgB₂ product decompose into MgB₄ at such high temperature. So the experiments at lower temperature, such as 600°C needs to be done,

Similar to the previous product analysis, we will focus on the XRD and SEM result for the product, and for this section, we will mainly talk about the 900°C sample(results from 800°C sample looks very similar), and briefly demonstrate the product at extremely high temperatures. Overall, before heating, the compressed Mg-Cu-B disc has a clear boundary between B and Mg-Cu mixture based on the color of these elements. Afterwards, the boundary disappears and the product is completely black. The only thing interesting is that on the place where the sample in contact with the AlN substrate, we found a greenish color which is completely different from other part of the product(Figure 4.17). Besides, after the heating, the originally attached two layers sep-



FIGURE 4.17: Visual image of the bottom of the 900°C sample. For the products at higher temperatures, or even different parts under the same temperature, the color is completely black. But from this one, we observe some interesting color change.

arated, and the metallic color Mg-Cu layer becomes black as well. This suggests the reaction between Mg and B at 900°C, but for the higher temperatures, the products are still bounded into one single disc. Therefore, for the 900°C sample, we examined the two layers of the product separately(namely, top and bottom), and we will start with the XRD analysis first.

The XRD result for the bottom layer(the colored region) was very inspiring. The result is demonstrated in Figure 4.18. As from the XRD pattern, MgB_2 has the greatest intensity among all other possible compounds. There are some other peaks in the XRD pattern, and from the analysis, they are mainly CuO and Mg_2B_{25} . CuO is possibly coming from the oxidization after taking out the sample, and Mg_2B_{25} is the product of decomposition of MgB_2 at high temperature. The XRD result gives very reasonable result for the possible composition after the reaction.

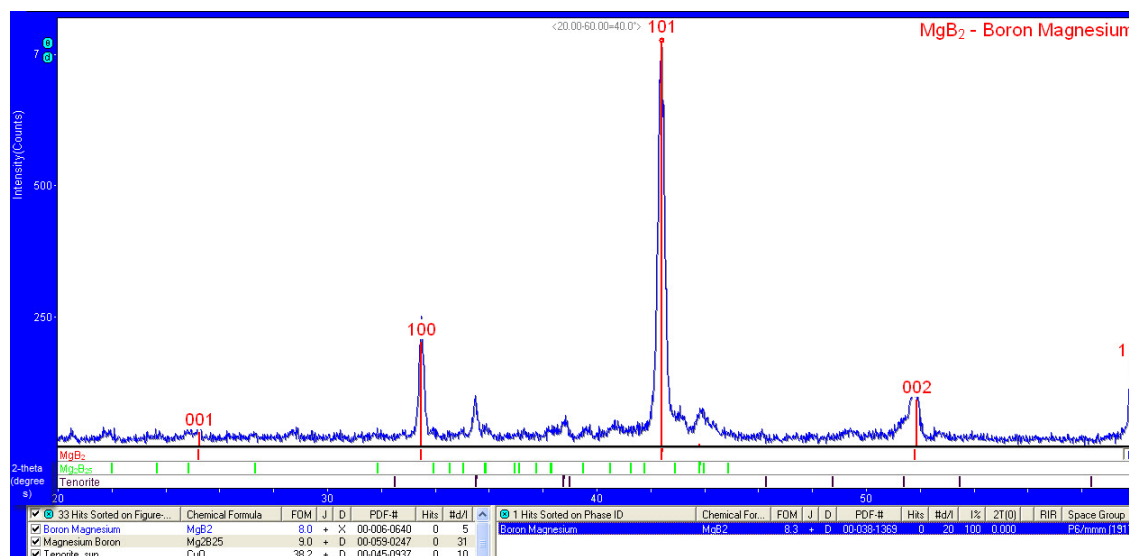


FIGURE 4.18: XRD result for the bottom layer of the compressed disc. The result has very sharp peaks for MgB_2 . The other existing peaks are mainly CuO and Mg_2B_{25} .

However, comparing to the bottom layer, the top layer shows great difference. The result is demonstrated in Figure 4.19. There is no dominating material that shows great intensity comparing to others. There are many peaks for the sample and they correspond to MgB_2 , CuO, MgB_4 , Mg_2B_{25} and C. The discovery of Mg_2B_{25} validates the temperature is too high and the product of MgB_2 . The other thing we found is that the decomposition starts from the top of the sample, and then gradually going to the bottom. The dilemma happens here, since if we go to high temperature, the product of MgB_2 decomposes, but if keep the temperature low, there will no be enough reaction or the heating duration will be dramatically prolonged.

Then we used SEM to look at the sample. From the microscope, we found very nice crystal structure for all the products independent of the temperature setting. Figure 4.20 is the image we have for 900°C, and the structure of other products looks rather similar to this one. So there is not much knowledge we can learn only based on the structural looking of the product. However, we can still use the X-ray mapping from the SEM to further analyze the product.

