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Superconducting Properties of High-J_c MgB_2 Coatings

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ABSTRACT

We report the fabrication and superconducting properties of ~0.5 μm thick, fine-grained polycrystalline coatings of MgB_2 on single-crystal substrate surfaces. The films exhibit large critical current densities, implying little effect from the grain boundaries. Analyses for thermal activation effects are inconclusive, and evidence is presented that the irreversibility line is dominated by the combined influences of H_{c2} anisotropy and polycrystallinity. Comparative studies of the magnetic persistent currents and electrical transport properties reveal excellent agreement over a wide range of temperature and magnetic field. This result is contrary to similar comparisons on high-temperature cuprates, where disparities arise from the effects of large flux creep and the diverse electric field regimes probed by the two techniques. The MgB_2 films exhibit extremely sharp voltage-current relations away from the irreversibility line, in qualitative agreement with observed large J_c values and low rates of magnetic flux creep.

INTRODUCTION

The discovery of superconductivity at 40 K in MgB_2 has created interest for use of the material in the field of superconducting power applications, where, due to the simplicity and low fabrication cost, this compound might substitute for the more complex high T_c cuprates.[1] For electric power applications, the advantages of MgB_2 as compared to YBCO or BSCCO for fabricating low-losses superconducting wires are still controversial. The lower critical temperature of MgB_2 represents a serious challenge for the engineering and economics of cryogenic refrigeration systems. Moreover, the critical current behavior in magnetic field, as reported for bulk samples and polycrystalline or uniaxial textured films, is still weaker than that of BSCCO tapes in large magnetic fields. On the other hand, advantages of MgB_2 include the smaller anisotropy of the electronic structure and strong-linked properties of the grain boundaries[2]; the latter act as a major obstacles to current flow and are problematic for scale-up of YBCO-based high-J_c coated conductors[3]. The investigation of the H-T phase diagram and electrical transport properties of MgB_2 in forms that have potential practical application is very important in order to fully understand this material, particularly the features that limit the current conduction in high magnetic fields and the mechanisms that can expand the operating field.

Here we report electrical transport and magnetization measurements of polycrystalline MgB_2 films grown on Al_2O_3 substrates. The transport voltage-current characteristics were measured in a temperature range from 5 to 40 K, up to magnetic fields of 15 T and electric fields of 0.25 V/cm. From these measurements we deduced an upper critical field line $H_{c2}(T)$, and identified important considerations regarding characterization of the irreversibility line and resistive transition to the superconducting state in an applied external magnetic field.

EXPERIMENT AND RESULTS

The MgB_2 films investigated in this study were prepared by post-annealing of ~0.5µm thick boron precursor films deposited by electron-beam evaporation on R-plane oriented Al_2O_3 substrates.[4] After deposition, the B films were sandwiched between cold-pressed MgB_2 pellets, along with excess Mg turnings, and packed inside a crimped Ta tube. The Ta tube containing the precursor film was introduced into a quartz tube, evacuated to 1×10^{-5} Torr, and sealed. The sealed quartz tube was placed inside a box furnace, where the films were heated rapidly to 890 ºC for 60 minutes, and then furnace-cooled to room temperature. Using this process we obtained

