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Critical current distribution of hot isostatically pressed PbMo_6S_8 wires

B. Seeber ^a, N. Cheggour ^a, J.A.A.J. Perenboom ^b, R. Grill ^c

^a *Groupe de Physique Appliquée, Université de Genève, 20 rue de l'Ecole-de-Médecine, CH-1211 Genève 4, Switzerland*

^b *High Field Magnet Laboratory and Research Institute for Materials, University of Nijmegen,
Toernooiveld, NL-6525 ED Nijmegen, The Netherlands*

^c *Metallwerk Plansee, A-6600 Reutte, Austria*

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Abstract

The PbMo_6S_8 Chevrel phase has an important potential for the construction of ultra-high-field superconducting coils. The critical current density of hot isostatically pressed (HIP) PbMo_6S_8 wires with a stainless steel matrix and a molybdenum diffusion barrier was investigated in fields up to 25 T. The field dependence of J_c is considerably improved in the high-field regime by going from a 990°C, 4 h to a 1225°C, 4 h HIP treatment at 110 MPa. However, a drop of J_c at unusually low fields as 15 T was observed. The appearance of a double peak in the critical current distribution, obtained by dI^2/dI^2 suggests that the origin of such a behavior is a strongly reduced effective upper critical field B_{c2}^* , presumably at grain boundaries. A detailed analysis of the critical current distribution reveals that only a few percent of the wire is in a dissipative state at an electric field criterion of $1 \mu \text{V cm}^{-1}$, indicating that the used HIP parameters are not yet optimized.

1. Introduction

The Chevrel phase PbMo_6S_8 (PMS) is one of the candidates of the third generation of superconducting wires for ultra-high steady-state magnetic fields above 20 T. The combination of commercially available materials like NbTi and Nb_3Sn allows to obtain magnetic fields slightly above 20 T, and further improvements seem to be unlikely, because the critical transport current density J_c falls very rapidly as the upper critical field B_{c2} is approached. Therefore significant progress towards higher magnetic fields will be obtained only with new materials with higher B_{c2} . PbMo_6S_8 has an upper critical field $B_{c2}(0) > 50 \text{ T}$, although the critical temperature is only 15 K. The B_{c2} of PMS is about double that of Nb_3Sn [1]. High-temperature superconductors (HTSC) have even

higher upper critical fields, but it is not clear if this may be obtained in a practical conductor at 77 K. In our opinion, with respect to ease of manufacturing, there is no obvious advantage of HTSC conductors when 4.2 K operation is necessary.

PMS wires cannot be fabricated like NbTi or Nb_3Sn and a completely different approach, dealing with powder metallurgy, has to be employed. The pre-reacted superconducting powder or a precursor powder (mixture of different powders) is cold pressed, machined and passed into a metal tube which serves as a diffusion barrier (Mo, Nb or Ta). Molybdenum is the ideal barrier because, in contrast to Nb and Ta, there is no chemical reaction at all between the PMS and Mo, even at very high temperatures. A molybdenum barrier, however, requires hot wire drawing, which is not a real difficulty since the technology is

available on an industrial scale. After sealing, a second matrix material for thermal and mechanical stabilization is required. For the latter copper and stainless steel (ss) is used. The presence of stainless steel, which has a relatively high thermal expansion, serves also as a thermal stress compensation in order to adjust the thermal expansion of the matrix (barrier and stabilization) to that of the PMS [2]. After wire manufacturing the wire must be heat treated because the superconducting properties are degraded during the deformation process or, in the case of precursor powder, the superconducting phase has to be synthesized (in situ route). In addition, the connection of powder particles must be extremely good and constant over the length of the wire. Taking into account that PMS has a rather short coherence length, in the order of 2.7 nm at 4.2 K, this is a very difficult task. It is worth mentioning that the short coherence length is a common problem of ultra-high-field superconductors.

2. Earlier HIP work

To improve the quality of grain boundaries (connection of powder particles) researchers started to investigate heat treatments of PMS bulk and wire samples under isostatic argon pressure (HIP) up to 200 MPa. An astonishing result was that, up to now, it was not possible to improve the transport J_c in wires above approximately $2 \times 10^8 \text{ A m}^{-2}$ at 20 T and 4.2 K. This value can also be obtained using an optimized heat treatment, but without HIP.

