Phase formation in Cu-sheathed MgB$_2$ wires

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Abstract

The phases in Cu-sheathed MgB$_2$ wires fabricated using very short annealing time are studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and critical current ($I_c$) measurements. By comparison with the XRD pattern of our synthesized MgCu$_2$, the XRD line located at $2\theta \approx 36.1^\circ$ for all Cu-sheathed MgB$_2$ wire samples is unambiguously identified to be due to the MgCu$_2$ phase. This line was previously unidentifiable due to its absence in the standard pattern of MgCu$_2$ recorded in the current powder diffraction file (PDF) database. We found that the XRD lines previously attributed to Cu atoms by other groups, are actually due to the CuMg$_d$ (with $d \approx 6\%$) phase, indicating that copper does not exist in the form of un-reacted atoms in the core materials of these Cu-sheath MgB$_2$ wires. For samples heat treated at $700^\circ C$ or below, the phases are basically the superconducting MgB$_2$ and impurity MgCu$_2$ phases. Quantitative analysis indicates that the molar percent of the MgB$_2$ phase in these samples is over 90%. For samples heat treated at $725^\circ C$ or above, two additional phases, CuMg$_d$ and MgB$_4$ phases, are also present. The content of CuMg$_d$ phase increases rapidly with the increase of the heat treatment temperature from $725^\circ C$ and $750^\circ C$. This increase in CuMg$_d$ content is one of the factors responsible for the dramatic decrease of $I_c$. These phase identification results are consistent with our SEM result and the published Cu–Mg phase diagram. It is also found that the variation of the MgB$_2$ fraction with the heat treatment temperature peaks at $700^\circ C$, well correlated to the variation trend of $I_c$ with heat treatment temperature.

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1. Introduction

Ever since the discovery of superconductivity at 39 K in magnesium diboride [1], MgB$_2$, much effort has been made in the fabrication and characterization of metal-sheathed MgB$_2$ wires/tapes [2–10] for large-scale high current applications [11]. Among all of the sheath metals such as iron (Fe), nickel (Ni), silver (Ag), copper (Cu) and their alloys [3–9,11–21], iron seems to be the best metal sheath material in achieving high critical current density ($J_c$) due to its best chemical compatibility (almost no reaction) with MgB$_2$. Mg at high temperatures. For Fe-sheathed tapes, $J_c$ with value above $10^5$ A/cm$^2$ has been achieved by several groups [3,7–9,12,14]. Recently, however, much attention has been drawn to the study of the Cu-sheathed MgB$_2$ wires/tapes [13,14,16–20] due to the fact that Cu is superior than Fe in terms of the following four advantages: (1) high thermal and electrical conductivity, (2) high ductility, (3) non magnetic nature, and (4) cost effectiveness. These four factors are critical to the cryogenic stability, wire drawing workability, AC loss, and large scale production of practical superconductors, respectively. Compared with Fe, the only drawback of Cu as a sheath material for MgB$_2$ is that Cu can react with MgB$_2$ or Mg more actively than Fe, resulting in a substantial degradation of $J_c$. While Fe does not
react with Mg or MgB₂, it does react with B to form insulating FeB or FeB₂, which could lead to long current transfer length [21]. On the other hand, the main product, MgCu₂, of the reaction of Cu with Mg, is a very stable metallic compound [22], presumably leading to shorter current transfer lengths and potentially better stability. Thus, in terms of the electrical property of the impurities produced by the reactions of Cu with Mg and Fe with B, Cu as a sheath material actually has an additional advantage over Fe. Recently, Wang et al. [7] found that MgB₂ can be formed with a heat treatment time as short as three minutes by reaction between Mg and B powders in a Fe-sheathed tape. This fast formation process was readily applied for Cu-sheathed MgB₂ wires, and it indeed demonstrated that \( J_c \) can be significantly enhanced by reducing the reaction time between the Cu sheath and Mg + 2B powders [13,14,16].