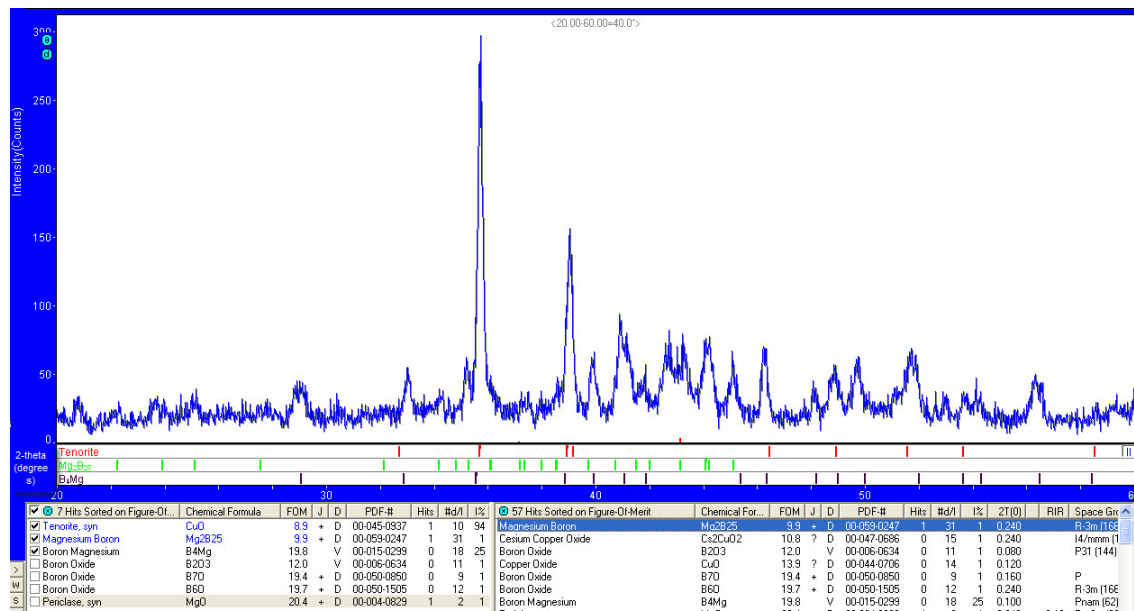


FIGURE 4.19: XRD result for the top layer of the compressed disc. The result has many sharp peaks for MgB_2 , CuO, MgB_4 , Mg_2B_{25} and MgO. Even though the peaks for MgB_2 are found, the product has very low purity and many unwanted compounds.

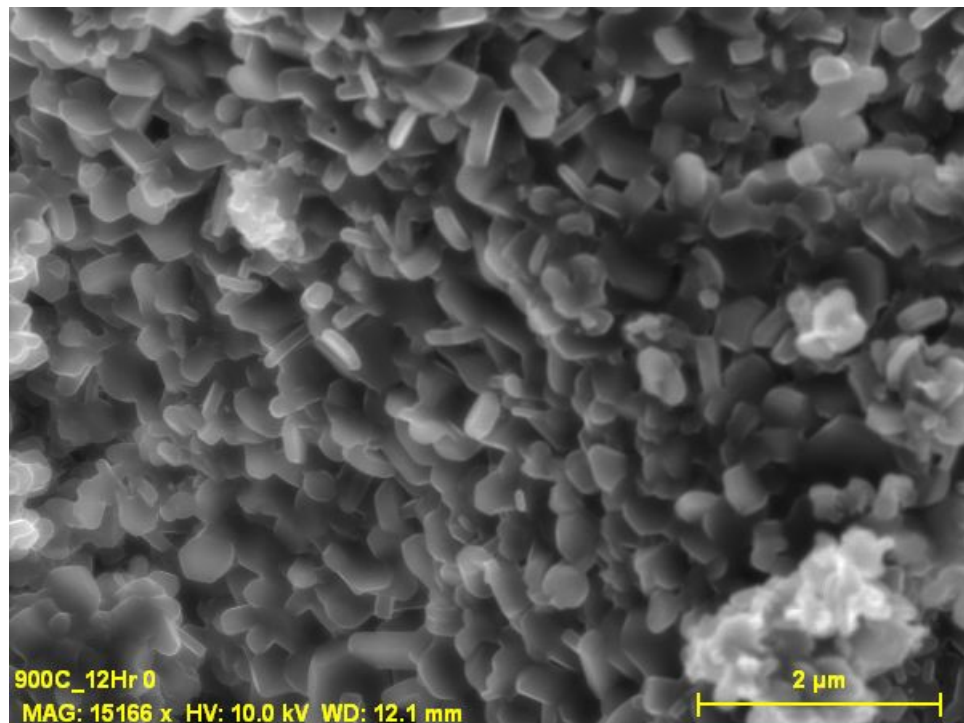


FIGURE 4.20: SEM image of bottom layer of the compressed disc. The result suggests very nicely formed crystal structure of MgB_2 . This is the first time we observe fine crystal structure of Mg-B compounds.

The X-ray analysis from SEM is concluded in Figure 4.21. The X-ray analysis shows that the ratio between Mg and B is 1 to 2.5. This is smaller to the theoretical value of 1 to 2 mainly because of the decomposition into MgB_4 or other compounds. Also, we found very small amount of oxygen and copper from the result, but no other contaminations. This X-ray analysis validates the XRD result we have earlier. The mixture of MgB_2 and other Mg-B compounds result in the formation of $Mg_1B_{2.5}$ according to the X-ray, and the small amount of Cu and O reflects the peaks we found for CuO on XRD. Therefore, based on the results from SEM and XRD, we can conclude that that bottom layer of the compressed product is in high purity of MgB_2 . The issues for this layer are the oxidization of copper and the decomposition of MgB_2 . Experiments on lower temperatures are necessary in order to eliminate all these problems.