Kubo et al. [3] were the first to apply the HIP technique on 400 mm long PMS wires with Ta/Cu matrix wound to a coil of OD 38 mm. HIP heat treatments of the coil have been carried out between 850°C and 1050°C for 1–3 h and pressures of 100–200 MPa. The best J_c was in the order of $2.15 \times 10^8 \text{ A m}^{-2}$ at 10 T and 4.2 K but the most important result, in our point of view, was the relatively high B_{c2}^* (4.2 K) = 45.2 T obtained by the extrapolation of a Kramer plot to $J_c = 0$ [4]. In later work, the critical current density could be substantially increased ($J_c = 1.3 \times 10^8 \text{ A m}^{-2}$ at 23 T and 4.2 K) by optimizing the powder composition and replacing the tantalum with a niobium barrier, but without HIP treatment. Rimikis [5] also used HIP heat treatment for

SnMo₆S₈ wires with a tantalum and a niobium barrier at 1000°C for 1 h and 100 MPa. With respect to a conventional annealing without pressure, nearly the same J_c have been obtained. Yamasaki et al. [6,7] were the first to apply HIP to PMS wires with a molybdenum barrier. It has been observed that conventionally annealed PMS wires show an important porosity and the J_c is limited to about $2 \times 10^8 \text{ A m}^{-2}$ at 8 T and 4.2 K. In addition, the ratio of $J_c(H_{\parallel})/J_c(H_{\perp})$ is near unity, suggesting a non-unidirectional, percolation-type current flow through the wire. The same wire treated by HIP at 1200°C for 12 h and at 200 MPa shows a substantial increase of $J_c > 5 \times 10^8 \text{ A m}^{-2}$ at 8 T and 4.2 K resulting in an improved high-field performance with $J_c = 9.7 \times 10^7 \text{ A m}^{-2}$ at 23 T and 4.2 K. In this case the current flow is much more unidirectional and the ratio $J_c(H_{\parallel})/J_c(H_{\perp})$ increases up to about 4. High-resolution SEM pictures indicate a clear improvement of the connectivity of PMS powder particles. By changing from an ordinary molybdenum quality to an ultra-high-purity, electron-beam-melted molybdenum the reproducibility could be improved by HIP at 1200°C for 2 h at 200 MPa [8]. Very recently, Hamasaki and Watanabe [9] started to investigate PMS wires with a Nb/ss matrix and with Sn doping (Pb_{1-x}Sn_xMo₆S₈ with $x=0, 1.1$ and 1.2) by HIP. With a heat treatment of 1100°C and for 45 min at 200 MPa, J_c may be increased from $\sim 1 \times 10^8 \text{ A m}^{-2}$ at 20 T and 4.2 K for $x=0$ to $\sim 1.7 \times 10^8 \text{ A m}^{-2}$ at 20 T and 4.2 K for $x=1.1$ and 1.2. No values have been given for conventional annealing without pressure.

PMS bulk samples have also been HIP treated. Goldacker et al. [10] used this technique in order to synthesize several kg of PMS as a starting material for wire drawing. Le Lay et al. [11] studied Pb_{1-x}Sn_xMo₆S₈ (x between 0 and 1.0) samples fabricated by a two-step procedure. After a first synthesis between 800°C and 900°C for 20 h in quartz tubes, a second treatment was performed at the same temperature and for 8 h, but under 200 MPa argon pressure. For this purpose, samples were wrapped in a Mo foil and sealed in an evacuated stainless steel tube. Although the morphology of the bulk samples shows substantial better connectivity of the HIP-treated samples with respect to pressureless sintered samples, J_c measured by magnetization did not change very much. The observation that magnetization scales

with the sample size suggests that there is no intrinsic granularity. This observation has been confirmed by Bonney et al. [12] in HIP-treated SnMo_6S_8 bulk samples by comparing $J_c(\Delta H)/J_c(\Delta M)$ where ΔH is the reversed external field to invert the critical state and ΔM is the magnetization hysteresis at a given external field. In the case where the ratio $J_c(\Delta H)/J_c(\Delta M)$ is approaching unity the better grains are connected, and deviations above 2 are characteristic for granular behavior [13]. HIP treatment has been carried out at 800°C for 8 h and at 200 MPa in a stainless steel container with the sample wrapped in a molybdenum foil. Without post-heat treatment a J_c of $8.2 \times 10^8 \text{ A m}^{-2}$ (9 T, 4.2 K) was deduced from magnetization measurements and this represents a new record for bulk samples. The same sample showed a T_c shift of 0.2 K by increasing the excitation field from 1 to 940 μT (103 Hz) of an AC-susceptibility measurement. Such a small shift is usually only observed in PMS single crystals [14]. The $J_c(\Delta H)/J_c(\Delta M)$ ratio is 0.9, again indicating a non-granular behavior.

Although the connectivity of grains can be improved by HIP, the modest increase of the critical transport current density suggests a more detailed study. In this paper we report the preliminary results on HIP treated PMS wires with Mo/ss matrix in order to obtain a better fundamental understanding. We have chosen a wire with a molybdenum barrier because, as it has been already mentioned, there is no chemical reaction between the PMS superconductor and the barrier, allowing rather high annealing temperatures.

3. Samples and heat treatments

The pre-reacted PMS powder for the manufacturing of the wire was synthesized by a 'conventional' method mixing Pb, MoS_2 and Mo with a stoichiometric composition and sealing the powder mixture in a quartz ampoule. After a first heat treatment at 1050°C for 50 h the powder was wet grinded in a WC ball mill. The powder was subsequently dried at 500°C under clean vacuum (turbomolecular pump) of about 10^{-5} mbar and subjected to a second annealing in a sealed quartz tube, again at 1050°C for 50 h. Before wire fabrication the PMS powder was sieved < 20 μm .