To further improve \( J_c \) and understand superconducting properties for Cu-sheathed MgB₂ wires, a clear understanding about different phases and phase formation conditions is important. Knowledge concerning the phase formation can help in producing samples with better properties. Previously, some groups have carried out certain studies on the phase formation in Cu sheathed MgB₂ wires/tapes by XRD measurements [13,14,17–20]. However, in spite of such effort, three questions remain open and need to be answered. The first question is about the existence of unreacted Cu atoms in the cores of the Cu-sheathed MgB₂ wires. For example, Wang et al. [13], Beilin et al. [17], and Kovac et al. [20] identified some lines in their X-ray diffraction (XRD) pattern for the Cu-sheathed MgB₂ wires as due to pure Cu, indicating that Cu can diffuse from the Cu sheath into the cores of the wires and stay there as unreacted Cu particles. This seems very unlikely because it is well known that Cu can easily react with Mg to form certain copper–magnesium phases, such as the MgCu₂ phase. Thus, whether or not there are elemental Cu particles in the cores of the MgB₂ wires remains an open question and needs to be clarified. The second question that needs to be answered is whether or not the XRD line located at about 36° for 2θ [14,18] is due to the MgCu₂ phase, or due to other impurity phases. Since the currently available powder diffraction file (PDF) database for MgCu₂ (#01-1226) [23,24] does not list any XRD line near 2θ ≈ 36°, it has made it very difficult to identify the phase of this line. Since the powder XRD study on the crystal structure of MgCu₂ was reported by Hamawalt et al. [23], single crystal MgCu₂ and many other compounds of the type of crystal structure, commonly referred to as the MgCu₂-type Laves phase, have been synthesized and studied [25–33]. However, to our knowledge, none of these studies, which include the single crystal and powder XRD studies of MgCu₂ by Ohba et al. [25] and Kubota et al. [26], reported a more complete XRD pattern (with the use of Cu Kα X-ray radiation) of MgCu₂ than that reported by Hamawalt et al. [23,24]. This might be the reason why the data of Hamawalt et al. has been placed in the PDF file 01-1226 for many years as the standard XRD pattern of MgCu₂ for crystal structure analysis or phase identification of materials. To unambiguously identify the line near 2θ ≈ 36° as due to the MgCu₂ phase, it is necessary to synthesize MgCu₂ compound and obtain more complete XRD data using Cu Kα X-ray radiation than the existing PDF database. The third question concerns about how the fraction of the superconducting MgB₂ phase in the Cu-sheathed MgB₂ wires varies with heat treatment temperature for such short time heat treatment fabrication process. Currently, there is no any quantitative analysis made on XRD patterns of Cu-sheathed MgB₂ wires to address this question. The clarification on this question is very valuable for optimizing the fabrication conditions for producing high quality Cu-sheathed MgB₂ wires. This paper is intended to address all of these three questions by a combination of XRD, scanning electron microscopy (SEM), and \( I_c \) measurements.

2. Experimental

Cu-sheathed MgB₂ wires were prepared using a standard powder-in-tube (PIT) method. Mg powder (99.8% purity and 325 mesh) and amorphous B powder (99.99% purity and 325 mesh) from Alfa Aesar were stoichiometrically mixed. The mixed powder was then milled by a Spex-8000 high-energy ball mill for 2 h. During the milling process, stainless steel balls and vial were used as a milling medium and the mass ratio of ball to powder was 20:1. The milled Mg + 2B powder was loaded into a Cu tube with one end sealed, and then the remaining end was crimped mechanically. The copper tube, which conformed to ASTM B75, had an outer diameter of 6 mm and a wall thickness of 1 mm. The entire filling procedure was carried out in an argon atmosphere. The packing density was about 1.5 g/cm³. The powder-filled Cu tube was then drawn to a square wire with a cross-sectional area of 1 mm by 1 mm using a groove rolling mill.

Short length wire samples of about 15 cm in length were heat treated at four different temperatures: 650°C, 700°C, 725°C and 750°C, respectively, for 5 min and then quickly cooled down to room temperature. A flow of high purity argon gas was maintained throughout the heat treatment process.

MgCu₂ was synthesized using Mg (1–5 mm pieces, 99.98%) and Cu (powder 100 mesh 99.999%) from Alfa Aesar. Stoichiometric amounts of Mg and Cu (ratio 1:2) were loaded into a Nb tube that was then welded under an Argon atmosphere. This, in turn, was jacketed within an evacuated fused silica container. Then the assembly was heated in a resistance furnace at 850°C under a liquid zone for 10 h, it was then slowly cooled down to 350°C at a rate of about ~0.1 °C/min.

The powder XRD measurement was made using a Rigaku X-ray diffractometer with Cu Kα radiation. The data were analyzed with XRD analysis software Jade 6.1 provided by Materials Data, Inc. (MDI). All of the XRD patterns presented in this paper are also background
subtracted and Kx2-line removed using this XRD analysis software (Jade 6.1). The Kx2 stripping was performed using the Rachinger algorithm together with the removal of the background. All of the XRD data presented in this paper were calibrated using Si as the standard by measuring the samples with added Si powder. To make sample slides for XRD measurement, the core material of the Cu-sheathed MgB2 wires was obtained by peeling the Cu metal sheath to expose the core. The SEM images were taken using a JEOL JSM-6330F Field Emission Scanning Electron Microscope. The critical current, \( I_c \), of the MgB2 wires was measured by standard four-probe method using a pulse current source and a voltage criterion of 1 \( \mu V/cm \). SEM images were used for examining the micro-structure of the wires.

3. Results and discussion

3.1. XRD result for MgCu2

The powder XRD pattern for one of the synthesized MgCu2 samples is shown in Fig. 1. The pattern was obtained after subtracting the background and stripping the Kx2-lines from the raw data. All of the lines in the pattern can be indexed with a cubic structure of space group Fd3m. The pattern shows that our synthesized MgCu2 sample is in single phase. The lattice constant obtained from cell refinement is 7.0309 Å.

