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Infield Heat Treatment of Magnesium Diboride Tapes

Abstract

5 at.% vanadium-doped MgB_2 wires and tapes were heat-treated infield with their longitudinal axis at orientations of 0°, 45°, and 90° to the magnetic field, as well as in the absence of field. I_c measurements suffered from irreproducibility due to the highly resistive and electrically unstable stainless steel sheath, and no solid conclusions could be drawn from I_c data. The T_c of the vanadium-doped MgB_2 was confirmed to be depressed to 36°K, indicating that V was substituted into the MgB_2 matrix. Magneto-optical images suggest that samples processed normal to the magnetic field experience an enhanced ability to repel flux and may be better overall superconductors. Optical images were not useful to discern anything about the static and infield processed samples; SEM and other further analysis is needed to investigate the effects of infield processing on the grain structure and superconducting properties of MgB_2.

Introduction

In 1911, H. Kamerlingh Onnes discovered a shocking drop in the electrical resistivity of Mercury when it reached a temperature of about 4.2K. It was herein that the phenomenon known as superconductivity was first discovered. Superconductors exhibit two astonishing properties; firstly, below their critical temperature T_c they exhibit vanishing resistance to the flow of current. Current held in a superconducting loop that remains cooled below its critical temperature can have a decay time exceeding tens of thousands of years. Secondly, superconductors below their T_c behave as perfect diamagnets, canceling out any incoming magnetic flux by expelling an equal and

opposite amount of flux (up to a certain limit). There are actually three limits on the superconducting state; the critical temperature, T_c, the critical magnetic field, H_c, and the critical current density, J_c. When plotted on a three-dimensional domain, these three points are connected by a curved surface known as the critical surface. As long as the state of the superconductor is confined to a point somewhere within the bounds of the critical surface, the superconducting state can exist.

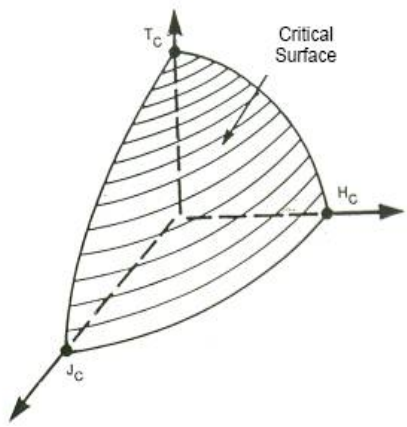

Figure 1: A diagram of a theoretical superconducting critical surface. Materials can only exhibit superconducting behavior inside of this surface.

The physics of superconductivity and the reasons why the limiting critical surface exists are chiefly described by the BCS theory of superconductivity. In 1972 the Nobel Prize in physics was awarded to John Bardeen, Leon Cooper, and Robert Schrieffer for this theory. Basically, it describes how the superconducting state can come about, through the pairing of electrons into units called Cooper pairs. These Cooper pairs form through an electron-phonon interaction; an electron moving through the lattice attracts the atoms of the lattice towards it, creating a region of positive charge, which can attract an additional electron. The two electrons form a pair, separated by a distance called the coherence length, which can be on the order of tens of nanometers. The Cooper pair can

then freely flow through the material without colliding with atoms in the lattice (electron collisions with the lattice are the interactions which lead to electrical resistance), because the electrons tend to drag each other through the lattice smoothly. However, this pairing of electrons can only occur when the energy binding the electrons exceeds that of the vibrational energy of the lattice, and since the vibrational energy of the lattice is a function of temperature, the existence of a limiting critical temperature T_c only under which superconductivity can occur is explained.

As the magnetic field increases, the amount of screening current on the superconductor's surface increases to cancel out the incoming magnetic field, and eventually a limit is reached. This limit, H_c, exists simply because for field strengths above it, it is energetically favorable for the superconductor to revert to the normal state. The third limit on superconductivity, the critical current J_c, exists because the flow of current through the superconductor will induce a magnetic 'self-field'; then, for the same reasons as the existence of the limit H_c, if this magnetic field becomes high enough, the superconductor will revert to the normal state.