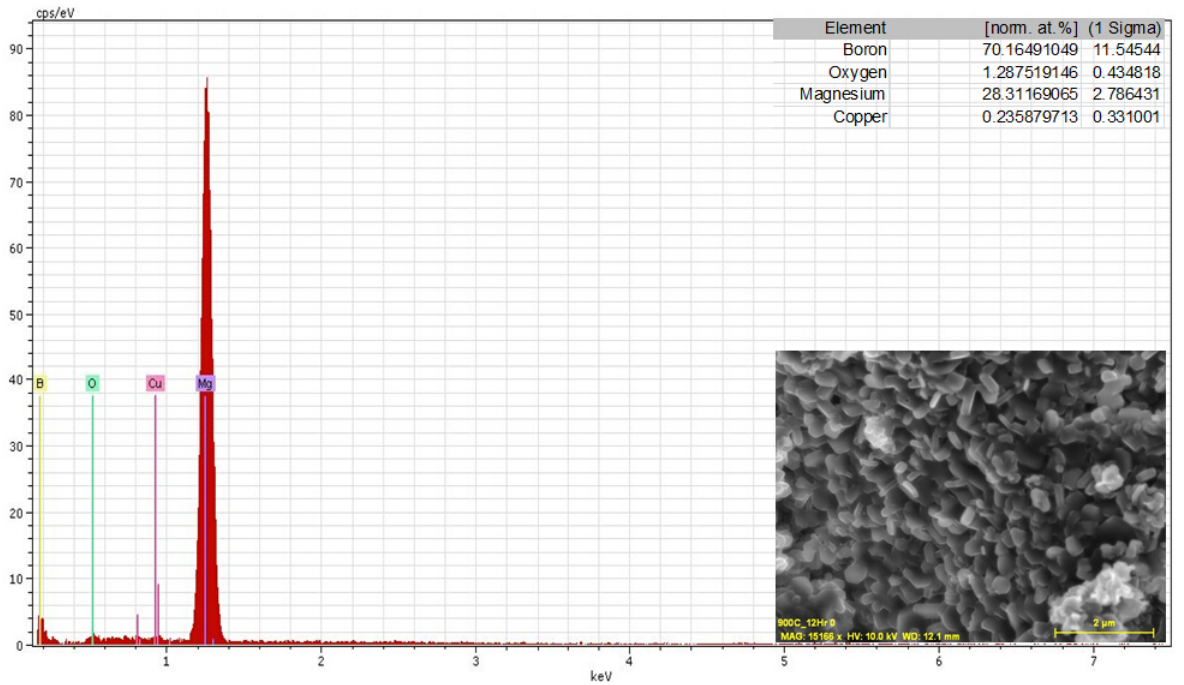


FIGURE 4.21: X-ray analysis of the selected area on the bottom layer. The element identification shows that the Mg to B ratio is 28% to 70%, which is close to the ideal value of 1 to 2. There is no many contamination according to the X-ray identification.

In the end, we did X-ray mapping of the each individual element for the bottom layer. The result shows uniform distribution of the elements, except those regions having cavities and appears to be black in Figure 4.22. This further confirms the success synthesis of MgB_2 . The problem as shown from the X-ray mapping, is that there some cavities that may hurt the properties of the superconductor. Hot-compressing can be used to possibly remove these cavities during sample preparation.

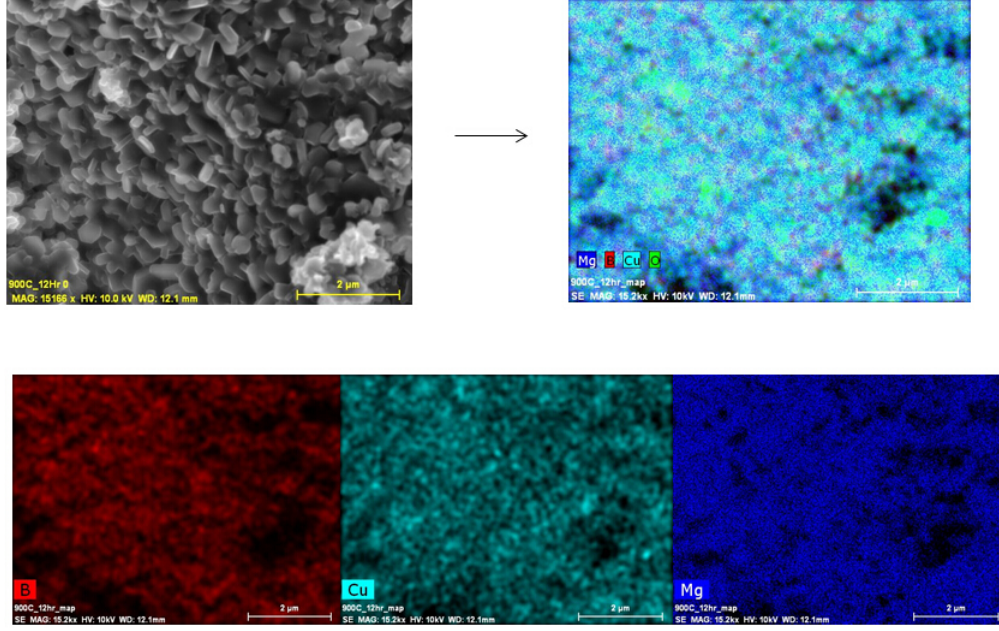


FIGURE 4.22: X-ray mapping of the bottom layer. The elements are uniformly distributed among all the region except those areas having cavity (dark region in the picture).