The (220) line, which is missing in the PDF database file 01-1226, is seen in the XRD pattern for our MgCu2 sample. The 2h value for this line is about 36.09°. The percent intensity for the (220) line is quite prominent, with a value of 11.7% of the maximum intensity at line 311. Due to the absence of the (220) peak in the PDF file #01-1226, people [14] in the past either could not unambiguously or experimentally identify the phase of this line in their XRD pattern for Cu-sheathed MgB2 wires. Our XRD pattern shown in Fig. 1 has clearly proven experimentally that the peak appearing at 2h/° C36.09 (see Fig. 2) for all Cu-sheathed MgB2 wires belongs to the MgCu2 phase.

3.2. Phase identification on Cu-sheathed MgB2 wires

Fig. 2 shows the XRD patterns for the core material of the Cu-sheathed MgB2 wires heat treated for 5 min at temperatures of 650 °C, 700 °C, 725 °C and 750 °C, respectively. For phase identification purpose, we also show in Fig. 2 the XRD patterns for three reference compounds: MgB2, MgCu2, and Cu powder. The powder for MgB2 and Cu was obtained commercially from Alfa Aesar.

For samples heat treated at 650 °C and 700 °C, all the peaks can be identified with the MgB2 and MgCu2 phases. In Fig. 2, the peaks due to the MgB2 and MgCu2 phases are labeled respectively by letters “o” and “v”. As mentioned above, the peak observed at 2θ ≈ 36.09° for all of the Cu-sheathed MgB2 wires can be identified as the (220) peak of the MgCu2 phase by comparison with the measured XRD pattern of our MgCu2 reference sample. Thus, we conclude that in these two MgB2 wire samples there is only one impurity phase, the MgCu2 phase.

For the two samples heat treated at 725 °C and 750 °C, two additional impurity phases, the CuMg6 (0 < δ < 7%) or Cu32.3Mg1.04 phase [34–36], and the MgB4 phases, are present. No any peaks, due to pure Cu, are found in the XRD patterns. Those small peaks for MgB4 phase are labeled by the solid circles in Fig. 2. The 2θ values of these peaks are very close to that listed in PDF database file #15-0299 for MgB4. The peaks for the CuMg6 are labeled by letter “C” in Fig. 2 and indexed in Table 2. The crystal structure of CuMg6 is cubic of space group Fm3m, same as that for Cu metal. The lattice constant values of CuMg6 in the 725 °C and 750 °C samples are found to be 3.647 Å and
3.649 Å, respectively. We also observed in Fig. 2 that the two MgB2 phase peaks, i.e., the (100) peak at 33.5° and (110) peak and 59.9°, disappear for the 750 °C sample, while the intensities of the C'-peaks of the CuMg6 phase become stronger when going from 725 °C to the 750 °C samples. This variation of peak intensity for different phases indicates that the content of the superconducting MgB2 phase decreases while the non-superconducting impurity CuMg6 phase increases with the increase of the heat treatment temperature from 725 °C to 750 °C.

The (101), (002), and (201) peaks of the MgB2 phase shown in Fig. 2 overlap with some peaks of the MgCu2 phase due to the proximity of the positions of the corresponding peaks from these two phases. To better see such overlap, the 2θ region between 41.8° and 43.8° is zoomed and shown in Fig. 3 as an example. It is clear that the MgB2(101) peak located at about 42.4° overlaps with the MgCu2(311) peak located at about 42.6°. To confirm such overlap, we have studied the peak positions and widths of these peaks by fitting them with pseudo-Voigt functions provided by the XRD data analysis software package Jade 6.1. For the double peak feature (labeled by o+v and C' in Fig. 3) of the samples heat treated at 725 °C and 750 °C, a pair of pseudo-Voigt functions were used for the fitting. The fitting values for the peak positions and full width at half maximum (FWHM) are listed in Table 1. The data in Table 1 can be well explained by the overlapping of the MgCu2(311) peak and the MgB2(101) peak. Table 1 shows that the 20 positions for the MgCu2(311) peak and the MgB2(101) peak are 42.630° and 42.442°, respectively. The FWHM value for MgCu2(311) peak is 0.236° ± 0.006°, which is about 0.106° smaller than the value of 0.342° ± 0.007° for the MgB2(101) peak. If a material contains these two compounds, then the small difference (0.188°) between the peak positions of the MgCu2(311) and the MgB2(101) peaks could produce a quite small variation in the width for the overlapped peak (labeled by o+v in Fig. 3). Indeed, Table 1 shows that for the samples heat treated at 650 °C and 700 °C, the values of FWHM are 0.404° and 0.405°, respectively, which are significantly larger than the FWHM values of both the MgCu2(311) and MgB2(101) peaks. This is a clear indication of the broadening of the peak due to the overlap of these two neighboring peaks. Table 1 also shows that when the heat treatment temperature increases from 700 °C to 725 °C and then to 750 °C, the FWHM value decreases from 0.405° to 0.346° and then to 0.325°. Such decrease in FWHM reflects the decrease of the percentage content of MgB2 (or increase of the percentage content of MgCu2) because the FWHM (0.236°) of the MgCu2(311) peak is much smaller than that (0.342°) for the MgB2(101) peak. This result is fully consistent with our quantitative analysis on the MgB2 content to be discussed later. The variation of the width of the peaks suggests that it is unlikely for MgCu2 and MgB2 to form some kind of solid solution in these Cu-sheathed MgB2 wire, because such a solid solution would not change the width of the peak. The difference in the crystal structures of MgCu2 and MgB2 also does not allow them to form such a solid solution.