The onset of the critical temperature was at 13.2 K with a significant tail down to 7 K. The reduced T_c onset is typical for PMS powders prepared in quartz tubes and is due to oxygen contamination. The T_c tail may be attributed to an incomplete chemical reaction. The investigated wire was manufactured by Metallwerk Plansee and its fabrication is described elsewhere [15]. The outer diameter was 0.4 mm. About 10% of the total cross section was PMS, 22% Mo and 68% stainless steel. The pre-reacted PMS powder contained 10 wt.% precursor powder (PbS , MoS_2 and Mo) which is advantageous for the wire drawing process. HIP treatments at 990°C, 4 h and 1225°C, 4 h at ~ 110 MPa argon pressure were carried out on straight pieces of wire with a length of 13 cm and with sealed ends. The HIP cycles are quite arbitrary, but were imposed for cost reasons. As a reference, we also carried out heat treatments at 990°C, 4 h, but without applying isostatic pressure. A summary of the wire samples, together with the heat treatments, are given in Table 1. In Fig. 1 a micrograph of the wire is shown after a HIP cycle at 990°C, 4 h. Note the interdiffusion layer between the molybdenum barrier and the stainless steel matrix. The thickness of this layer varies as a function of temperature and annealing time. In particular, at temperatures above 1200°C, depending on the thickness of the barrier, it may happen that the barrier breaks and the PMS superconductor is contaminated by the stainless steel, resulting in an abrupt decrease of T_c and J_c . As an example, the critical thickness of the Mo barrier at 1225°C, 4h is about 50 μm .

4. Measurements and analysis

The following described wire samples are representative for several wires (2–3) treated under the

Table 1
Summary of the investigated PbMo_6S_8 samples and the applied heat treatment after wire manufacturing

Sample	Temperature (°C)	Time (h)	Pressure (MPa)
#1	990	4	ambient
#2	990	4	110
#3	1225	4	110

Fig. 1. Micrograph of Sample 2, heat treated at 990°C for 4 h under 110 MPa argon pressure (HIP). The sample has been etched in order to make visible the interdiffusion layer between stainless steel matrix and the molybdenum barrier.

same HIP condition. In a first step, the critical current density J_c of the straight wires, 13 cm in length, was measured at 4.2 K in a split coil system up to 7.5 T. Voltage taps were placed in the middle of the sample with a separation of 2 cm. Later, the samples were cut to a length of 3.5 cm in order to fit perpendicularly to the field in the cold bore of a hybrid magnet at the Nijmegen High Field Magnet Laboratory. After cutting, the wire ends were squeezed with a pair of tongs. Two pairs of voltage taps were made, each sensing about 0.7 cm of the wire. Fig. 2 shows J_c vs. a transverse applied magnetic field for wires with different heat treatments. As a criterion $1 \mu\text{V cm}^{-1}$ was used and the current density was calculated by dividing the critical current with the PMS cross section. In comparison to sample 1, which was annealed without pressure, applying HIP with 110 MPa at 990°C, 4 h and 1225°C, 4 h leads to a considerably improved J_c . Although far from being optimized, the field dependence of J_c is obviously better for 1225°C, 4 h, 110 MPa with respect to 990°C, 4 h, 110 MPa. However, in magnetic fields above 15 T, one can observe an anomalous bending of J_c to lower values which is an indication that the B_{c2}^* , determining the transport current, is not optimized [16]. Finally attention

Fig. 2. Critical current density vs. transverse applied magnetic field. Sample 1 is a reference for a normal heat treatment without HIP. Note the important increase of J_c for Sample 3 by cooling at 1.8 K. The bending down of J_c at fields above 15 T is due to a reduced B_{c2}^* of the path of current flow, in particular due to grain boundaries, as shown in the text. The dashed lines are a guide to the eye for non-granular behavior at high fields.

Fig. 3. n -exponent of the V - I characteristic ($V \propto I^n$) vs. applied field at 4.2 K of Samples 1–3. Note the important increase for the HIP treated samples and also for Sample 2 at 1.8 K.

should be drawn to the important increase of J_c by reducing the temperature to about 1.8 K.