For the samples heated at higher temperatures, we mainly observe large amount of MgB_4 as the product. So the Mg-Cu and B reacts and forms MgB_2 in the beginning. Then because of the high temperature and long heating duration, MgB_2 decomposes into MgB_4 and Mg_2B_{25} . For the sample heated at 800°C we observe very similar results as from the 900°C sample. Later, we cut the two samples (800°C and 900°C) and measure the thickness of the MgB_2 layer on the bottom using the SEM. For the 900°C sample, the thickness is found to be 0.012mm, and the 800°C sample a thickness of 0.051mm. Therefore, lowering the temperature is able to result in less decomposition of MgB_2 into other compounds. After the heating, the product has a thickness of around 1mm. So it is still possible to increase the thickness of MgB_2 layer by either lowering the temperature or reducing the reaction time. These tests are very good next steps to work on in order to fully understand the diffusion mechanism and form thick layer of MgB_2 .

Chapter 5

Superconducting test, errors and outlook

5.1 Introduction

As from last section, we have successfully fabricated MgB_2 sample using compressed Mg and B disc. We have confirmed the structure and composition of our product using XRD and SEM. Then, it is natural to perform superconducting test on the sample to know the transition temperature of the sample and verify its superconducting property. For this section, we will show the result of resistance measurement at low temperatures. The resistance measurement indeed indicate the superconductivity of our sample. Then, we will discuss some errors and difficulties during the experiment, so whoever may use our synthesis method later should avoid these errors. In the end, we would like to talk briefly about the possibility and issues regarding large-scale application, namely the superconducting cavity. There are still a lot of hidden problems that we may not realize at this moment, but from the process and result of current synthesis, it is very possible to build a superconducting cavity using this method.

5.2 MgB_2 superconducting test

In last section, we described our journey to the successful synthesis of MgB_2 , and in the end, we used both XRD and SEM to verify the composition of our product. The XRD and SEM actually showed very delightful result, and we have observed nice crystal structure after the reaction of Mg and B disc. Then, our final step to test the quality of our sample is to have a superconducting test and find out the critical temperature. From

other references, we have seen that different fabrication method will lead to different critical temperature of the MgB_2 product. The reported critical temperature is found to be from 35K to 39K based on different method. The established value of MgB_2 critical temperature is 39K, which sets the standard for high quality MgB_2 .

In this section, we performed a resistance measurement on our sample using Quantum Design Physical Property Measurement System (PPMS) provided by CCMR. Due to timeliness, we only measured the critical temperature of our sample, and we did not have any insight on the critical current or field. However, the critical temperature we find is very close to the established value of 39K, and we shall describe the superconducting test in the following. The PPMS consist of a 9 Tesla superconducting magnet

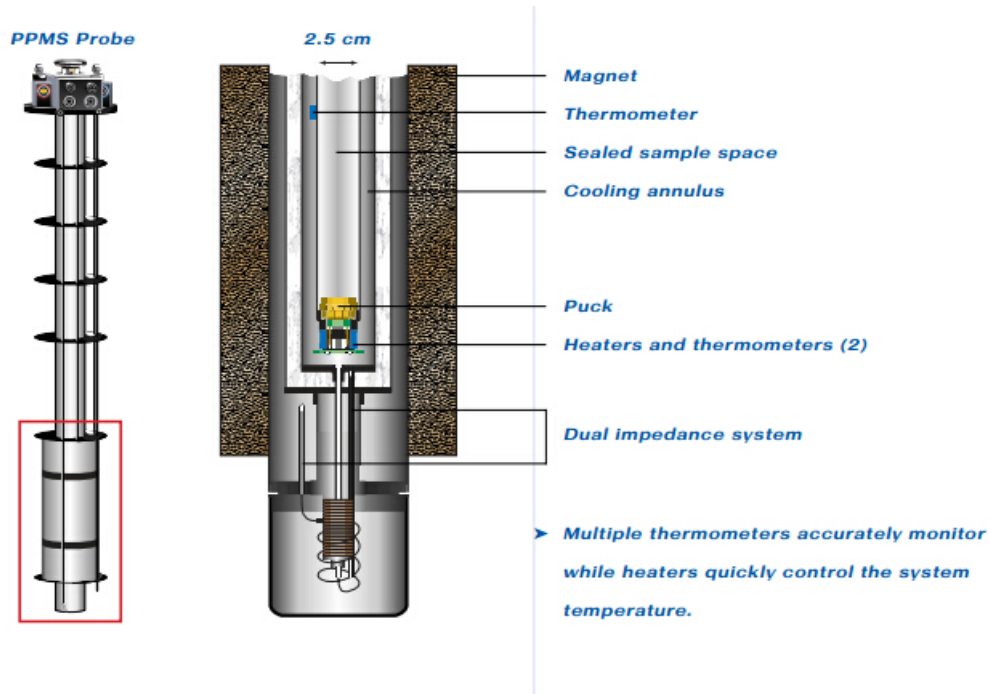


FIGURE 5.1: This figure illustrate the basic design of the PPMS system. Sample is loaded on the puck and placed in the sealed sample space. Temperature and magnetic field is controlled from outside terminal.