The above phase identification is also consistent with the SEM result shown in Fig. 4. In Fig. 4(a)–(d), we show the SEM photographs for the core areas of the four wire samples. In Fig. 4(e), the SEM image for the entire cross-section of the core area of the 725 °C wire is shown. For the samples heat-treated at 650 °C (Fig. 4(a)) and 700 °C (Fig. 4(b)), the basic structure is that the grey islands are embedded in the mutually connected dark matrix materials. There is no significant microstructure difference between these two samples. Previously, Wang et al. [13] identified the dark matrix material as MgB2 and the less dark islands as MgCu2. We believe that the dark matrix contains predom-

![Fig. 3](image-url)  
Fig. 3. The zoomed region of Fig. 2 in the 2θ range of 41.8° ≤ 2θ ≤ 43.8°, which shows a big shift of 2θ between the (111) line of Cu, labeled by letter C, and the (111) line for CuMg6, labeled by C'. It also shows the overlap between the MgCu2(311) and MgB2(101) lines.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak 2θ (°)</th>
<th>Miller index</th>
<th>FWHM (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCu2</td>
<td>42.630</td>
<td>(311)</td>
<td>0.236 (0.006)</td>
</tr>
<tr>
<td>750 °C wire sample</td>
<td>42.640</td>
<td>Mainly (311)</td>
<td>0.325 (0.033)</td>
</tr>
<tr>
<td>725 °C wire sample</td>
<td>42.554</td>
<td>(311)+(101)</td>
<td>0.346 (0.040)</td>
</tr>
<tr>
<td>700 °C wire sample</td>
<td>42.496</td>
<td>(311)+(101)</td>
<td>0.405 (0.004)</td>
</tr>
<tr>
<td>650 °C wire sample</td>
<td>42.490</td>
<td>(311)+(101)</td>
<td>0.404 (0.004)</td>
</tr>
<tr>
<td>MgB2</td>
<td>42.442</td>
<td>(101)</td>
<td>0.342 (0.007)</td>
</tr>
</tbody>
</table>
inantly MgB$_2$ phase whereas the material in the grey islands contains mainly the MgCu$_2$ phase. Indeed, detail energy dispersive spectrometry (EDS) analysis reveals that the ratio of Mg to Cu content in the material of the dark matrix for the 700 $^\circ$C sample is about 4.58:1, corresponding to about 89% MgB$_2$ mixed with 11% of MgCu$_2$. The material in the grey islands is primarily MgCu$_2$ mixed with minor MgB$_2$. For the sample heat treated at 725 $^\circ$C (Fig. 4(c)), another material with whitish color presents in the area near the left side of the SEM image, indicating that an additional phase exists in this samples. This area is located near the wall of the Cu sheath. In Fig. 4(c) and (e), a small patch of the whitish materials is labeled by “area W”. We believe such whitish material is due to the CuMg$_5$. Our EDS analysis reveals that the content ratio of Cu to Mg in the whitish material is about 100:5, corresponding to a $\delta$ value of 0.05 for CuMg$_5$. This value is quite close to the $\delta$ value of 0.056 estimated below in Section 3.3 by the lattice parameter result. Fig. 4(e) shows that such whitish material appears in the outer region of the core for the 725 $^\circ$C sample, i.e., near the inner wall of the Cu sheath. The central portion of the core is essentially the same as the image in Fig. 4(b), that is, it consists of grey islands and a dark matrix. Fig. 4(d) shows the SEM image for the sample heat treated at 750 $^\circ$C. One can see that the whitish material spreads over the entire cross-sectional area of the core. This suggests that the content of CuMg$_5$ in the 750 $^\circ$C sample is much more than in the 725 $^\circ$C sample. The above SEM and EDS results can be qualitatively explained with the Cu-Mg equilibrium phase diagram [36], which is shown in Fig. 5. In Fig. 5, the eutectic-temperature line [37] between MgCu$_2$ and CuMg$_5$ lies right at 725 $^\circ$C. For the samples heat treated at 650 $^\circ$C and 700 $^\circ$C, during the cooling, the liquid solution or liquid + MgCu$_2$ should start to solidify crystals of primarily the MgCu$_2$ solid phase. Since the solid-state reaction is much slower than liquid-state reaction, the possibility of forming CuMg$_5$ phase (or Cu–Mg solid solution with small content of Mg), which is labeled by (Cu) in the phase diagram in Fig. 5, is extremely low. This explains why CuMg$_5$ phase is not observed in the XRD pattern for the samples heat treated at 650 $^\circ$C and 700 $^\circ$C. For the sample heat treated at 725 $^\circ$C, which is the eutectic tem-
temperature, both solid-state and liquid-state reactions can coexist. Thus, a slight temperature fluctuation can transfer solid-state reaction to liquid state reaction. In such case, the eutectic reaction should yield the production of CuMg₅ in the region of the wire close to the inner wall of the Cu sheathed. For the sample heat treated at 750°C, more solid-state reactions are transformed into liquid-state reactions. When temperature is decreased from 750°C to room temperature, the CuMg₅ can be produced by both the solidification above 725°C and the eutectic reaction at 725°C, resulting in much more production of CuMg₅ in the sample treated at 750°C than the sample treat at 725°C.