There are two basic classifications of superconductors. Type I superconductors repel all incoming magnetic flux until the magnetic field strength is equal to H_c, at which point the superconductor immediately reverts to the normal state and allows for complete flux penetration through its interior. Type II superconductors respond to magnetic fields in the exact same way (as a perfect diamagnet) up until a field strength H_{c1}, the lower critical field. From H_{c1} up until the upper critical field H_{c2}, there is a mixed state in which the superconducting material allows some penetration of magnetic flux through cylindrical-shaped regions; these normal regions are called Abrikosov vortices. Type I

superconductors are mostly unusable for application because of their extremely low critical field H_c. Type II superconductors, due to the existence of the mixed state, allow for much higher magnetic fields as they allow some penetration of magnetic flux into their interiors. If left unchecked, these magnetic vortices will move through the sample due to a Lorentz force, and, because of Faraday's law of induction, an electromotive force will be produced. This voltage will lead to a resistance, and thus a dissipation of power and the generation of heat, which will quickly cause the superconductor to become normal. However, the increased upper critical field of type II superconductors can be made useful if the movement of these magnetic vortices can be prevented. Due to a phenomenon called flux pinning, non-superconducting regions such as impurities, precipitates, and grain boundaries can hold the flux lines in place. The density of the matrix of Abrikosov vortices is derived from an expression containing the magnetic field strength; as the strength of the magnetic field increases, so does the density of the flux vortex matrix. Additionally, as the magnetic field increases, the Lorentz force attempting to move the vortices off of the pinning sites and through the sample increases. Thus, a type II superconductor can remain superconducting (and thus be useful for application) as long as there are enough pinning sites to hold the magnetic vortices, and as long as the force of pinning is greater than the Lorentz force.

In January 2001, Professor J. Akimitsu was credited with the discovery of superconductivity in magnesium diboride, MgB_2. MgB_2, a simple binary material arranged in a hexagonal lattice (see figure 2), exhibits superconductivity at a temperature of approximately 39°K, which places above the realm of low temperature superconductors (LTS) such as NbTi and Nb_3Sn, but below the high temperature

superconductors (HTS) such as BSCCO-2212 and YBCO-123. It is a type II superconductor, and while its H_{c2} and J_c values were discouraging at first, through doping and other experimentation, advances have been made.

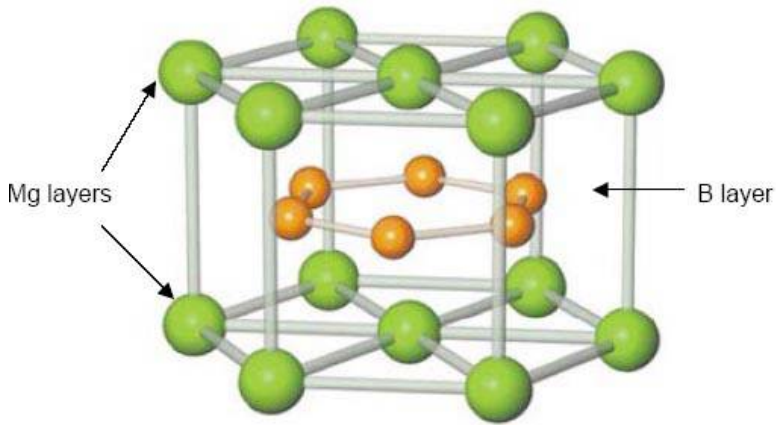

Figure 2: The hexagonal structure of MgB_2. Supercurrent flows smoothly between the B and Mg planes when the material is superconducting.

The purpose of this project was to test the effects of the application of a magnetic field during heat treatment (infield processing) on MgB_2 tapes. Since infield processing had been observed to provide better grain alignment and texturing in BSCCO superconductors, the hypothesis was that the infield processing might also have effects on the growth of grains in MgB_2 during the heat treatment process. The strength of the magnetic field applied during infield processing in this experiment was approximately 3 Tesla, and tapes would be processed infield at orientations of 0°, 45°, and 90° angles between the longitudinal direction of the sample and the magnetic field.

Experimental Procedure

The first step in the experiment was to decide on what types of samples to use and how to make them. 5 at.% vanadium doped, stainless steel sheathed wires, as well as tapes fabricated by rolling the wires in a rolling mill, were used. The vanadium doped

wires were used because they were the samples on hand, but additionally, vanadium doped MgB_2 has been shown to have enhanced critical current and magnetic field due to better flux pinning.[1] Tapes were fabricated for infield treatments because wires are isotropic due to their cylindrical geometry, and thus, the effects of various orientations of the magnetic field during processing would not have been able to be studied.