in a helium dewar with sample temperature range of 1.9-400K. The PPMS is able to perform a multitude of measurements, such as resistivity, AC transport, and magnetic susceptibility. For our purpose, we only use the resistivity option and determine the critical temperature based on the resistivity measurements. The resistivity option is used for making basic DC resistance measurements by applying a current and measuring the resulting voltage. If desired, resistance of the sample can also be measured using AC, which is probably necessary for the application of cavity. The basic design is suggested in Figure 5.1 and sample chamber is suggested in Figure 5.2. The resistivity option of PPMS performs a 4-point resistance measurement on up to three channels at a time. We

used only one channel at this moment to avoid any complexity associated with the device. The sample is then prepared to fit the puck with recessed area of $11.6\text{mm} \times 13.6\text{mm}$, and the puck has pre-mapped pads for current and voltage measurements. An insulating and adhesive layer is needed between the base of the puck and the sample. Electrical contact between the sample and the channel input pads is made using four spring-loaded press golden pins. In fact, two of the four pins are used for current measurements and two for voltage. The connection between sample and channel input can be tested in advance of insertion into PPMS by ohm meter.

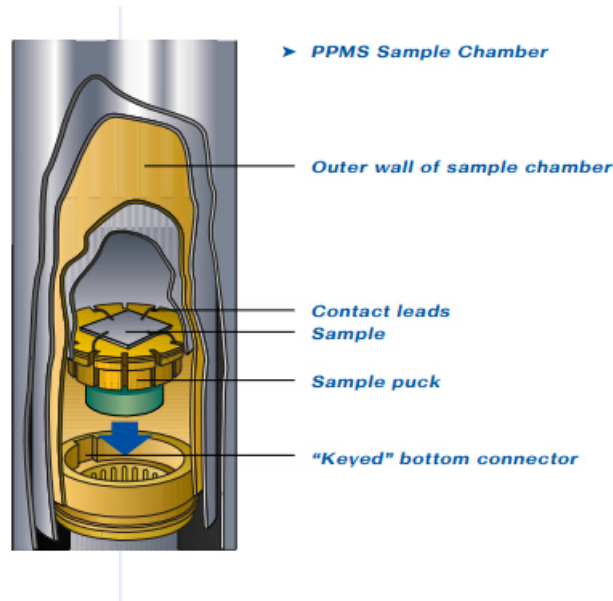


FIGURE 5.2: This figure illustrate the design of the sample chamber and the puck. Sample is prepared to fit on the puck, and then placed on the "keyed" bottom connector, which gathers information of the sample.

For our measurement, we cut the sample first to fit in the resistivity puck. During the sample preparation, we find it is very difficult to machine the sample into desired shape, and the sample is not as brittle as it seems. Then we attached the four-pin to the sample and measured the resistance with a hand Ohm meter. The separation of the inner two pins are 5mm and outer two pins are 10mm. The ohm meter reads $2.5m\Omega$ and $4.2m\Omega$ for the inner and outer pin combination respectively. As a reference, the resistance measured later by the device corresponds to the resistance between the inner two pins. The reading suggests the sample is conducting well at room temperature. Then we inserted the puck into the PPMS, and starting the resistance measurements at low temperatures. We use the samples prepared by compressed Mg and B disc heated at 800°C and 900°C for 12 hours. The results of resistance(between the inner two pins) measurements of the two samples are shown in Figure 5.3 and Figure 5.4.

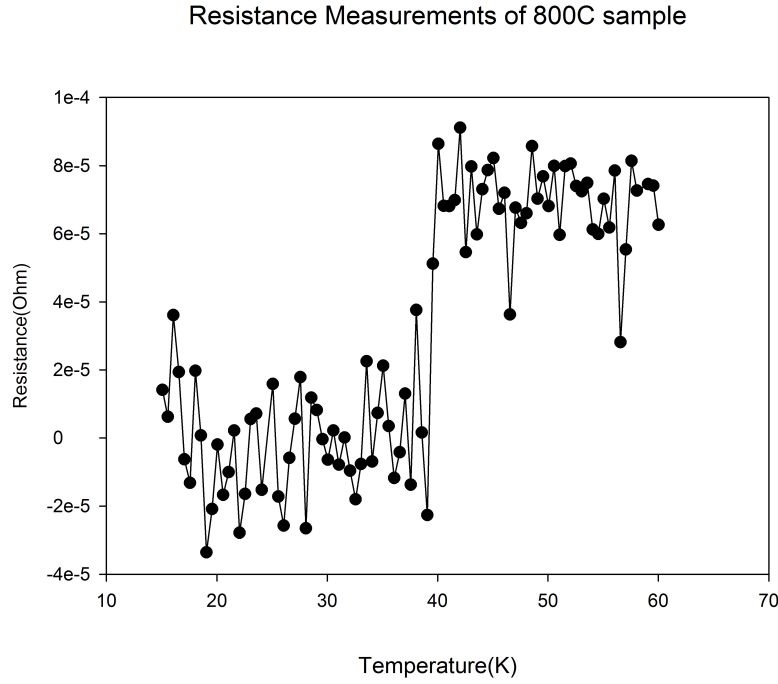


FIGURE 5.3: In this figure, we measure the 800°C sample’s resistance at temperature range of 15K to 60K. The measurements are performed at each 0.5K increment starting at 15K. The measurements at around 0Ω are largely due to noise, since there are negative readings for resistance. However, a clear transition of resistance can be observed at around 39K(0 to $5 \times 10^{-5}\Omega$). Even though the figure is rather noisy due to the capability of the device, we can still demonstrate the critical temperature of our sample is at 39K, or even a slightly above. Several measurements are performed to verify the result, and they look almost identical with a great resistance leap at 39K.