The V - I characteristic in a critical current measurement can be described by $V \propto I^n$. Plotting $\log V$ vs. $\log I$ yields the n -exponent, which is a measure of the abruptness of the transition. In commercial superconductors (NbTi and Nb₃Sn) n varies typically between 10 and 100. It can also be shown that the higher n is, the more homogenous the conductor is with respect to the distribution of the critical current density [17]. In Fig. 3 the n exponent for all three wire samples is plotted as a function of the applied

field. There is a clear increase of n in the low-field regime (< 10 T) by applying HIP. For instance, at 7.5 T and 4.2 K the n changes from 29.7 to 42 after a heat treatment at 990°C, 4 h without and with 110 MPa pressure, respectively. Presumably with HIP at 1225°C, 4 h, the n is still higher (it was not possible to measure n at fields < 15 T due to thermal instabilities of the wire). At higher fields n flattens out but is still above 20 for sample 3 (1225°C, 4 h, 110 MPa) at 20 T and 4.2 K. The n -exponent can considerably be improved by reducing the temperature from 4.2 to 1.8 K. There is an increase of a factor of about two indicating that n at 20 T may be as high as 40.

Further, the flux flow regime of the V - I characteristic can be analyzed by calculating the second derivative d^2V/dI^2

$$\frac{d^2V}{dI^2} = Af(I).$$

This gives directly the distribution of the critical current $f(I)$ times a constant A , which describes the dissipative current flow processes [18]. In principle, information on the flow of magnetic flux can be obtained by analyzing A but the measurement must be deconvoluted due to current sharing between the superconductor and the surrounding matrix requiring an appropriate model [19]. One can define the mean critical current $\langle J_c \rangle$ by

$$\langle J_c \rangle = \frac{\int_0^\infty If(I) dI}{\int_0^\infty f(I) dI}$$

or the fraction of the wire dissipating energy at a particular current I

$$FD(I) = \frac{\int_0^I f(I') dI'}{\int_0^\infty f(I) dI}.$$

Our I_c measurements are computerized and the calculation of the critical current distribution by numerical means is straightforward. The set of measured V - I pairs were smoothed and differentiated twice following the method of Savitsky and Golay [20]. The smoothing consists in selecting m data points on both sides of the point of interest and to fit them by a quadratic curve. The second derivative can then be calculated at this point. The complete d^2V/dI^2 curve is obtained by shifting the $2m+1$ data points stepwise through the whole data set. It has been

shown by Warnes et al. [18] that the choice of m is not very critical for the position of peaks as well as the calculation of $\langle J_c \rangle$ and $FD(I)$, but the detailed features of the I_c distribution may be oversmoothed (m too big) or they may disappear in the noise (m too small). In the analysis presented here, a value of $m=5$ was always used.

In Fig. 4 the distribution d^2V/dI^2 for samples 1, 2 and 3 at 7.5 T and 4.2 K is shown. Supposing a constant cross section of the superconducting filament, the current can be transformed to a current density. The critical current density as obtained by the $1 \mu V$ cm $^{-1}$ criterion and the mean critical current density $\langle J_c \rangle$ is also indicated. Note the pronounced improvement of critical current densities by HIP treatment, going from 2.5×10^8 A m $^{-2}$ ($\langle J_c \rangle = 3.0 \times 10^8$ A m $^{-2}$) to 4.3×10^8 A m $^{-2}$ ($\langle J_c \rangle = 4.8 \times 10^8$ A m $^{-2}$), for a heat treatment at 990°C, 4 h without and with 110 MPa argon pressure, respectively. The relative difference between J_c and $\langle J_c \rangle$ is decreased by employing HIP indicating a sharpening of the J_c distribution. For sample 3, which was HIP treated at 1225°C, 4 h at 110 MPa, there is a further modest improvement of J_c up to 4.5×10^8 A m $^{-2}$ but the complete distribution could not be obtained for thermal instability reasons.

Fig. 4. Distribution of the critical current density d^2V/dI^2 ($m=5$) at 7.5 T and 4.2 K for Sample 1 (990°C, 4 h) and the HIP treated Samples 2 and 3. For Sample 3 not sufficient data points are available in order to calculate the complete distribution.

Fig. 5 presents the J_c distribution for sample 2 (990°C, 4 h at 110 MPa) at 4.2 K between 17.5 and 22.5 T. Obviously with increasing field there is a broadening of the peak together with the appearance of a low- J_c tail. Because the $1 \mu\text{V cm}^{-1}$ criterion is very sensitive to this low- J_c tail, the bending down of J_c vs. field in Fig. 2 can be explained. The broadening can be quantified by calculating $J_c/\langle J_c \rangle$ which yields 0.807, 0.676 and 0.607 by going from 17.5 to 20 and 22.5 T, respectively. The increase of the HIP treatment temperature from 990°C, 4 h to 1225°C, 4 h brings a sharper J_c distribution at high fields (Fig. 6). With respect to sample 2 in Fig. 5 the $J_c/\langle J_c \rangle$ is now 0.727 and 0.636 for fields of 20 and 22.5 T, respectively. Note also the indication for a shoulder on the left side of both distributions which will be discussed later.

The effect on the critical current distribution of sample 2 at 15 T (highest field for the 1.8 K measurement) by reducing the temperature is shown in Fig. 7. Comparison with sample 3 was not possible because the wire is thermally unstable under these conditions. For 1.8 K there is not only a spectacular shift of J_c to higher values, there is again a sharpening; $J_c/\langle J_c \rangle$ goes from 0.812 to 0.885.