3.3. CuMg₅ vs. Cu

One of the issues we hope to clarify is whether, during the heat treatment process, the Cu atoms diffused from the Cu-sheath into the cores of the MgB₂ wires can remain as un-reacted Cu-element form. According to the Cu–Mg phase diagram in Fig. 5 [36], there is a small solubility of Mg into Cu, maximizing 6.93 at.% at 725°C, the eutectic temperature. This solubility could allow the formation of the CuMg₅ (0 < δ < 0.07) solution with the substitution of Cu atoms in pure Cu metal (δ = 0) by small amount of Mg atoms. According to this phase diagram [36], when temperature decreases from the eutectic temperature, 725°C, the precipitate does not come out as the pure metal Cu, but rather, the CuMg₅ solution with δ near 0.07.

For δ as small as a few per cent, the 2θ positions of the (111) peaks (labeled by C' in Figs. 2 and 3) for CuMg₅ could be quite close to the (111) peak (labeled by C) for Cu metal (δ = 0). Due to this reason, people in the past attributed the C' peaks observed in the Cu-sheathed MgB₂ wires to Cu particles. However, our data in Fig. 3 shows that the 2θ values of the C' peak for the 725°C and 750°C samples do not match the 2θ values of the peaks for Cu. By fitting the peaks, including the double peak features, using the pseudo-Voigt function provided by the Jade 6.1 analysis package, it was found that the (111) peak for Cu is located at 2θ = 43.310° ± 0.002°, while the (111) peaks for the 725°C and 750°C MgB₂ wire samples are located at 2θ = 42.903° ± 0.010° and 42.906° ± 0.012°, respectively. In our XRD measurement, the scan step for 2θ was set to be 0.02°. Usually, the error of the peak positions determined by the peak fitting procedure of Jade 6.1 is less than 0.04°. Thus, such a big shift (i.e., about 0.4°) in 2θ between the C and C' peak in Fig. 3 clearly indicates that the C' peaks observed for the MgB₂ wire samples cannot be attributed to Cu particles.

Such a big shift in 2θ between peak C and C' does not only occur for the peak at 2θ ≈ 43.3°, but also for all other Cu peaks of higher 2θ values. In Table 2, the 2θ values for Cu standard as well as for the CuMg₅ phase in the 725°C and 750°C samples are listed. One can find from the data in Table 2 that the values of the difference in 2θ, Δ(2θ), between the peaks for Cu and the MgB₂ wires are about 0.4°, 0.4°, 0.8°, and 1.0°, respectively, for the (111), (200), (220), and (311) peaks. Such big Δ(2θ) values clearly show that there are no elemental Cu particles presented in the cores of the Cu-sheathed MgB₂ wires, at least...
not to the concentration level detectable by our XRD measurement. The shift of 2θ toward lower angle side with the substitution of Cu by Mg atoms can be understood by the fact that the ionic radius of Mg (1.60 Å) is larger than that of Cu (1.28 Å) [38].