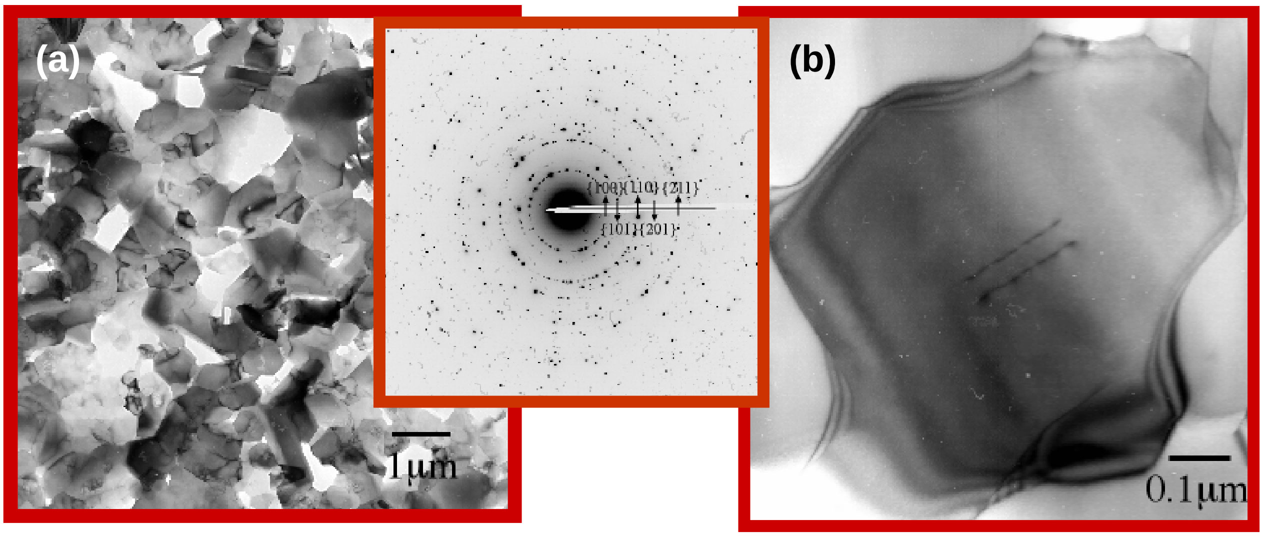

Fig. 1. (a) Plan view TEM image of an MgB_2 film. The inset is an electron diffraction patterning showing the grain orientations are random, and the sizes range from 0.2 to 1.2µm. (b) Individual grains are relatively defect free.

reproducible MgB_2 films with a T_c of 39 K, a resistivity at 300 K of 10-13 µΩ-cm, and a residual resistivity ratio (ρ(300K)/ ρ(40K)of nearly 3. The resulting MgB_2 coatings are polycrystalline, with grain sizes in the range of 0.2 – 1.2 µm, as shown in the plan view TEM image of Fig. 1. The large-area electron diffraction of several hundred grains shows a developing ring pattern that can be indexed by MgB_2 reflections, underscoring the polycrystalline structure. Figure 1(b) shows the existence of two dislocation lines within a typical grain, but little evidence of other defect contrast at the scale of the image.

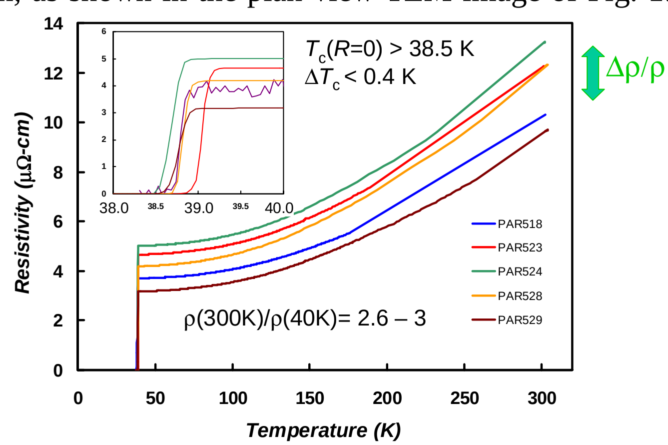

Fig. 2. The temperature-dependent electrical resistivity of five independently-fabricated samples. The double-ended arrow represents uncertainty due to sample roughness.

Figure 2 shows the temperature dependence of the resistivity, ρ(T), for several independently synthesized samples. Several features regarding the reproducibility are evident. While the $\rho(T)$ are consistent with values measured by others,[5] variations in the magnitude among the different samples is partially accounted for by the uncertainty in sample thickness due to the rough nature of the sample surfaces. This geometric uncertainty in the room-temperature resistivity is represented by the double-ended arrow; the values of the resistivity ratio $\rho(300K)/\rho(40K) = 2.6 – 3$ are consistent with this conjecture. Zero-resistance T_c values are greater than 38.5 K, with a spread among the different samples of less than 0.5 K, and with transition breadths of less than 0.4 K. These results indicate good reproducibility in the fabrication process and the resulting electrical properties.