The figures are rather self-explanatory. From both figures, we can see that there is a great resistance leap at the temperature between 39K and 40K. Below 39K, we see points fluctuating around 0Ω , and there are some negative readings. We believe this is due to the noise of the system, and we have averaged the data below 39K and the result is extremely close to 0. Therefore, we conclude that the samples become superconducting when below 39K. However, it is more important that we have seen a transition when above 39K. The resistance goes up to $5 \times 10^{-5}\Omega$ afterwards, and there are no negative readings since then. We have confirmed the result with several more measurements using different contacting locations between the golden pin and the sample. The resulting patterns are all very similar to Figure 5.4. Therefore, we can conclude that our sample

is superconducting with critical temperature of 39K.

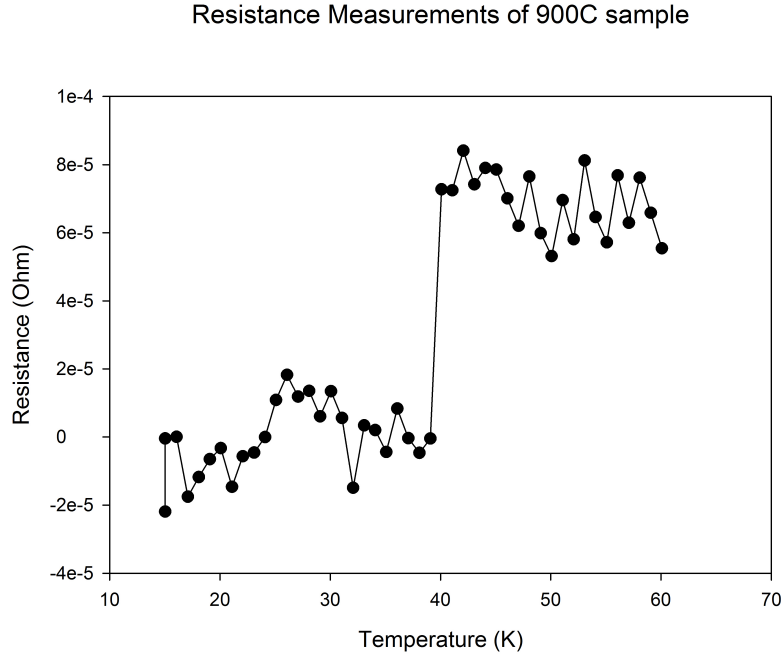


FIGURE 5.4: In this figure, we measure the 900°C sample’s resistance at temperature range of 15K to 60K. We use less but averaged points to show the transition more clearly. Again, like the sample prepared at 800°C, we found the transition temperature at around 39K.

We do not have enough time for the complete measurements from 10K to 300K. An individual measurement at 300K indicate $2.2m\Omega$ resistance, which is close to the reading from ohm meter. Also, we are not able to measure the critical field and current of our sample, even though these are important properties for a superconductor. But we are pleased with the critical temperature measurements, and conclude the experiment at this point.

5.3 Discussion of Error Origins

During the fabrications, we have encountered numerous problems and difficulties. In this section, we would like to record some of these issues, so the result of our tests can

be fully understood and people who employ our method can at least try to avoid these problems.

5.3.1 Contamination

The biggest challenge we encounter during the synthesis of MgB_2 is the contamination. The contamination is almost unavoidable, but we still try very hard to eliminate the influence of unwanted chemicals. The contamination of other elements, such as oxygen and carbon, happens through out the synthesis process. For instance, we have used XRD to analyze the composition of our boron powder. Even though it is labeled with high purity, we still find a lot of peaks corresponding to carbon element, which is later confirmed by SEM exam. Then, it is very important to choose non-reactive substrate and container for the reaction. We use AlN substrate with BN bar for the reaction and Al_2O_3 as the heating tube. Theoretically our choice should be compatible with the reaction between Mg and B. In reality, the furnace tube shows signs of reaction at high temperatures, and so does the boat and substrate. In the end, the inert gas is also one source of contamination. We use argon as the gas input to avoid oxygen coming into reaction. But we still observe oxygen element from SEM, and it is only possible to have oxygen from the gas environment based on our design.

For our experiment, we see unwanted reactions from almost every test, and sometimes a larger amount of impurities will simply destroy the sample. When going up to high temperatures, even small amount of impurities will have dramatic influences. There are several ways we used to prevent the damage from impurities. First, since the disc of Mg and B are very thin, it is very possible for the contamination to be happened at the surface. For the later experiment, we use another disc of Mg placed on top of our Mg-B combination as a shield to the surface contamination. Second, since BN is very easy to machine, we can clean the BN bar effortlessly after each reaction to avoid the residues from previous experiment by simply rubbing off the surface. However, despite the effort we try to have a clean environment for the reaction, we still observe CuO and carbon from the XRD and SEM analysis. Although these elements do not show any sign of impact on the superconducting test, we still believe it is necessary to eliminate as much contamination as possible.

5.3.2 Powder size

We have discussed the impact of powder size in last section of MgB_2 fabrication. In this subsection, we will talk about some experimental error introduced by the powder size. For our experiment, we only use a small amount of Mg, Cu and B for each test.