The Cu–Mg phase diagram shown in Fig. 5 suggests that for the sample heat treated at 725 °C and 750 °C, the Cu–Mg solution (or CuMgδ) formed by the eutectic reaction is primarily given by the extremities of the eutectic-temperature line (or maximum solubility line for Mg in Cu), i.e., at composition of 93.07 at.% Cu and 6.93 at.% Mg, which corresponds to a value of δ = 7.4% for CuMgδ. The solvus line shown in Fig. 5 for the Cu–Mg solution suggests that when temperature drops from 725 °C (the eutectic temperature) to room temperature, the solubility of Mg in Cu decreases from 6.93 at.% Mg to about 4.3 at.% Mg, corresponding to δ = 4.5% for CuMgδ. Thus, during the fast cooling of the samples from 725 °C to room temperature in the sample preparation, the Cu–Mg solution must be pinned at the maximum solubility line for Mg in copper. This means that only a small amount of CuMgδ, with δ in the range of 4.5% < δ < 7.4% can be produced during the fast cooling process. Thus, if the average value of δ is measured for the 725 °C and 750 °C samples, one would expect the δ values to be slightly smaller than 7.4% and close to each other. Indeed, our estimate of δ using the measured lattice parameter confirms this prediction. The Mg content δ of CuMgδ for the Cu-sheathed MgB2 wires heated at 725 °C and 750 °C can be estimated by comparing the measured lattice constant values with those previously reported for CuMgδ with δ in the range of 0 ≤ δ ≤ 0.03 [35]. The lattice constant, a, calculated using the 2θ data in Table 2, are 3.647 Å and 3.649 Å for the CuMgδ phase in the 725 °C and 750 °C samples. Culjaev and Trusova [35] studied how lattice constant a varies with Mg content δ in CuMgδ for δ in the range of 0 ≤ δ ≤ 0.03. In Fig. 6, the values of their lattice constant, a, are plotted against δ using solid squares. It can be seen that the data points fit pretty well with a linear relationship between a and δ. The lattice constant a for Cu obtained by Culjaev and Trusova [35] was 3.608 Å, which was 0.007 Å smaller than the more accurate value of 3.615 Å obtained both from the crystallographic PDF database # 04-0846 (see Table 2) and from our XRD measurement for Cu. The small error in lattice constant could be due to the old practice of labeling patterns according to copper radiation. The wavelength of copper X-ray radiation were standardized after this old practice. This systematic error could also arise from the use of the old X-ray diffractometer in the time of 1950s. Such kind of error could also occur for their data on other CuMgδ (0 ≤ δ ≤ 0.03) samples. To our knowledge, in spite of the extensive studies on the properties of the Cu–Mg alloys as reported in the literature [39–45], there was no other result on the δ dependence of the lattice parameter reported for the Cu–Mg solution in the range of (0 < δ ≤ 0.07). Thus, the original lattice parameter data of Culjaev and Trusova [35] in the range of 0 < δ ≤ 0.03 are calibrated with the correct lattice constant 3.615 Å for Cu and plotted (i.e. shifted up by 0.007 Å) as open circles in Fig. 6. If the linear relationship between a and δ is used for the CuMgδ phase in the 725 °C and 750 °C samples, then the lattice constant 3.65 Å for these two samples would correspond to a δ value of 0.056, or 5.6%. This value is almost the same as the value of 5.0% estimated from our EDS result. It is also quite consistent with the prediction made above based on the Cu–Mg phase diagram that the average δ value for these two samples should be slightly smaller than the maximum value δ = 7.4%. The values of the lattice constant for the Cu powder (δ = 0) and the CuMgδ phase in the 725 °C and 750 °C samples are plotted as solid triangle symbols in Fig. 6.

### 3.4. Quantitative analysis

#### 3.4.1. MgB2 vs. MgCu2

To better understand the superconducting properties of the Cu-sheathed MgB2 wires, it is useful to estimate the

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**Table 2**

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>2θ (°)</th>
<th>Cu Powder Sample</th>
<th>Cu-sheathed MgB2 Wire Heat Treated at 725 °C</th>
<th>Cu-sheathed MgB2 Wire Heat Treated at 750 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (PDF file # 04-0846)</td>
<td>2θ (111)</td>
<td>43.329</td>
<td>43.310</td>
<td>42.903</td>
</tr>
<tr>
<td>Cu powder sample</td>
<td>2θ (200)</td>
<td>50.433</td>
<td>50.422</td>
<td>49.950</td>
</tr>
<tr>
<td>Cu-sheathed MgB2</td>
<td>2θ (220)</td>
<td>74.130</td>
<td>74.114</td>
<td>73.404</td>
</tr>
<tr>
<td>Wire</td>
<td>2θ (311)</td>
<td>89.931</td>
<td>–</td>
<td>88.885</td>
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<tr>
<td>Cu-sheathed MgB2 wire sample</td>
<td>a (Å)</td>
<td>3.615</td>
<td>3.615</td>
<td>3.647</td>
</tr>
</tbody>
</table>

*a 2θ was measured in degrees.*

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**Fig. 6.** Lattice constant for CuMgδ at different δ values. Solid squares: original data of Culjaev and Trusova [35] for 0 ≤ δ ≤ 3%; the solid line is the linear fit to the data points. Open circles: lattice constant shifted up from the values of Culjaev and Trusova to match our measured lattice constant for Cu. Solid triangles: lattice constant measured for our Cu sample (located at δ = 0) and two Cu-sheathed MgB2 wire samples which were heat treated at 725 °C and 750 °C (both located at δ ≈ 5.6%).
percent content of the superconducting MgB$_2$ phase in the wires. In this section, we use an equivalent version of the internal-standard technique [46] to perform a quantitative analysis on the XRD patterns shown in Fig. 2 to obtain the MgB$_2$ content in the samples. The advantage of this method is that it is linear absorption coefficient independent and thus the relationship between the relative intensities and relative percentage volume (or weight) is linear. In our analysis, the XRD scans of two mixtures of known amount of the two compounds, MgB$_2$ and MgCu$_2$, are taken to obtain a calibration line. Then the percent weight of these components in an unknown sample which contains these two components can be determined by measuring the relative intensities of the selected reflection lines. The percent weight, $w_A$, of a component (here MgB$_2$) can be written as $w_A = K(I_A/I_S)$, where $I_A$ and $I_S$ are intensities of the two selected reflection lines of component A and standard S (here MgCu$_2$), respectively; $K$ is a constant which only depends on the miller indices of the selected reflection lines [46]. Two criteria should be applied for selecting the reflection lines: first the selection of a reflection line from the standard is based on the proximity on the XRD pattern of this reflection to that of the component sought; secondly, the reflection line of the standard S should not overlap with the reflection line of the component A. Thus, according to these two criteria, the (110) line at $2\theta \approx 59.9^\circ$ for MgB$_2$ and (331) line at $2\theta \approx 57.1^\circ$ for MgCu$_2$ (see Figs. 2 and 1) were selected for our quantitative analysis.