Electrical transport properties in the superconductive state were measured using a standard four-terminal technique, as a function of temperature and magnetic fields to 15 Tesla. For these measurements, the samples were mechanically patterned to typical bridge dimensions of 100 - 400 μm wide x 3 - 4 mm long. Figure 3 shows a typical family of voltage-current, $V(I)$, characteristics for several temperatures ranging from 30 to 37 K. The data were acquired for a 0.5 μm thick film in a magnetic field of 1 T applied perpendicular to the film surface. In Fig. 3, T_{irr} = 33.2 K is the temperature at which the corresponding $V(I)$ curve shows a power-law behavior with an exponent of 2 over a wide range (~ four decades) of voltage. This is the criterion used in the present transport measurements to define the irreversibility line $H_{irr}(T)$. Rigorously, T_{irr} can also be described as the temperature at which, for a given applied magnetic field, the linear resistive component of $V(I)$ vanishes. For temperatures greater than T_{irr}, $V(I)$ has a linear component at low currents that terminates with the normal state characteristic at about 37 K. With decreasing $T < T_{irr}$, the curves exhibit a finite J_c with a progressively larger power-law exponents n, where $V \propto I^n$.

In many cases $V(I)$ was measured over a voltage range of 7 orders-of-magnitude. This was possible due to the low normal-state resistivity of MgB_2 and the consequent high thermal stability of the measured film at currents significantly larger than J_c. It is interesting that such extended $V(I)$ characteristics cannot be measured in YBCO films (or HTS in general) that exhibit a normal state resistivity nearly 20 times higher. Because of the large accessible range, measurements of $V(I)$ in MgB_2 provide an opportunity for comparing different regimes of voltage dependence on current with those predicted by models of dissipation in superconductors. The low-level linear dependence can be identified with a resistive behavior, similar to the thermally activated flux flow (TAFF) in HTS at higher temperatures. Analysis of this portion was accomplished by plotting as V/I vs. I on a linear scale enables

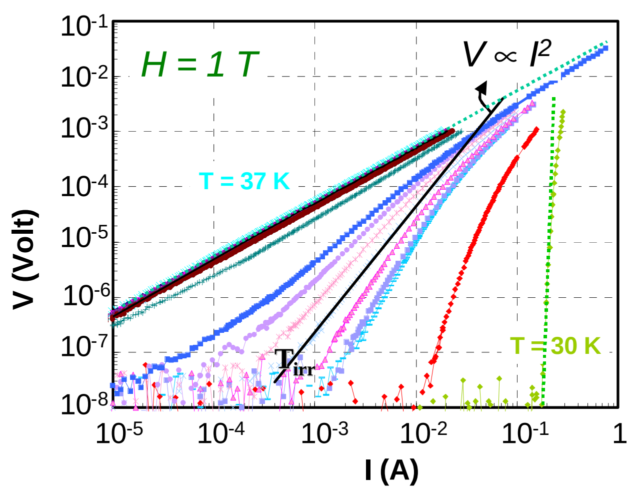

Fig. 3. Voltage-current relations for various temperatures in an applied field of 1 Tesla. The irreversibility temperature, T_{irr} = 33.2 K, is defined for a power-law characteristic $V \propto I^2$. A linear resistance component occurs for higher temperatures, and sharply increasing power-law exponent curves, $V \propto I^n$, result at $T < T_{irr}$. The dotted lines at 37K and 30K represent the normal state ohmic behavior and a $V(I)$ initial power-law with n=53, respectively.

extrapolation of the quadratic component to determine the ohmic component, from the *V/I* intercept, in the limit $I \rightarrow 0$. At intermediate currents the voltage response is highly nonlinear and consists of an upward-curvature region followed by a region of transition to a second linear behavior that persists to the largest voltages investigated. However, the slope of the high-current linear asymptote at high voltages is not that expected from Bardeen-Stephen model of flux flow resistance [$R_f = R_n(H/H_{c2})$], but rather approaches the normal state residual resistance R_n (see Fig. 3).