Sample 3 was re-measured about six weeks later

Fig. 5. Distribution of the critical current density d^2V/dI^2 ($m=5$) at 4.2 K and fields between 17.5 and 22.5 T (Sample 2 990°C, 4 h, 110 MPa). J_c was determined by the $1 \mu\text{V cm}^{-1}$ criterion. The mean $\langle J_c \rangle$ is also indicated.

Fig. 6. Distribution of the critical current density d^2V/dI^2 ($m=5$) at 4.2 K and fields at 20 and 22.5 T (Sample 3 1225°C, 4 h, 110 MPa). J_c was determined by the $1 \mu\text{V cm}^{-1}$ criterion. The mean $\langle J_c \rangle$ is also indicated.

Fig. 7. Distribution of the critical current density d^2V/dI^2 ($m=5$) at 4.2 and 1.8 K and a field of 15 T, the highest available field for the 1.8 K measurement (Sample 2 990°C, 4 h, 110 MPa). J_c was determined by the $1 \mu\text{V cm}^{-1}$ criterion. The mean $\langle J_c \rangle$ is also indicated.

because it was planned to complete the J_c data at 1.8 K. Surprisingly, the high-field values of J_c could not be confirmed and there was a degradation (Fig. 8). By analyzing the J_c distribution a double peak was

Fig. 8. Critical current density vs. transverse applied magnetic field remeasured six weeks later at 4.2 and 1.8 K for Sample 3, heat treated at 1225°C for 4 h under 110 MPa argon pressure (HIP). The dashed lines indicate the earlier observed J_c as in Fig. 2.

Fig. 9. Distribution of the critical current density d^2V/dI^2 ($m=5$) at 4.2 K and fields between 19 and 25 T remeasured six weeks later with respect to the measurement of Fig. 6 (Sample 3 1225°C, 4 h, 110 MPa). J_c was determined by the $1 \mu\text{V cm}^{-1}$ criterion. The double peak can be attributed to inter-grain J_c (left peak) and to intra-grain J_c (right peak).

discovered. This is shown in Fig. 9 for measurements at 4.2 K and fields between 19 and 25 T. A very similar behavior was observed on the second pair of voltage taps, separated by about 0.7 cm. Note that the peak on the left has a strong field dependence, whereas that on the right does not move very much. In the following section arguments are given that the dou-

ble peak may be attributed to inter-grain J_c (strong field dependence) and intra-grain J_c (small field dependence).

Kramer plots were tempted for an estimate of the upper critical field B_{c2}^* , limiting the critical current density at high fields. This is shown in Fig. 10 for samples 2 and 3. J_c values were taken generally above 10 T because below there is a deviation from a straight line. Note that the extrapolated B_{c2}^* is between 33.1 and 33.3 T, nearly the same for both samples. However, the slope is quite different, reflecting the better J_c performance below B_{c2}^* of the sample HIP treated at 1225°C, 4 h. These anomalously low B_{c2}^* are often observed in bulk and wire samples where a critical current is flowing, either as a transport or a screening current. In Fig. 11 a Kramer plot of sample 3, re-measured six weeks later is shown. The extrapolated B_{c2}^* ($1 \mu\text{V cm}^{-1}$) is now reduced to 30.0 T, by 3 T with respect to the earlier measurement. Due to a different field dependence of the peaks in the critical current density distribution in Fig. 9, it is also interesting to make a Kramer plot using the J_c peaks. The extrapolated B_{c2}^* by using the J_{c1} peak gives 31.4 T, a value quite similar to that using the $1 \mu\text{V cm}^{-1}$ criterion. More exciting is the observation of a B_{c2}^* of 46.4 T by taking the J_{c2} peak. This high B_{c2}^* is very near that of bulk samples measured by specific heat in high fields, an experiment where the properties of

Fig. 10. Kramer plot for Sample 2 990°C, 4 h, 110 MPa and Sample 3 1225°C, 4 h, 110 MPa yielding a B_{c2}^* of 33.1 and 33.3 T at 4.2 K, respectively.

Fig. 11. Kramer plot for Sample 3 1225°C, 4 h, 110 MPa remeasured six weeks later (with respect to Fig. 10) showing a double peak in the J_c distribution. Taking the position of the two peaks results in a B_{c2}^* at 4.2 K of 31.4 and 46.4 T. Note that the data, obtained before degradation, are nearly on the same line as the J_{c2} -peak data.

the grains (not of the grain boundaries) are investigated [23].