0.2g for B and Mg, and 0.05g for Cu. Also, we have Mg powder in rather large size (few hundred micron), while the other elements in micron level. Issue comes when we try to mix Mg with Cu. Cu powder can be easily attached to the weighting paper or the compressing device. Since we only use a very small amount of Cu as catalyst for the reaction, the loss during sample preparation can not be negligible. We try to mix a large amount of Cu and Mg at once, but Cu is then attached to the wall of container instead of Mg. The problems with Cu also apply to B due to their similar powder size. As a result, we do not have a very accurate molar ratio of these elements before putting the prepared sample into the furnace, and the amount of Cu as catalyst has huge impact on the product. Therefore, it is very necessary to be extremely careful during the process of sample preparation, and high accuracy weighting device is required in order to eliminate the loss of small powders.

5.3.3 Furnace

The last important issue is associated with the furnace we use for heating. This issue is not necessarily true for other furnaces, but we find out it is noteworthy about how the furnace can add uncertainty into the experiment result.

We have tried to use several different types of furnace for our experiment. These furnaces can be categorized into vacuum furnace and controlled atmosphere furnace. As the names suggest, the main distinction between these two types of furnace is that one has sample heated in vacuum while the other in certain gas environment. For the vacuum furnace, it can be hardly applied to our purpose mainly due to the loss or evaporation of Mg at low pressure. We tried to use the vacuum furnace, but we not only get product mainly made of Cu and B, but also contaminate the vacuum tube because of the evaporated Mg. For controlled atmosphere furnace, we use argon as inert gas to avoid the presence of oxygen, and the heating is performed at atmospheric pressure. These features satisfy our demands well, but there are some other issues can be hardly ignored. First, we do not have a external thermal couple associated to the furnace we use, i.e., the LabTemp furnace. We did several interesting experiment on the furnace, and it turned out that the temperature setting is not completely trustworthy. First, we tried to heat the Mg powder at 650°C, which was the melting point of Mg, but the product was not melted. Later we tried to repeat the test by setting temperature at 670°C, and this time we see the diffusion of Mg powder. Therefore, the temperature setting is not completely reliable for our furnace. Second, the furnace is designed that the center of the heating tube has the temperature set by the control panel. In another words, the center of the heating tube has the highest temperature in the furnace. Then, we have to insert the sample into the heating tube by estimation, and there will be some

human error centering the sample inside the tube. At last, the furnace does not have a temperature profile for the experiment we have, and the furnace does not have a linear heating or cooling option. Therefore, we only know how long the sample is heated at the set temperature but have no understanding at all for the other period. If the furnace takes excessive time to cool, then it is possible for some reactions to occur during the cooling period. In total, the furnace propose us great uncertainty during the experiment, and the result of this report has certain amount of relations with the furnace we use.

5.4 Outlook on large-scale application

As we have suggested in the beginning, our experiment is the only beginning to the construction of MgB_2 superconducting cavity. However, we choose fabrication method that can be possibly applied to the building of a cavity. In this section, we will talk about such possibility and some issues we can imagine at the moment right now.

Initially, we plan to fabricate a larger MgB_2 disc(10cm×10cm) after the current successful synthesis. Then, the next step is to build a cylindrical cavity made of MgB_2 based on the same method. There are several possible techniques can be applied to the fabrication of a superconducting cavity: coating of MgB_2 on a cavity surface, making a composite of MgB_2 and other metal, and building a bulk MgB_2 cavity. We consider the coating of MgB_2 on the surface of an existing cavity to be the best way at this moment. There are several reasons we interested in the coating of MgB_2 rather than other fabrication methods. First, MgB_2 has very low thermal conductivity comparing to other metals. So we would like some other material to remove the excessive heat during the usage. Second, since RF field only penetrates a few penetration depths into the superconducting cavity, a coating of hundreds nanometers on a metal cavity should demonstrate no issue in the RF cavity performance.

Then, we propose the following process of building MgB_2 superconducting cavity using our method. First, we need to construct a metal cavity into the desire shape. There are several choices for the structural metal, for instance, Mo, Ta or even some stainless steel. The criteria of choosing the structural material is that they do not react with Mg or B at high temperatures, and they have similar thermal expansion coefficient to MgB_2 , so that the coating will not crack or peel off during heating. Second, we have B powder to be cold pressed on the existing cavity surface, followed by an extra amount of Mg-Cu mixture cold pressed on the B layer. For our experiment, 10k psi is enough for the reaction to take place, and this should be easily achievable by current industrial situation. Then the cavity is put into a furnace for heating with protective gas in the cavity, such as argon. During the thermal process, rotation of the cavity is necessary to

ensure the product having homogeneous MgB_2 layer. Afterwards, we will have to polish the inner surface to get a smooth surface of MgB_2 .

However, this is the method that is the closest to what we have been doing so far, and we believe this approach is very possible to be applied. There are several other fabrication techniques in industry can be used as well, such as hot isostatic press(HIP). HIP uses a much higher pressure to facilitate the reaction. Similar to what we described earlier, we can fill B and Mg-Cu powder between two shells of the metal cavity. Then we put the assembly into a HIP furnace. After the reaction, we remove the inner metal surface to get MgB_2 layer.

Overall, it is very possible that our approach can be used in the construction of MgB_2 superconducting cavity. But from a small MgB_2 sample to a large cavity for particle acceleration, there is still a long way to go. There are still many issues remain unclear, not even including those remain hidden but can be catastrophic. For instance, we found CuO and some other contamination after the synthesis. Although they do not show any problem during the resistance measurements, we are not sure if these unwanted material will keeo docile when applying RF field. Also, the homogeneity of the large product is not worry-free. Our successful fabrication of small MgB_2 disc does not guarantee the quality if we plan to make it larger and in curved shape. However, our approach can be improved and other new techniques can be introduced, so we believe a MgB_2 superconducting cavity, demonstrating superior performance, is in the near future.