For temperatures below $T/T_c < 0.7$ ($T <$ ~30 K), $V(I)$ become extremely sharp, with exponent values n of several hundred, in contrast to observations of HTS materials where smaller n values result from the apparent combined effects of large anisotropy and thermal activation. A related aspect of this behavior in MgB_2 is the very low flux creep rates, $S = -dlnJ/dlnt$, observed in magnetic studies,[6] in semi-quantitative agreement with the transport measurements through the relation $S = 1/(n-1)$.[7]

Due to the sharpness of the $V(I)$ for $J \geq J_c$, the measured critical current value is less dependent on the specific voltage criterion used for its definition. In particular, we observed a remarkable similarity between J_c values obtained by transport measurements, using a criteria of 1 μV/*cm*, and measurements of the current density obtained magnetically, using the Bean model, where the effective criterion is orders of magnitude lower. A comparison between transport and magnetic data is shown in Fig. 4, which plots values for J_c versus applied field H for two different films at a temperature T = 25 K. We notice that the J_c values are very similar in the low field region and slightly divergent above 1 T, with the transport data lying higher than the magnetization data. This behavior can be qualitatively explained by the change in the shape of the $V(I)$ relations at high fields, where the superconductive system approaches its irreversibility line and characteristics show a progressively smaller power-law exponent. The data are compared with magnetization measurements made on isolated powder particles of bulk-processed MgB_2, and with the recent J_c results of Kim, *et al.*,[8] measured on *c*-axis textured MgB_2 films. Apparently, the texture provides no significant advantage in field, implying the strongly-linked character of the grain boundaries in the present films. In addition, the close correspondence with the values of bulk powder may indicate that naturally occurring defects in the MgB_2 grains are relatively effective in pinning vortices over a substantial range of magnetic fields. However, as yet it is unknown whether the powder particles represent a single grain, or are multi-grained, with possible similar effects from the grain boundaries as in the films.

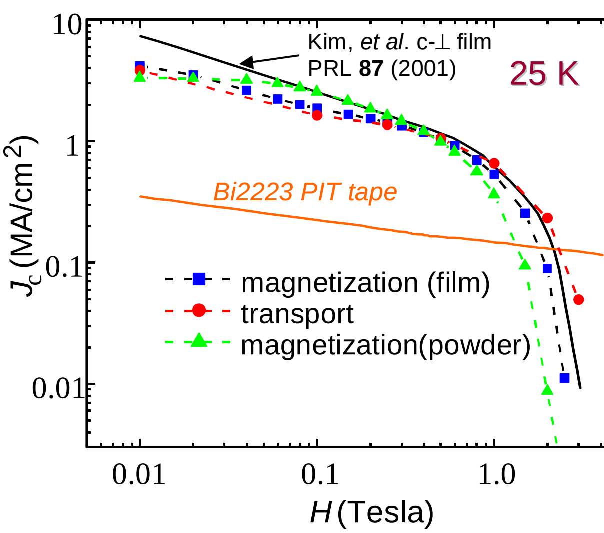

Fig. 4. The critical current density $J_c(H)$, measured by both electrical transport and magnetization hysteresis. For comparison are magnetization data obtained on isolated powder particles of bulk MgB_2, those published for the *c*-axis aligned thin films of Kim, *et al*, and data for BSCCO powder-in-tube tapes.

The operating temperature of 25 K is interesting for possible applications using cryo-coolers or liquid neon cryogen, so we have included for comparison the J_c properties determined for the HTS Bi2223 powder-in-tube tapes. For operation in modest fields (< 2 Tesla), the economics of MgB_2 fabrication,[1] and its stability and high J_c values could provide advantage for some applications.

