Irreversibility line and granularity in Chevrel phase superconducting wires

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A Chevrel phase monofilamentary wire was hot isostatically pressed (HIPed) under 2 kbar of argon pressure at 940 °C for 1.5 h. Transport critical current densities (J_c) were measured from 2.7 to 11 K, in magnetic fields up to 15.5 T. Compared to previous results for a sample HIPed at 900 °C for 0.5 h, the irreversibility field $[B_{irr}(T)]$ has been improved by 3 T to 34.5 T at 4.2 K. The J_c has also been enhanced at 14 T and 4.2 K to the highest reported value of 6.7×10^8 A/m^2. The reduced pinning force data show excellent temperature scaling. Resistivity measurements in high magnetic fields confirm an improvement in $B_{irr}(T)$ and provide evidence that the improved properties are due to better superconducting properties at the grain boundaries. © *1998 American Institute of Physics.* [S0021-8979(98)06016-2]

I. INTRODUCTION

Nb_3Sn and ternaries based on Nb_3Sn are the most widely used superconducting material in manufacturing high field magnets up to 21 T. To make magnets operating significantly above 21 T, another generation of wires incorporating a different class of superconducting material is required. In spite of the discovery of the high T_c superconductors, low T_c materials are still candidates for these new magnets. The very recent development of transformed Nb_3Al conductor offers high J_c, high upper critical field (B_{c2}), and an excellent tolerance to strain as compared to Nb_3Sn.[1] Chevrel phase superconductors (Pb,Sn)Mo_6S_8 (PSMS) are also a possibility since B_{c2} of this material is about 55 T at 4.2 K.[2] Very recently, a new benchmark for the overall critical current density of Chevrel phase wires of 105 and 60 A/mm^2 at 20 and 24 T at 1.9 K has been set.[3] In spite of these high values, the irreversibility line $[B_{irr}(T)]$ of these wires lies far below the $B_{c2}(T)$ curve.[4,5] Nevertheless, magnetic measurements on bulk samples have shown that Chevrel phase materials may not be intrinsically granular despite their short coherence length.[6,7] To develop the potential of Chevrel phase materials, it is essential to bring $B_{irr}(T)$ as close to $B_{c2}(T)$ as possible. In this article, further significant improvements in these state-of-the-art wires are reported by heat treating the wire using a hot isostatic press (HIP) operating at a higher temperature for longer time (940 °C for 1.5 h compared to previous work using 900 °C for 0.5 h). Variable temperature $J_c(B,T)$ data obtained in fields up to 15.5 T are presented that show an improvement in the irreversibility field of 3 T at 4.2 K. Consistent with previous work on wires which found that the heat treatment at ambient pressure influences the superconducting properties of grain boundaries,[8,9] resistivity and susceptibility data are used to provide evidence that improved sintering between grains is responsible for the increase in $B_{irr}(T)$.

II. SAMPLE PREPARATION

The powder used in the fabrication of the Chevrel phase wire is a mixture of $Pb_{0.6}Sn_{0.4}Mo_6S_8$+0.2 at % Sn+10 wt % of precursors (Pb, MoS_2, Mo). The main component, $Pb_{0.6}Sn_{0.4}Mo_6S_8$ (PSMS) powder, is obtained by reacting Sn and Pb with the stoichiometric precursor Mo_6S_8 in a sealed molybdenum crucible. The Mo_6S_8 powder is obtained by first making the Chevrel phase $Ni_2Mo_6S_8$. Ni is then withdrawn by immersion in hydrochloric acid. This desintercalation leads to chemical grinding which produces small grain size Mo_6S_8.[10,11] Preliminary transmission electron microscope (TEM) investigations on the final wire show very small PSMS grain size, ranging between 20 to 300 nm.[12] Such small grain size is favorable for obtaining very high J_c's.[13] The powder is surrounded by a melt-processed niobium sheet, an intermediate sheet of CuNi30% and a stainless-steel outer jacket. After the HIP treatment, the final wire diameter is about 0.58 mm. Only 6.4% of the cross section of the wire is the superconducting core, but recent results show that without degrading J_c in the core the superconducting cross section can be increased to 20% by removing the CuNi30% sheet. Full details of the wire fabrication can be found elsewhere.[3,14]