5. Discussion

One of the most striking properties of PbMo_6S_8 is the strong temperature dependence of J_c . As seen in Fig. 2, by changing the temperature from 4.2 to 1.8 K the critical current density can be raised more than 50%, depending on the magnetic field. At the same time J_c vs. applied field is improved in the high-field regime. The behavior of PMS can be explained by considering a scaling law for the volume pinning force, $P_v = J_c B = g B_{c2}^{*m} b^p (1-b)^q$, assuming that the Ginzburg–Landau parameter κ does not change in the considered temperature range. g is a pre-factor, essentially given by the microstructure of the superconductor, b is the reduced field $b = B/B_{c2}^*$ and m , p and q are exponents determined by experiment. B_{c2}^{*m} describes the temperature dependence and $b^p (1-b)^q$ the field dependence. In well prepared PMS samples this scaling law is valid, indicating a unique pinning mechanism working over the considered temperature and field range [16,21].

Specific heat measurements of PMS bulk samples

revealed that samples with a small T_c distribution, on the order of < 1 K, have an m -exponent of 2.4 ± 0.2 [21]. In the case of a large T_c distribution, and consequently of a more inhomogeneous material, m can increase above 3. Knowing the critical temperature of the sample, as well as B_{c2}^* at a particular temperature, one can calculate B_{c2}^* for other temperatures and then estimate the increase of J_c going from 4.2 to 1.8 K. In order to calculate $B_{c2}^*(T)$ the following formula for a superconductor in the dirty limit was used [24]. $B_{c2}^*(t) = 3.56 B_{c2}^*(0) \rho_{AG}(t)$ with $\rho_{AG}(t)$ the Abrikosov–Gorkov function and $t = T/T_c$, the reduced temperature. For instance taking $T_c = 12$ K as an average T_c of the used PMS powder, one can calculate the increase of B_{c2}^* by changing the temperature from 4.2 to 1.8 K. For $B_{c2}^*(4.2 \text{ K}) = 33.3$ T of sample 3 (without degradation) one obtains $B_{c2}^*(1.8 \text{ K}) = 39.6$ T. Finally, a value of $m = 2.4$ would yield an improvement of J_c of 52%, the right order of magnitude to account for the measurements. The situation is similar in NbTi where the m -exponent for optimized wires is between 2.0 and 2.1 [31]. However, most important is the relative change of B_{c2} upon variation of the temperature. The ratio $B_{c2}(1.8 \text{ K})/B_{c2}(4.2 \text{ K}) \approx 1.3$ and 1.2 for NbTi and PMS, respectively. Nb₃Sn does not show an important temperature dependence because $B_{c2}(1.8 \text{ K})/B_{c2}(4.2 \text{ K})$ is nearly unity.

Changing the HIP temperature from 990°C to 1225°C improves the field dependence of J_c in an important way. If there would not be the bending down of $J_c(4.2 \text{ K})$ above 17 and 15 T of samples 2 and 3, respectively, one would end up with higher, and quite different B_{c2}^* , instead of the nearly equal 33.1 and 33.3 T. It seems that a HIP treatment at 1225°C, 4 h at 110 MPa is of advantage but not optimal. One comes to the same conclusion by analyzing the critical current density distribution. Comparing the high-field J_c distribution of Fig. 5 (sample 2) with that of Fig. 6 (sample 3) shows an important improvement of J_c and a slight sharpening by increasing the HIP temperature from 990°C to 1225°C. As already mentioned, the low- J_c tail is responsible for the determination of J_c by an electric field (i.e. $1 \mu\text{V cm}^{-1}$) or a resistivity criterion (i.e. $10^{-14} \Omega \text{ m}$). The ratio of $J_c/\langle J_c \rangle$ is a measure how far J_c is from the mean $\langle J_c \rangle$ and finally from an optimized heat treatment. In Table 2 the $J_c/\langle J_c \rangle$ ratio, together with $\text{FD}(J_c)$, the

Table 2

The ratio of J_c ($1 \mu\text{V cm}^{-1}$) and the mean $\langle J_c \rangle$, obtained from the J_c distribution, $J_c/\langle J_c \rangle$, as well as the fraction of the wire dissipating energy at J_c ($1 \mu\text{V cm}^{-1}$) $\text{FD}(J_c)$, for HIP treated samples 2 and 3 at fields between 17.5 and 22.5 T at 4.2 K

B (T)	#2 990°C, 4 h, 110 MPa		#3 1225°C, 4 h, 110 MPa	
	$J_c/\langle J_c \rangle$	$\text{FD}(J_c)$	$J_c/\langle J_c \rangle$	$\text{FD}(J_c)$
17.5	0.807	0.0280		
20.0	0.676	0.0141	0.727	0.0026
22.5	0.607	0.0346	0.636	0.0020

fraction of the wire creating $1 \mu\text{V cm}^{-1}$ (dissipative state), is summarized. Referring to the work of Warnes et al. [18] the ratio $J_c/\langle J_c \rangle$ can go up to 0.97 and 0.91 for NbTi and Nb₃Sn, respectively. The J_c criterion of Warnes et al. is more severe ($10^{-14} \Omega \text{ m}$) than ours ($1 \mu\text{V cm}^{-1}$) so representing a lower bound estimate. The general feature, to have a broadening of the J_c distribution near B_{c2} , can also be seen in our data. More striking is the observation that in the high-field regime $\text{FD}(J_c)$ is only 0.0141–0.0346 for sample 2. In the case of sample 3 this is one order of magnitude lower: 0.0020–0.0026. As indicated in Fig. 7, the situation may be improved at 1.8 K. The $\text{FD}(J_c)$ increases from 0.004 to 0.025 and the $J_c/\langle J_c \rangle$ from 0.812 to 0.885.