The next step in the experiment was to attempt to match critical current (I_c) values achieved in previous work on MgB_2 samples by Oscar Castillo. A heat treatment temperature of 750°C was chosen for simplicity (Oscar's thesis showed the highest average I_c values at 750°C for some of his samples; additionally, MgB_2 is not as sensitive to heat treatment temperature as many superconductors), and several samples were treated in a static (in the absence of magnetic field) furnace.

During this portion of the project, a furnace was being constructed for the bore of the 3 Tesla magnet that would be used for infield processing, so before samples could be processed infield, I_c measurements were taken on the samples that had been heat treated.

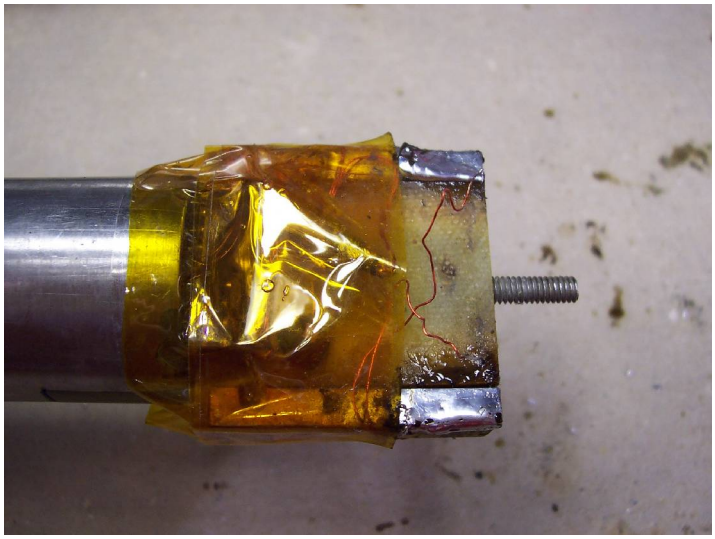

Figure 3: The end of the sample probe for I_c measurements, where the sample is attached. The two shiny areas on the top and bottom are the current leads where the sample was soldered on. The two thin copper wires pictured are attached to the sample as voltage taps, and the distance between them is measured and entered into the

computer so that the voltage due to resistance in the sample can be measured in volts per unit length.

The I_c measurement system consisted of a sample probe (see figure 3) to which the sample was soldered on in a simple 4-point configuration. The stainless steel sheath of the MgB_2 wires and tapes was difficult to solder, so an etch was used to create disorder and a high-energy surface to which solder would be more likely to attach to. Additionally, small bits of copper wire were wound around the ends of the sample to improve conductivity and reduce heating at the points where the current leads were soldered on, since the stainless steel sheath is highly resistive and electrically unstable.[1] After the sample was soldered in and secured, the probe was attached to an apparatus to measure the temperature near the sample. Then, the sample probe was slowly lowered into a dewar of liquid helium. The temperature was monitored as the sample cooled, in order to maintain a slow rate of cooling as to not damage the probe or the sample; a cooling rate of approximately 1°K/s was optimum for most of the cooling process. (Unfortunately, towards the end of the project, the temperature sensor ceased to function correctly and instead the cooling rate was monitored by watching the total resistance of the system, which could be read through the attached cable. At room temperature, the resistance of the system was about 3.8Ω, and at liquid helium temperature of 4.2°K, it was approximately 3.0Ω; thus, the cooling rate could be roughly monitored by keeping the rate of resistance drop reasonably slow.) After complete cooling to liquid helium temperature and attachment of power cables to the current inputs of the sample probe, current was passed through the sample using a voltage ramp generator. The rate at which the amount of current that flowed through the sample increased, as well as the maximum current limit, could be altered using the ramp generator. A LabVIEW console was used

to record data. The computer program recorded the voltage that arises from resistance as a function of current, with the I_c value recorded when the voltage was 1 μv/cm. An absolute voltage limit (at which point the system would stop taking data points) of 5 μv/cm was used. After a few tests were done and I_c values were recorded, the sample was pulled out of the liquid helium bath and allowed to slowly cool in helium vapor before bringing it to room temperature.

A short experiment was also performed to confirm the T_c of the samples. This was done because the samples were vanadium-doped, and doping in MgB_2 tends to lead to a depression of T_c. Using a similar probe and 4-point measurement system, the T_c was measured by reading the resistance of the sample to a very small amount of current at many temperatures as cooling was performed. When the resistance dropped to zero at T_c, the data points recorded took on the form of a typical superconducting transition curve.