A wire sample 70 cm long was wound on a thin walled stainless steel sample holder. After the HIP cycle, the wire together with the sample holder were electroplated with cop-

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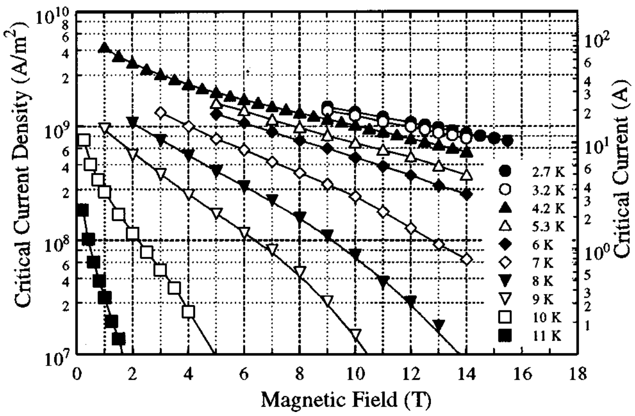

FIG. 1. $J_c(B,T)$ results using the 0.1 μV/cm criterion, for a Chevrel phase wire HIPed under 2 kbar argon pressure at 940 °C for 1.5 h. At 4.2 K, the values shown for fields below 8.5 T correspond to quench currents.

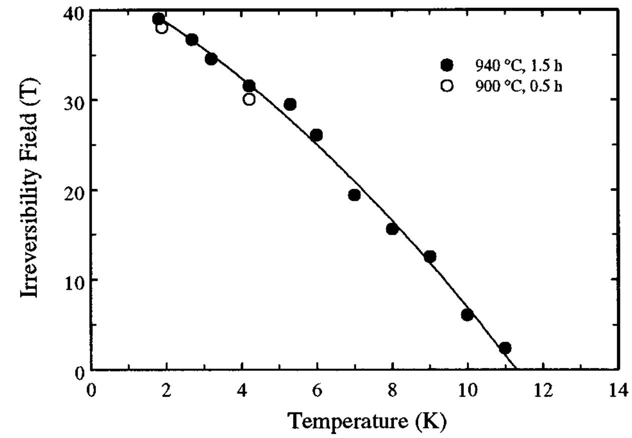

FIG. 3. Irreversibility line from Kramer plots, for two Chevrel phase wire samples HIPed under 2 kbar argon pressure, at 940 °C for 1.5 h (●) and for 900 °C for 0.5 h (○) (Refs. 3 and 14). The point $B_{irr}(1.8\text{ K})$ for the (940 °C for 1.5 h) HIP treatment is from the measurements of J_c up to 23 T.

per and soldered together. For $T>4.2$ K, transport $J_c(B,T)$ measurements were carried out under vacuum to ensure good temperature control.[15] The uncertainty in the temperatures quoted is estimated to ± 0.2 K. For $T \leqslant 4.2$ K, vapor pressure thermometry was used with the sample directly immersed in liquid helium.