Chapter 6

Summary

In this chapter, we conclude the thesis by the following order. First, we summarize the entire fabrication and identification process to our final MgB_2 product. We will describe the process based on the time-line of our experiment. Then, we discuss briefly about the result, the limitations and uncertainties of our method, and the next steps to a large-scale application. In the end, we will talk about the possible fabrication superconducting RF cavity using our method, and the difficulties we may encounter.

We start our MgB_2 superconducting RF cavity from scratch. The first thing we did is to test the available facilities by melting Mg powder in a carbon crucible. What we learned based on our experimental setup (LabTemp furnace with Argon) is that, Mg powder is possible to evaporate even below its boiling point. We saw dramatic Mg loss at high temperatures around 1000°C . Also, due to the active nature of Mg metal, we observe signs of contamination from the surrounding. As a result, we did not think it is viable to have Mg and B react together in powder form because of the large Mg loss. At this point, we also tried to use the vacuum furnace for the experiment. However, the vacuum furnace demonstrated more problems since Mg is more easily to evaporate at low pressure. Therefore, we thought about several fabrication methods that can be possibly applied to a cavity. Among the choices we believe that if we add Cu as catalyst, the issue of Mg loss should be eliminated.

Then we repeated our Mg melting test with small amount of Cu. We confirmed that adding Cu as catalyst could lower the melting point of Mg, and then avoid the problem of Mg loss. There might be other issue associated with Cu if we would like to apply this method for superconductivity, since Cu is not a superconductor. But we later found that Hg, as a superconductor, is a good substitute for Cu. So we keep using Cu, hoping that if Cu works well, we could repeat the experiment with Hg. Since the mixture of

Cu-Mg melted successfully without losing Mg, we continued the experiment by adding B element and tried to synthesize MgB_2 directly.

We have tried three methods for sample preparation. First, we mixed the Mg, Cu and B powder completely, and then compressed the product into a disc. The disc was heated in the furnace, and we examined the result afterwards. The result from XRD and SEM showed signs of MgB_2 , but the result is not uniform at all. The main reason for the inhomogeneity is due to the powder size. We have B and Cu powder in micron level, but the Mg powder is rather large. So the reaction could not be complete, and thus we abandoned this method. To avoid the issue based on the powder size, we tried to compress Mg-Cu mixture into one disc, and B as the other. Then we place the Mg-Cu mixture on top of the B disc and let them react. Again, we looked at our product, which has four layers (including the AlN substrate), and found homogeneous MgB_2 exist at one of the four layers. Also, we found that Mg was diffused through the B, but there were large bulks of B preventing the formation of uniform MgB_2 layer. Finally, after we have two separate discs of Mg-Cu and B, we compress them together. This time, we chose high temperatures from 800°C to 1100°C to ensure the reaction, and we successfully found homogeneous MgB_2 product at 800°C and 900°C . We took our sample at 800°C and 900°C for XRD and SEM test, and we saw sharp peaks for MgB_2 from XRD for multiple locations and nice crystal structures of MgB_2 from SEM. We also performed resistance measurements for the products, and the transition temperature we found was 39K.

From the XRD and SEM test, we confirmed that the product was MgB_2 , and based on the superconductivity test, we believed that the product has very high quality. However, there were several issues that might affect the result significantly. These issues included the difference in powder size, the contamination from the surroundings, the inaccurate temperature control of the furnace, etc.. We recorded these problems so our approach could be more easily applied and the quality of product can be further improved.

Because of timeliness, we conclude our experiment at the point when we found the products heated at 800°C and 900°C for 12 hours were superconducting at 39K. There were still many things can be done to make the thesis more comprehensive. First, we could use even lower temperature, such as 600°C to see if MgB_2 could be formed. The problem of heating at high temperature was that MgB_2 decomposed into MgB_4 and other Mg-B compounds. We have tried to 600°C using a different furnace because of the shut down of LabTemp furnace in the end. But the product was heavily contaminated and could not be used for further exam. Then, the LabTemp came back when we had no time for further test. Second, all of our heating time was set to be 12 hours. We would like to know if the different heating time could have impact on the quality

of the sample. For instance, we saw a lot of MgB_4 product from the sample heated for 12 hours. We wondered if shorten the heating duration could actually prevent the decomposition of MgB_2 . Third, we would like to perform the AC transport, critical field and current measurement for the MgB_2 product we had. But we only had the chance to do the resistance measurement because of the difficulties in preparing the product into the PPMS.

After the fully understanding of our fabrication technique and finding out the best reaction conditions(time, temperature, pressure, etc.), we would like to extend our approach to a larger disc, and consequently, a superconducting RF cavity. From last chapter, we discussed briefly about the process of applying our approach to a cavity. But currently, we could hardly envision the potential issues. From our point of view, applying our method to a curved surface, avoiding contaminations and achieving outstanding performance in superconducting cavity test, are the obstacles that we have to overcome. Besides, the available facilities may also prevent us reaching the destination, since our method needs some different fabrication conditions to be satisfied. However, we are confident in our fabrication method, and believe that a superconducting RF cavity made of MgB_2 , having superior performance than the current Nb cavity, will be successfully fabricated soon.

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