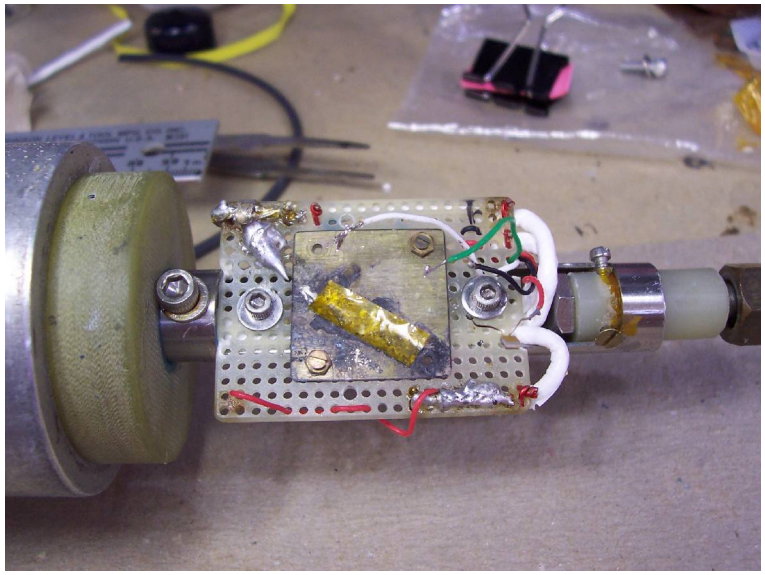

Figure 4: The simple 4-point probe used to measure T_c. The green and white wires were attached as voltage taps and the sample was soldered diagonally across the surface to the current leads.

The next portion of sample characterization was the use of magneto-optical imaging to estimate the overall quality of the samples. The magneto-optical imaging

apparatus is able to convert magnetic information into optical information due to the use of a garnet slab above the sample and the application of a weak magnetic field. Inside of this garnet, light experiences a polarization due to the magnetic field; the stronger the magnetic field, the more the rotation of the orientation of the light wave. Thus, the garnet can display in what fashion and with what intensity the magnetic flux penetrates the sample; in areas where the field is stronger, the camera will record a higher intensity of color. The magneto-optical images taken using MgB_2 tapes processed infield and in the absence of magnetic field were used to give a general sense of the quality of the superconducting state in the sample.

The final method of characterization that was performed was microstructural analysis. Unfortunately, the environmental scanning electron microscope (ESEM) was not available for use, so images were instead acquired with the use of an optical microscope.

Results

The aim at the beginning of the experiment was to process and test the I_c of several samples heat treated in the absence of a magnetic field to check the I_c values against literature values. Unfortunately, this initial step became a problem. Due to the high resistivity and instability of the stainless steel sheath, the I_c measurements yielded values that were much lower than literature values, as well as being seemingly random. The copper wire wound around the ends of the samples helped but did not alleviate the problem. The very first sample tested had a critical current greater than 600A, but all subsequent samples had I_c values between 0 and 200A. This was very detrimental because the I_c values would have been a way to easily see if the effects of infield

treatment at different orientations to the magnetic field had any patterns. Table 1 shows the measured values of I_c for samples.

Sample	I_c (A)	Sample	I_c (A)
Static Wire 1	>600	**Infield Tape 1 90°**	44.56
Static Wire 2	50.2	**Infield Tape 2 90°**	25.9
Static Wire 3	114.41	**Infield Tape 3 45°**	128.46
Static Wire 4	33.6	**Infield Tape 4 45°**	128.78
Static Wire 5	35	**Infield Tape 5 0°**	184.33
Static Tape 1	90.4	**Infield Tape 6 0°**	24.88
Static Tape 2	0		
Static Wire 6	120.4		
Static Wire 7	50.3		
Static Tape 3	5.4		
Static Tape 4	0		

Table 1: A list of I_c values measured. One sample processed in the static furnace had an excellent critical current, at greater than 600A, but all subsequent samples suffered from seemingly random I_c values.