In well manufactured and heat treated technical superconductors, such as NbTi and Nb₃Sn, $\text{FD}(J_c)$ is in the order of typically 0.20–0.30 [18]. The latter mentioned value can be much smaller, 0.02–0.03, where sausing of the superconducting filament appears (NbTi) or the heat treatment was not appropriate (Nb₃Sn). Obviously this leads to the suggestion that in the PMS wire samples, presented here, similar mechanisms are responsible. Sausaging is not regularly observed in the PMS wires, at least at the above mentioned length scale. It is supposed that primarily the HIP heat treatment is not optimized. Due to a better $\text{FD}(J_c)$, it seems that the 990°C 4 h heat treatment is closer an optimum than in the case of sample 3 (lower $\text{FD}(J_c)$). However, J_c of sample 3 is higher, although the $\text{FD}(J_c)$ is very small. This indicates also that there is a more important potential for improvement at 1225°C.

HIP parameters may certainly be improved, but longer annealing times at 1225°C or even higher temperatures must be excluded because of the interdiffusion layer between stainless steel and the molyb-

denum barrier. One possibility is to increase the pressure which is equivalent to a higher temperature. This is also a way to decrease the temperature for the same result but with less reaction between the matrix materials. Although not optimal, the rather high temperatures are probably related to the PMS powder. Up to now experience gained with other wire constructions and other types of powders indicate that temperatures can be reduced.

A further argument for a non optimized HIP treatment may be the observed degradation of J_c with time (aging) by comparison of Figs. 6 and 9. As mentioned, there were six weeks between the two measurements. The beginning of degradation can already be seen in Fig. 6 by a little shoulder on the left side of the peak. In Fig. 9 one observes a dramatic broadening of the J_c distribution towards lower J_c . Very striking is the appearance of two peaks, suggesting two mechanisms responsible for the transport J_c . By investigating the field dependence of both peaks, as in Fig. 11, one can deduce two upper critical fields 31.4 and 46.4 T at 4.2 K. In earlier work, Cattani [21,22] plotted the J_c of PMS bulk samples, determined from total flux measurements, as a function of B_{c2} , measured by AC susceptibility in DC fields. Depending of the preparation condition, B_{c2} can vary considerably and there is a clear improvement of J_c with increasing B_{c2} . Some of these samples were measured calorimetrically (specific heat) in magnetic fields. It was found that the $B_{c2}(0)$ from specific heat measurements yield values between 51 and 53 T ($T_c = 14.4$ – 14.8 K) and there is no correlation with J_c . Due to the fact that a specific heat measurement senses essentially the bulk properties of the sample leads to the suggestion that the so obtained B_{c2} values belong to the grains. This is true where the fraction grain volume/grain boundary volume is high. Sup-

posing a mean grain size of 5 μm , as in conventional PMS powders, and the thickness of the grain boundary of 1 nm, this ratio is in the order of 830. Such a high ratio could not be resolved with the specific heat experiment. However, B_{c2} obtained by χ_{AC} measurements in DC fields or by critical current measurements are sensitive to the path where the critical current flows. The measuring current senses the physical properties on this path, including grains and grain boundaries. For reasons given above, it is suggested to call the upper critical field, estimated by experiments with critical current flow B_{c2}^* , the effective upper critical field.

Finally, one has to check, if the B_{c2} (4.2 K) of 46.4 T in Fig. 11 is a realistic value. Cors [23] was able to measure initial slopes $(dB_{c2}/dT)_{T=T_c}$ for various PMS bulk samples by specific heat up to 25 T. The knowledge of these slopes together with the corresponding critical temperatures allows to calculate $B_{c2}(T=0)$ by $B_{c2}(0) = 0.693 T_c (dB_{c2}/dT)_{T=T_c}$ and B_{c2} at 4.2 K as mentioned above [23]. However, it is important to note that this kind of calculation is only valid for a superconductor in the dirty limit. An interesting result found by Cors was that starting with a T_c of 14.5 K the initial slope was -5.5 T/K resulting in a $B_{c2}(0) = 55$ T. Reducing T_c to 14.0 K, by changing the nominal composition of sulfur, the initial slope increased to -6.0 T/K with $B_{c2}(0) = 58$ T. Another sample was contaminated by oxygen and had a $T_c = 11.3$ K. In spite of this strongly reduced T_c , the initial slope was -6.8 T/K leading to $B_{c2}(0) = 53$ T. Although $T_c(\text{onset})$ varies between 14.5 and 11.3 K, $B_{c2}(0)$ varies only between 55 and 53 T, respectively. Such behavior is characteristic for a superconductor in the clean limit and the values given are therefore lower bound estimates. In reality one can expect higher B_{c2} [25]. However, a $T_c(\text{onset})$ below 11.3 K leads also to a substantial reduction of $B_{c2}(0)$ which indicates that the material changed from the clean limit to the dirty limit [23,25]. The extrapolated 46.4 T at 4.2 K in Fig. 11 fits well to these data supposing a T_c between 11.3 and 14.0 K. It seems to be reasonable, consequently, to attribute the low- J_c peak in Fig. 9 to the J_c of the grain boundaries and the high- J_c peak to grains.