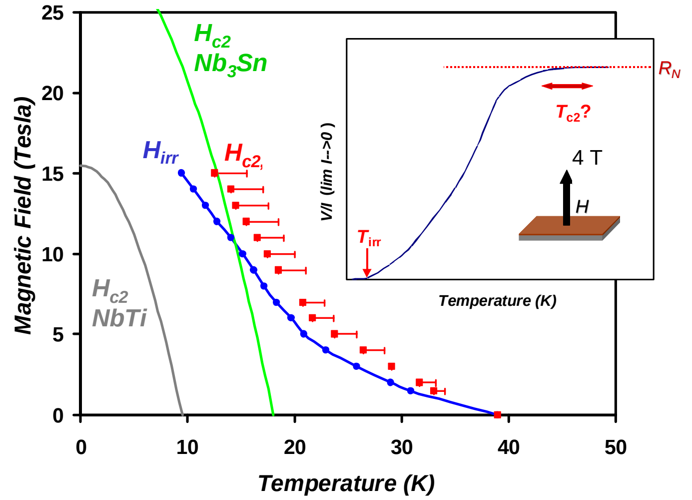

Fig. 5. The measured irreversibility curve, $H_{irr}(T)$, based on the vanishing of the linear resistance in the $V(I)$ characteristics. The upper critical field, H_{c2}, is estimated from the onset decrease in $R(T)$ from its normal-state value. The H_{c2} phase boundaries of NbTi and Nb_3Sn are included for comparison.

Figure 5 shows the *H*-*T* phase diagram as obtained by transport current measurements. The indicated $H_{c2}(T)$ line represents a level of uncertainty based on the observed, gradual onset decrease of resistance from that of the normal state, as shown in the example of the inset. In principle, this broadening could be due to a number of factors, including the anisotropy in H_{c2}, or possibly thermal smearing effects. If anisotropy is the dominant influence, then the measured phase boundary will reflect the maximum H_{c2} values. The H_{irr} line is much better resolved, since it defined by the vanishing of the linear resistance in the $V(I)$ curves, as described above. For comparison, we have included the H_{c2} phase boundaries of two common LTS materials, NbTi and Nb_3Sn. Again, these results indicate a possible advantage for operation of MgB_2 in the temperature range 20 – 25 K.

While the irreversibility line does fall not far below the H_{c2} curve, the origin of this suppression is of interest. We have attempted to analyze the data for thermal activation effects, as would manifest themselves through the characteristics of vortex glass or thermally activated flux flow (TAFF) behavior in the vicinity or above the irreversibility line. A definitive signature of these effects could not be discerned, although vortex glass scaling of the $V(I)$ curves was recently reported for uniaxially textured films.[8] Alternatively, we may analyze for the effects of anisotropy alone as a possible source of these differences. Recent studies on single crystals[9] and uniaxially textured films,[10] indicate anisotropy ratios $\gamma = H_{c2,ab}(0)/H_{c2,c}(0)$ in the range 1.3 to 3.2. In a polycrystalline or poorly textured MgB_2 film such an anisotropic behavior gives rise to a distribution of H_{c2} values, such that each single MgB_2 grain will be characterized by a different critical field according to its crystal orientation with respect to the direction of the external applied field. In this case, each MgB_2 grain composing the film will transition to the superconducting state at a different temperature for a given applied magnetic field. Therefore, the high-temperature onset of the resistive transition will coincide with the transition temperature $T_{c2,max}$ of those grains having the highest H_{c2} value, $H_{c2,max} = H_{c2,ab}$. Conversely, zero resistance may be realized at a temperature where a percolative zero-resistance path exists along grains having $H_{c2} > H$. This picture assumes $R = 0$ in the zero-current limit at H_{c2}, and would preclude a significant contribution from intrinsic mechanisms such as thermal fluctuations or thermal depinning, which could provide finite resistance in the superconducting state.

In this case, the $H_{irr}(T)$ line would simply indicate the existence of the onset percolative superconducting path in the zero-current limit, and dissipation incurred at increased current and/or temperature would result from the forced conduction through paths occupied by non-superconducting grains.