The samples suffered from two major problems. Firstly, the high resistivity of steel led to a large amount of heating and resistance at the beginning of every I_c test, which showed as a large spike in the measured voltage at low amounts of current in the graphs. This effect can be seen in figure 5. The other problem that caused inaccuracies in the I_c measurements was the issue of thermal runoff. In some samples, the computer would record zero voltage due to resistance for values of current exceeding 100A, but then suddenly would spike almost vertically past the voltage limit, ending the test. This is due to the high electrical instability of steel. Due to an effect that is not fully understood, during the ramping up of the current, sometimes the current can be partially

redistributed from the superconductor to the stainless steel sheath, and the current value is sufficiently high at that point that it dissipates enough power to heat the steel dramatically and thus the superconducting core as well, leading to an immediate quench of the superconductor and a reversion to the normal state. This can be observed in figure 6.

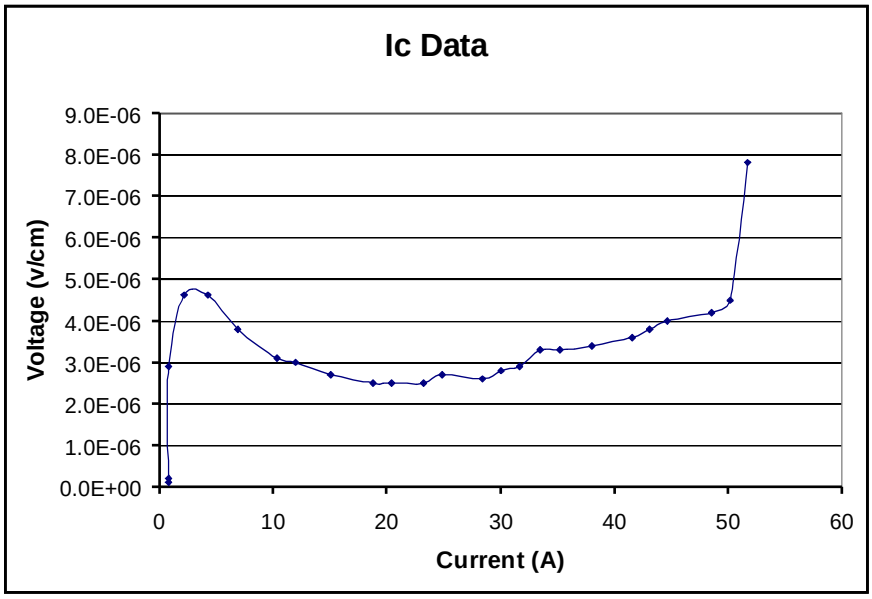

Figure 5: I-V curve showing initial heating in MgB_2 samples. At low values of current, the steel heats up so much that the test nearly ends because there is a large resistance; the voltage limit is nearly reached. The current gets mostly redistributed to the superconductor near 10A, but at the point enough heating has occurred that the superconductor can't fully recover, and thus it tends to become normal.

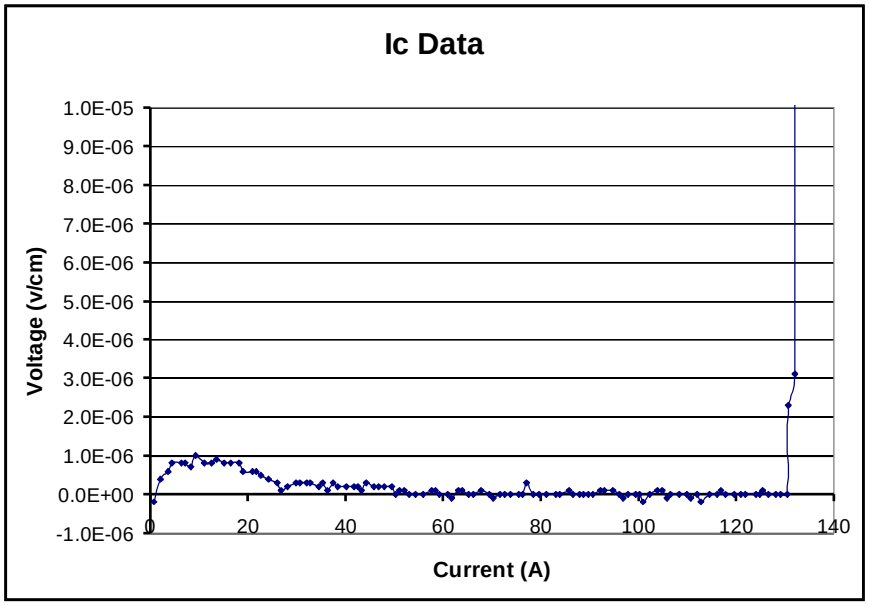

Figure 6: I-V curve showing thermal runoff that occurred in some MgB_2 samples. At about 130A, the current gets partially redistributed into the unstable steel sheath and leads to immense heating and the superconductor becoming normal.