III. RESULTS AND DISCUSSION

Using the standard 1 μV/cm criterion, the J_c calculated for the superconducting cross section reaches the highest reported value of 6.7×10^8 A/m^2 at 14 T and 4.2 K, confirming the excellent performance for this type of Chevrel phase wire.[3,14] At 15.5 T and 2.7 K, J_c is 7.9×10^8 A/m^2. The extrapolated B_{irr} is equal to 34.5 T at 4.2 K, an improvement of about 3 T. This result was confirmed by measurements carried out on the same sample in fields up to 23 T at the Grenoble High Magnetic Field Laboratory.[16] At low magnetic fields and low temperatures, $E(J)$ curves showed a very small round transition followed by a series of voltage steps of a few μV as has been reported before.[14,17] A low E-field criterion of 0.1 μV/cm was chosen which minimizes the effect of the shunt and the steps found at high E fields. $J_c(B,T)$ results using this criterion and the corresponding Kramer plots[18] are presented in Fig. 1 and 2. In Fig. 3, the irreversibility line, deduced from Kramer plots, is compared to results on the same wire HIPed at 900 °C for 0.5 h.[3,14] The slope $dB_{irr}/dT \approx -4.7$ T/K. Similar to the high temperature superconductors, the improvement of B_{irr} is criterion dependent.[19] In Fig. 4 the normalized volume pinning force is plotted against the reduced magnetic field $b=B/B_{irr}$ at different temperatures. The results show excellent temperature scaling, indicating that there is one pinning mechanism operating. The scaling function is: $F_p = 2.23 \times 10^7 (B_{irr})^{2.118} b^{0.5} (1-b)^2$. This Kramer field dependence is found in bulk[6,20] and thin film[21] Chevrel phase materials and is normally attributed to grain boundary pinning. Measurements in magnetic fields up to 23 T show that at 4.2 K, there is a crossover in J_c between this PSMS wire and the non-Nb J_c of transformed rod in tube Nb_3Al superconducting wires at about 21 T.[1]

Resistivity and ac susceptibility measurements were also carried out in magnetic fields up to 14 T on small pieces cut from samples of both HIP treatments used for transport measurements. Making the plausible assumption that the de-

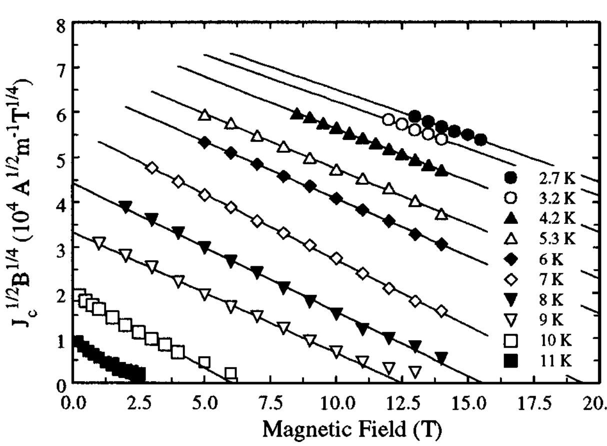

FIG. 2. Kramer plots at different temperatures for a Chevrel phase wire HIPed under 2 kbar argon pressure at 940 °C for 1.5 h.

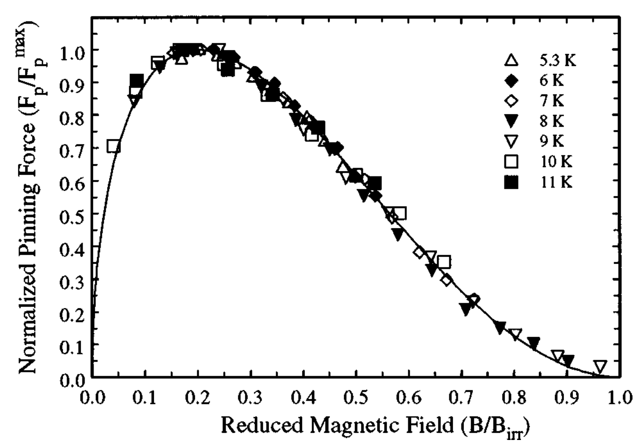

FIG. 4. Reduced pinning force as a function of reduced magnetic field for a Chevrel phase wire HIPed under 2 kbar argon pressure at 940 °C for 1.5 h. The continuous line represents the function $\alpha b^{1/2}(1-b)^2$.