This picture can also be confirmed by analyzing the reduced volume pinning force $P_v/P_{v\text{max}}$ vs. the re-

duced field b shown in Fig. 12. For the calculation of b the B_{c2}^* of the Kramer plot were used. The maximum of the volume pinning force for sample 2 is near a reduced field of $b = 0.2$. This indicates pinning of grain boundaries as in Nb_3Sn . Such a behavior is observed in many experiments with PbMo_6S_8 and one can show that the pre-factor g of the scaling law changes by varying the mean grain size [21,26]. Small mean grain size increases the volume pinning force. However, sample 3 HIP treated at 1225°C has the maximum of P_v near $b = 0.4$. This is an indication that grain boundary pinning is less relevant and pinning by precipitations and plane boundaries may become dominant [27]. After degradation of J_c , the maximum P_v is shifted to about $b = 0.35$.

It cannot be excluded that the observed degradation of J_c in the high-field regime has another origin. The thermal expansion of PMS is much higher than that for the molybdenum barrier [28]. By cooling from the annealing temperature to helium temperature the PMS comes under tensile strain. In order to compensate this behavior, and for mechanical reinforcement, the stainless steel matrix is added. To adjust the thermal expansion of the matrix to that of the PMS is a matter of the right fraction of stainless steel and molybdenum. In this way a state of minimum strain at low temperatures of PMS can be obtained resulting in an optimum J_c . Ekin et al. [29] carried

Fig. 12. Normalized volume pinning force $P_v/P_{v\text{max}}$ vs. reduced field $b = B/B_{c2}^*$. The upper critical field was obtained by a Kramer plot (see Fig. 10). As a guide to the eye the functions $b^{1/2}(1-b)^2$ and $b(1-b)^2$ are drawn.

out the first J_c measurements under uniaxial strain of PMS wires and tapes. B_{c2}^* was estimated by fitting a scaling law and it was found that the uniaxial strain dependence of PMS leads to a decrease from $B_{c2}^*/B_{c2m}^* = 1-0.86$ for a tensile strain of 0.4%. B_{c2m}^* is the highest observed value by plotting B_{c2}^* vs. strain. These data were completed by Goldacker et al. [30] for compressive strain. B_{c2}^*/B_{c2m}^* decreases from 1 to 0.95 for a compressive strain of 0.2%. The J_c degradation of sample 3, measured in a time interval of six weeks, is related to a reduction of $B_{c2}^* = 33.1-30.0$ T. Supposing that 33.1 T corresponds a nearly strain-free state, the reduction can be explained by a tensile (or compressive) strain of about 0.3%. The still open question is now why the wire should come preferentially under tensile strain as a function of time. We have already observed time dependence of J_c in earlier experiments where the wire samples were particularly short, typically 2.5 cm long. By sealing the ends or by increasing the length of the wire this time effect disappeared. The behavior can be explained by a relaxation of thermally induced stress (mismatch of thermal expansion) over the open, or not well sealed, ends of the wire. In the case where the stainless steel cannot further compensate the thermal expansion of the molybdenum barrier, the PMS core comes under tensile strain.

6. Conclusions

In conclusion, it was shown that the introduction of isostatic pressure for heat treatments of PbMo_6S_8 wires can be an interesting additional parameter. At 990°C a very pronounced increase of J_c was observed in the low-field regime (7.5 T) by applying 110 MPa argon pressure. By increasing the HIP temperature to 1225°C the J_c at low fields does not improve. In the high-field range around 20 T, where an excellent J_c performance is required for high-field insert coils, the 1225°C are clearly better than the 990°C because the field dependence of J_c is more flat. It was also possible to push the maximum of the volume pinning force at 4.2 K to reduced fields well above 0.2, signifying that other pinning centers than grain boundaries are active. However, at fields above 15 T a granular behavior is observed which is deemed responsible for

the anomalous depression of J_c . Analysis of the critical field B_{c2}^* as well as of the distribution of the critical current density suggests that the HIP treatment used is not yet optimal and, as a consequence, there is a degradation of J_c . Arguments were given to show that the quality of grain boundaries is most probably at the origin of degradation.

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