The confirmation of T_c was a simple procedure that went smoothly. The characteristic superconducting transition curve was recorded upon cooling and warming several times to confirm the T_c. (See figure 7.) The slight depression of T_c is due to vanadium substitution into the MgB_2 lattice, because impurity atoms in the lattice lead to a slight distortion of the lattice parameters, which changes the way that electrons form cooper pairs through electron-phonon interactions.

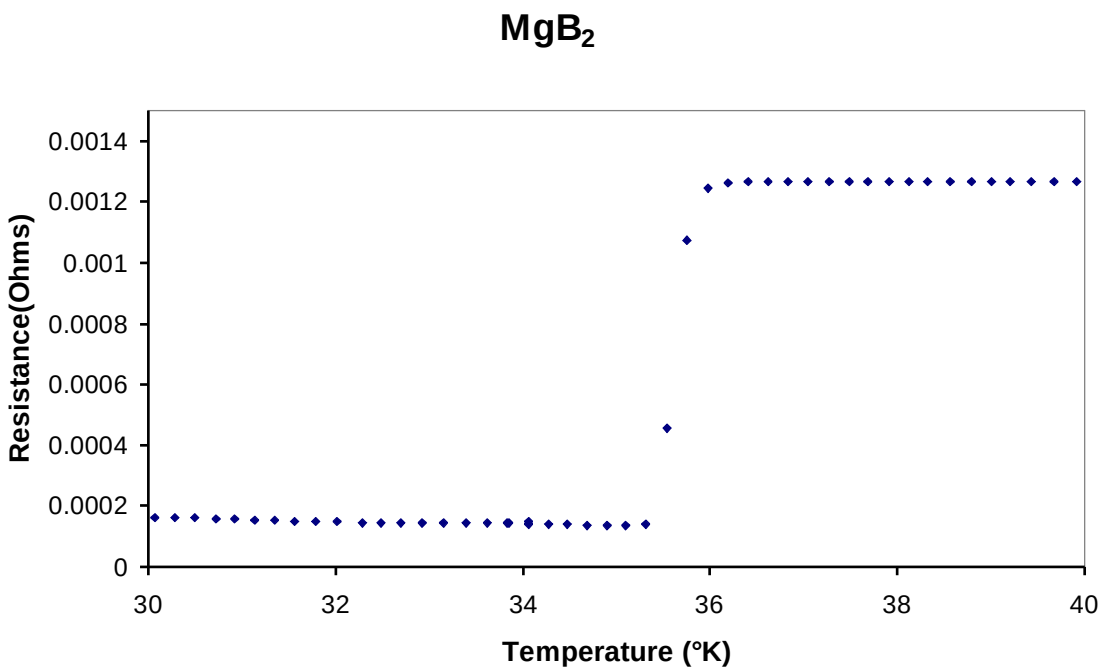

Figure 7: T_c measurement of an MgB_2 tape. V-doping led to a slight depression in T_c, which is expected. The onset T_c is approximately 36°K, with a ΔT (transition curve width) of approximately .5°K, which indicates a good, sharp transition to the superconducting state.

Magneto-optical imaging was used to compare the samples processed at various directions with respect to the magnetic field, as well as a static-processed sample. Composite images depicting the method of flux penetration into the sample were formed.