Two mixtures of MgB$_2$ and MgCu$_2$ powder with molecular (mol.) ratios of 50:50 and 80:20 were made for obtaining the calibration line. The relationship between the weight (wt.\%) $x$, and mol.\% $y$, for MgB$_2$ in the mixtures is given by formula $x = ry/(I_y-I_x)$, where $r = 0.3035$ which is the molar mass ratio of MgB$_2$ to MgCu$_2$. Fig. 7 shows the XRD patterns for these two mixtures, together with that for the four MgB$_2$ wire samples, in the 20 region where the MgCu$_2$(331) and MgB$_2$(110) lines are located. The measured values for the relative intensity, $I_{\text{ratio}}$, which is defined as $I_{110}(\text{MgB}_2)/I_{331}(\text{MgCu}_2)$, are 0.51 for the 50:50 mixture and 1.30 for the 80:20 mixture, respectively. In Fig. 8, the $I_{\text{ratio}}$ values for these two mixtures are plotted against weight percentage of MgB$_2$, $x$, by solid squares. The $I_{\text{ratio}}$ vs. $x$ data points in Fig. 8 can be well fit to a straight line (or called the calibration line) with equation $I_{\text{ratio}} = 2.22x$. The $I_{\text{ratio}}$ values measured for the four MgB$_2$ wire samples are also listed in Table 3. Using the equation $I_{\text{ratio}} = 2.22x$ and the measured $I_{\text{ratio}}$ values, the values of wt.\%, $x$, and mol.\%, $y$, of MgB$_2$ for these four samples are calculated and listed in Table 3. The values of $y$ for the samples treated at 650 $^\circ$C, 700 $^\circ$C, 725 $^\circ$C, and 750 $^\circ$C, respectively, are about 91\%, 94\%, 35\%, and 0\%, respectively. The $I_{\text{ratio}}$ vs. $x$ data for these four MgB$_2$ wire samples are plotted in Fig. 8 with open square symbols.

Our quantitative analysis suggests that for the 650 $^\circ$C and 700 $^\circ$C samples, more than mol. 90\% of the core mater-

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_{110}(\text{MgB}<em>2)/I</em>{331}(\text{MgCu}_2)$</th>
<th>MgB$_2$ wt.%</th>
<th>MgB$_2$ mol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%MgB$_2$ + 50%MgCu$_2$</td>
<td>0.51</td>
<td>23</td>
<td>50</td>
</tr>
<tr>
<td>80%MgB$_2$ + 20%MgCu$_2$</td>
<td>1.30</td>
<td>55</td>
<td>80</td>
</tr>
<tr>
<td>650 $^\circ$C MgB$_2$ wire</td>
<td>1.74</td>
<td>76</td>
<td>91</td>
</tr>
<tr>
<td>700 $^\circ$C MgB$_2$ wire</td>
<td>1.93</td>
<td>84</td>
<td>94</td>
</tr>
<tr>
<td>725 $^\circ$C MgB$_2$ wire</td>
<td>0.32</td>
<td>14</td>
<td>35</td>
</tr>
<tr>
<td>750 $^\circ$C MgB$_2$ wire</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
material is in the superconducting MgB$_2$ phase. For the 725 °C sample, since it contains two other additional phases, the CuMg$_3$ and MgB$_4$ phases, the mol.% fraction of MgB$_2$ in the core material should be less than the estimated 14% for $y$. Table 3 shows that the variation of percent content of MgB$_2$ with heat treatment temperature peaks at 700 °C and drops rapidly to less than 14% at 725 °C and then to 0% at 750 °C. Such trend of variation can also be observed in Fig. 7 by the variation of the intensities of the MgCu$_2$(331) and MgB$_2$(110) lines. Since the MgB$_2$ phase is responsible for the superconducting property, one would expect that the critical current, $I_c$, would also peak at 700 °C in a similar manner as the percent content of MgB$_2$ in these samples.

The critical current values at 20 K and self-field were measured for a similar batch of wire samples and the result is shown in Fig. 9. The sample treated at 700 °C has the highest $I_c$ of 152 A which corresponds to a critical current density ($J_c$) of $4.3 \times 10^4$ A/cm$^2$. The critical current increases with heat treatment temperature from 650 °C to 700 °C and then drops from 700 °C to 750 °C. The critical current of the sample treated at 725 °C is 80 A. This current is carried by the MgB$_2$ in the central region of the core which has the similar microstructure as the samples annealed at temperatures equal or below 700 °C. In the outer region of the core closer to the Cu sheath, the formed CuMg$_3$ phase (evidenced by the whitish materials in the SEM image in Fig. 4) breaks the flow of the superconducting current and thus reduces the $I_c$ substantially. It is no surprise that the sample treated at 750 °C is not a superconductor because this result is supported by our XRD analysis that the fraction of MgB$_2$ in this sample is almost vanished. In Fig. 9 we plot both $I_c$ and MgB$_2$ mol.%, $y$, against heat treat temperature. Indeed, Fig. 9 shows that both $y$ and $I_c$ reach maximum values at heat treatment temperature 700 °C and drops to zero at 750 °C.