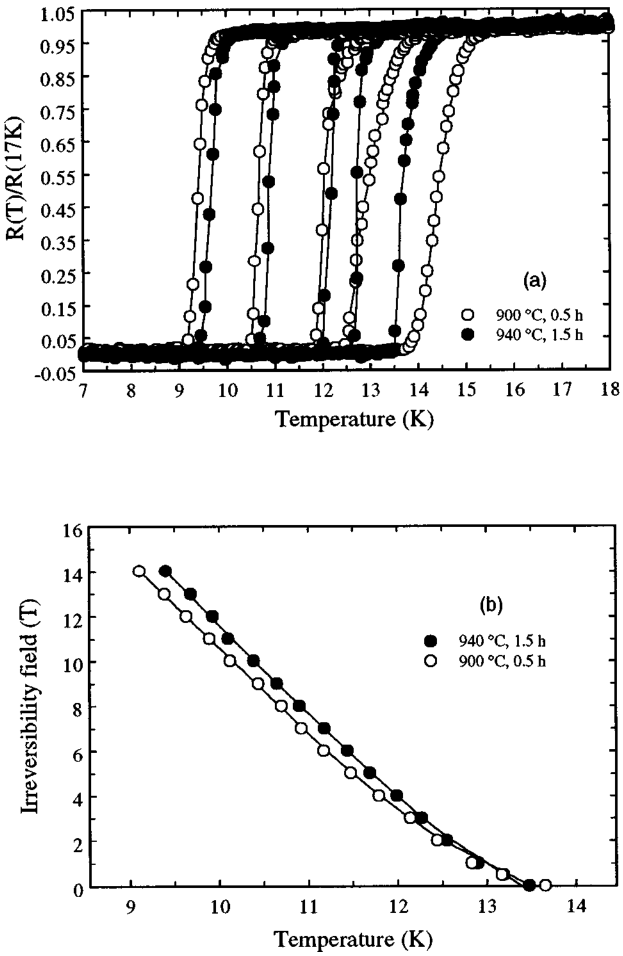

FIG. 5. (a) Comparison of $R(B,T)$ results for two Chevrel phase wire samples HIPed under 2 kbar argon pressure, at 940 °C for 1.5 h and 900 °C for 0.5 h. From right to left, $B=0$, 2, 4, 9, and 14 T. (b) Comparison of the irreversibility line deduced from $R(B,T)$ results using 1% of the $R(17\text{ K})$ criterion, for both Chevrel phase wire samples.

graded regions of superconductivity occur at grain boundaries, the first drop in resistance marks the superconducting transition of the grains. The zero-resistance state marks the beginning of the coherence between grains and coincides with the T_c onset for ac susceptibility measurements confirming long-range screening supercurrents.[20] Therefore, the temperature at which the zero-resistance state occurs characterizes the properties of the grain boundaries. Resistivity measurements in dc fields applied perpendicular to the current were carried out from 0 to 14 T using a current of 2 mA. Figure 5(a) gives a summary of the results. The broad transition observed at 0 T confirms a distribution of T_c in both samples. The smaller transition width for the 940 °C for 1.5 h HIP treatment (1.0 instead of 1.64 K) suggests that the sample is more homogeneous. Figure 5(b) shows $B_{\text{irr}}(T)$ defined at 1% of $R(17\text{ K})$ for both wires. This represents the lowest measurable resistance criterion with reasonable signal to noise. The irreversibility line thus defined is somewhat different from the one deduced from $J_c(B,T)$ measurements. This difference arises from the Kramer extrapolations underestimating the field at which J_c is zero. Kramer plots show deviations from a linear dependence at low currents and high fields consistent with this explanation. Nevertheless, $B_{\text{irr}}(T)$ is unambiguously enhanced in high magnetic fields for the wire HIPed at 940 °C for 1.5 h, in accordance with the improvement in $J_c(B,T)$ data. As discussed above, we attribute the improvement to better superconducting properties at the grain boundaries as a result of enhanced sintering between grains.

IV. CONCLUSION

In summary, using the standard criterion of 1 μV/cm, J_c values for a Chevrel phase wire are reported to be 6.7×10^8 A/m^2 at 4.2 K and 14 T with an irreversibility field improved by 3 T to 34.5 T. $R(B,T)$ measurements suggest that the enhancement is due to improved superconducting properties at grain boundaries. Homogeneity of superconducting properties throughout the sample has also been enhanced. Chevrel phase materials may yet meet the requirements for the next generation of high field magnets.

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