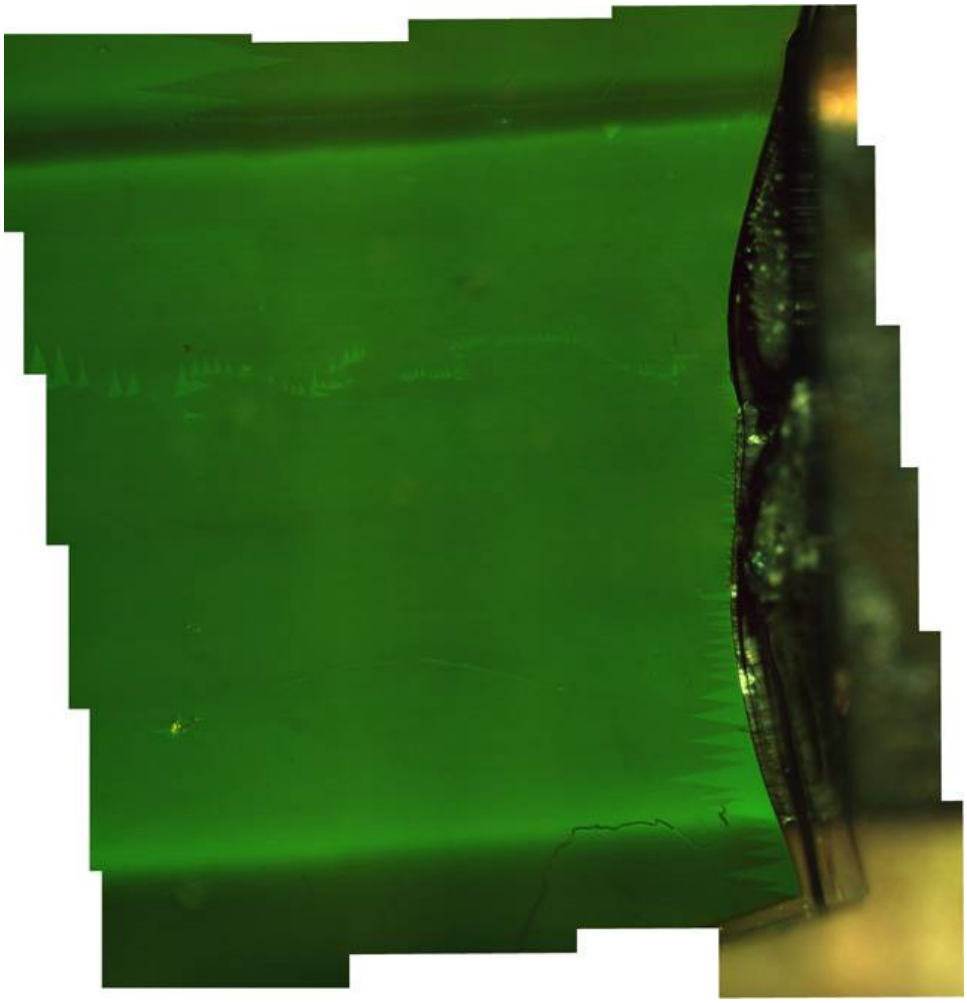

Figure 8: An example of a composite image that has been stitched together (sample processed parallel to the magnetic field). The intensity of the green inside the sample is an indication of how strongly the magnetic flux penetrates the sample at that point.

The slightly brighter regions at the top and bottom edges of the superconductor are the regions where the superconductor is repelling the magnetic flux away from its surface. To compare the samples' ability to repel magnetic flux (and thus their overall quality) at their surfaces, Scion imaging software was used to plot intensity profiles over these regions. Table 2 shows measurements of the relative intensity values; how bright the intense region is in comparison to the darker region outside of the superconductor.

	Static	Infield		
		Parallel	45°	Normal
1	1.285714	1.146316	1.443451	1.455341
2	1.211538	1.15	1.159661	1.359551
3	1.097345	1.201429	1.646528	2.080335
4	1.065217	1.068376	1.837184	1.639456
5	1.058412	1.135135	1.475556	1.597484
Average	1.143645	1.140251	1.512476	1.626433

Table 2: Relative intensities of the edge of the sample versus the darker background. Multiple measurements were taken and averaged for each sample.

The data table indicates that the samples processed with their longitudinal axis perpendicular to the magnetic field do the best job of repelling magnetic flux, which may indicate that they are better superconductors. The sample processed parallel to the magnetic field experienced no change with respect to the sample processed in the static furnace. The sample processed at 45° to the magnetic field experienced some improvement.

Due to the ESEM being down, microstructural analysis was not able to be done. Some images were obtained with the optical microscope, but the images were not very useful. Because MgB_2 does not sinter well during heat treatment, polishing led to the tearing off of chunks of the superconductor, leaving behind a rocky topography that was impossible to resolve at magnifications above 200x. Interesting areas of the microstructure that may show evidence of effects of magnetic field orientation are the inter- and intra-grain structures, as well as the steel-MgB_2 interface, but SEM analysis will be needed to see these small-scale features.

Figure 9: An image of the surface of the MgB_2 superconductor. Some of the image is out of focus due to the rough surface of the sample. The bright area at the bottom of the image is the stainless steel sheath, which is almost perfectly smooth. Magnification 200x.