### 3.4.2. CuMg$_3$ vs. MgCu$_2$

By comparing the XRD patterns in Fig. 2 between the 725 °C to 750 °C samples, one can observe that the intensities of the three C' peaks for the CuMg$_3$ phases increase with the increase of the heat treatment temperature from 725 °C to 750 °C. Since the compound CuMg$_3$ ($\delta \neq 0$) is currently not available, we could not obtain a mixture of CuMg$_3$ and MgCu$_2$ powder for determining a calibration line. However, by using the intensities of selected reflection lines of the CuMg$_3$ and MgCu$_2$ phases in the Cu-sheathed MgB$_2$ wire samples, we can still estimate the variation of the wt.% ratio of CuMg$_3$ to MgCu$_2$ for these two samples. In Table 4, the measured intensity ratios for the two pairs of selected lines are listed. The pair #1 consists of the CuMg$_3$(200) and MgCu$_2$(222) lines, and the pair #2 consists of the CuMg$_3$(220) and MgCu$_2$(511) lines. Now in the formula $w_A = K(I_A/I_s)$ [46], the letters A labels CuMg$_3$ and S labels MgCu$_2$. The measured ratios of the CuMg$_3$ wt.% for the 725 °C sample to that for the 750 °C sample, or $w_A$(725 °C)/$w_A$(750 °C), are found to be 43% (=0.42/0.99) and 45% (=0.58/1.28), respectively, for the selected line pair #1 and #2. This result indicates that CuMg$_3$ wt.% content in the samples increases rapidly (more than doubled) with the increase of the heat treatment temperature from 725 °C to 750 °C. As discussed previously at the end of Section 3.2, such a rapid increase in the production of the MgCu$_2$ can be explained by the transformation of certain solid-state reaction of the material at the eutectic temperature 725 °C (see phase diagram in Fig. 5) to the liquid-state reaction at 750 °C. Such a big increase in the content of the impurity CuMg$_3$ phase, accompanied with the rapid decrease of the content of MgB$_2$ phase, could destroy the superconductivity in the 750 °C sample completely.

### 4. Conclusions

We have fabricated Cu sheathed MgB$_2$ wires using ultra-fine precursor and very short heat treatment time (5 min). The effect of heat treatment temperature on the phase formation in these wires is studied by XRD, SEM, and $I_c$ (or $J_c$) measurements. The results can be summarized below.

The XRD pattern measured for our pure phase MgCu$_2$ sample and the Cu-sheathed MgB$_2$ wire samples unambiguously identified the XRD line located at $2\theta \approx 36.09^\circ$ as...
being due to MgCu₂ phase. This line was previously unidentifiable due to its absence in current PDF database for MgCu₂.

The XRD lines (C' peaks) previously attributed to pure Cu by some groups are shown to be actually due to CuMg₃ (δ ≈ 5.6%). No lines for pure Cu are observed in our XRD patterns. This result indicates that the Cu particles diffused from the Cu-sheath to the central region of the cores of the wires react with the Mg atoms to form CuMg₃. Our result suggests that Cu cannot exist in the core materials as un-reacted atoms.

For samples heat treated at 650 °C and 700 °C, the phases are basically the superconducting MgB₂ and impurity MgCu₂ phases. Quantitative analysis suggests that the mol.% fraction of MgB₂ phase in these samples is over the fraction with heat treat temperature is well correlated to and MgB₄ phases, also present. The content of MgB₄ phase increases rapidly with the increase of the heat treatment temperature peaks at 700 °C. This line was previously attributed to CuMg₃ by some groups are shown to be actually due to CuMg₃ (δ ≈ 5.6%). No lines for pure Cu are observed in our XRD patterns. This result indicates that the Cu particles diffused from the Cu-sheath to the central region of the cores of the wires react with the Mg atoms to form CuMg₃. Our result suggests that Cu cannot exist in the core materials as un-reacted atoms.

For samples treated at 650 °C and 700 °C, the eutectic temperature 725 °C, two additional phases, CuMg₃ and MgB₄ phases, also present. The content of MgB₄ phase in the samples is small. The production of CuMg₃ phase can be explained by the eutectic reaction between MgCu₂ and MgB₄ at 725 °C. The content of MgCu₂ phase increases rapidly with the increase of the heat treatment temperature from 725 °C and 750 °C, resulting in a decrease in the fraction of MgB₂ phase and critical current. These phase identification results are supported by our SEM result and can be qualitatively explained by the Cu–Mg phase diagram in Fig. 5.

The variation of MgB₂ fraction with the heat treatment temperature peaks at 700 °C. This variation trend of MgB₂ fraction with heat treat temperature is well correlated to the Ic measurement result.

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References