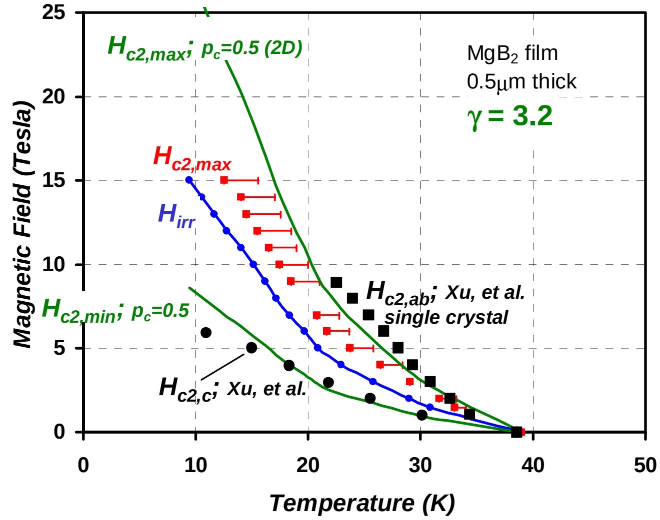

Fig. 6. Comparison of the data with calculated H_{c2} curves based on the measured irreversibility line, percolation in the two-dimensional limit, and an anisotropy ratio of 3.2. The latter value is taken from the experiments on MgB_2 single crystals of Xu, *et al*. Details are described in the text

Here we report a simple numerical analysis to assess this viewpoint, where we have calculated expected $H_{c2}(T)$ curves based on the observed $H_{irr}(T)$ and an array of randomly oriented grains. Since our film thickness (0.5 µm) is comparable to the grain (0.2 – 1.2 µm), we consider the simplest case of 2-dimensional percolation, for which an infinite, zero-resistance cluster should occur at a critical superconducting concentration of p_c=0.5.[11] In the calculation, for each grain randomly oriented with its *c*-axis at an angle θ from the applied field *B*, then the resistance is zero provided the ratio $B/H_{c2}(\theta) < 1$, with,

$$B/H_{c2}(\theta) = B/H_{c2,ab}\,[sin^2(\theta) + \gamma\, cos^2(\theta)]^{1/2}.$$

The mass anisotropy parameter γ = 3.2 is used, taken from the measurements of Xu, *et al*. on single crystal MgB_2.[9] Figure 6 shows the $H_{c2,max}$ and $H_{c2,min}$ generated from this calculation and our H_{irr} data. The resulting curves are in reasonable agreement with the measured $H_{c2,ab}$ and $H_{c2,c}$ of Xu, *et al*, but lie near the upper limit of the estimated range for our measured $H_{c2,max}$. Similar calculations, yielding similar qualitative agreement, were made for case of 3-D percolation, where the value of p_c can range from 0.195 to 0.425, depending on the nature of the percolation network.[12]

SUMMARY

We have reproducibly fabricated 0.5µm thick, polycrystalline MgB_2 coatings by *ex situ* reaction of evaporated boron precursor films in the presence of Mg. Away from the irreversibility line, transport measurements of J_c are in excellent agreement with those found from magnetization hysteresis, consistent with the observation of very sharply rising $V(I)$ relations, which render the definition of J_c insensitive to the diverse voltage criteria of the two techniques. Analysis of the measured $H_{c2}(T)$ and $H_{irr}(T)$, using the combined effects of anisotropy and percolative transition to the zero-resistance superconductive state, yields a consistent description, and implies that thermal activation may not be significant source of H_{irr}. In reality, it is likely that both anisotropy and thermal effects play a role in the suppression of $H_{irr}(T)$ below that of the H_{c2} line. For the present polycrystalline films, however, $H_{irr}(T)$ seems to lie midway between the range of H_{c2} anisotropy. Further analysis will assess the effects of the conjectured percolation on the observed dissipation levels near the threshold.

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