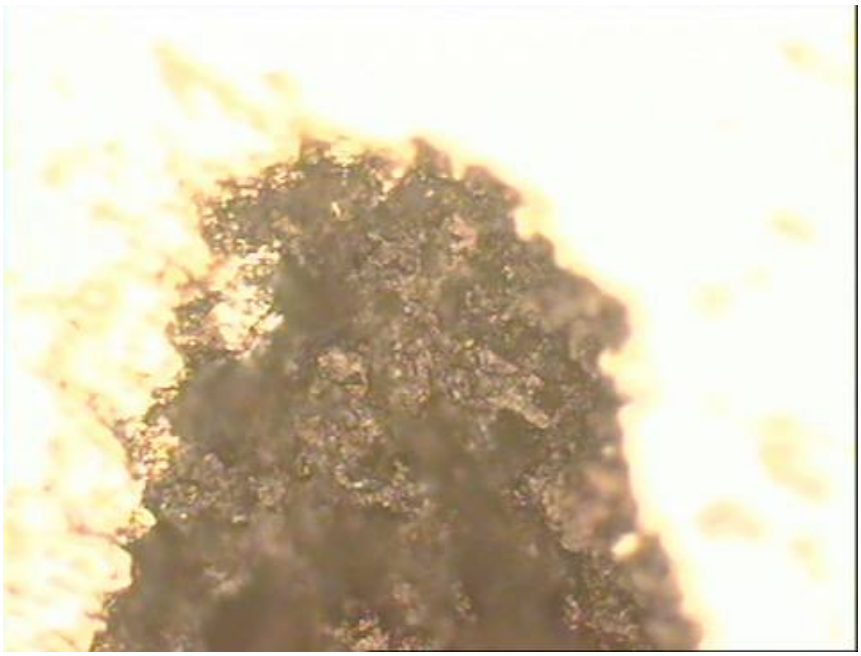

Figure 10: An image of the MgB_2/steel interface in a transverse cross-sectional sample. The way that the MgB_2 binds to the steel and how it is textured is interesting and may change within the three samples treated at different orientations to the magnetic field. SEM analysis is needed to see the grain structure at high magnifications. Magnification 1000x.

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Discussion

The T_c value of the samples was confirmed to be approximately 36°K, which affirms that there is V-substitution into the MgB_2 matrix. The I_c value of the first sample tested was greater than 600A; this is good evidence that the MgB_2 samples were able to superconduct and carry large amounts of current. Unfortunately, the stainless steel sheath led to many problems with the tests and an overall irreproducibility of data. It was impossible to establish a control range of I_c values in the static samples due to this. In spite of the inability to establish a control, samples were treated infield, and while table 1 shows that there may be a pattern in the I_c values (normal, 45°, and parallel, in increasing order), but there is no way to tell whether the I_c values achieved in the samples processed normal to the magnetic field are simply inaccurate due to aforementioned problems. In fact, the magneto-optical images suggest that the samples processed normal to the magnetic field are the best overall superconductors, as their ability to repel magnetic flux at the surface experienced the greatest enhancement. Bulk samples may also be a better choice, because of the lack of any sheath material that would impede I_c testing (as long as issues with bulk samples such as magnesium loss can be satisfied). By fabricating, processing, and testing many more samples with infield heat treatments, it may be possible to identify a relationship between magnetic field orientation during processing and superconductor characteristics, if one exists for MgB_2. Additionally, ESEM/SEM analysis is necessary to confirm if there are any effects on the microstructure of the superconductor.

Conclusion

5 at.% V-doped MgB_2 tapes were fabricated from wires and processed infield with their longitudinal axis at orientations of 0°, 45°, and 90° to the magnetic field of 3 Tesla. I_c measurements suffered from randomness and irreproducibility problems due to the highly resistive and electrically unstable stainless steel sheath, and no clear conclusions could be drawn from I_c data. The T_c was confirmed to be depressed to 36°K from MgB_2's normal T_c of 39°K, affirming that V had been substituted into the MgB_2 matrix. Magneto-optical imaging suggested that samples processed normal to the magnetic field experience an enhanced ability to expel magnetic flux at their surfaces. Optical microscopy yielded no useful images due to the rough topography of the samples; SEM analysis is needed to see if the grain structure of the superconductor is affected by infield processing.

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References

[1] Castillo, Oscar Eduardo. *Microstructural and Superconducting properties of V doped MgB2 Bulk and Wires.*