Critical Current Limiting Factors of Hot Isostatically Pressed (HIPed) PbMo₆S₈ Wires

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Abstract—PbMo₆S₈ wires with a molybdenum barrier and a stainless steel matrix were hot isostatically pressed (HIP) at 990 °C and 1225 °C for 4 hours at 110 MPa. The critical current density, its distribution, as well as the ac-susceptibility were investigated. The higher the applied HIP temperature, the better the critical current density becomes. A comparison of inductive Tc transitions suggests that HIPing is able to considerably reduce the width of the transition. In addition, at 1225 °C, the Tc onset is shifted from 12.4 K to 14.2 K. The high field behavior of Jc strongly depends on the effective upper critical field which is essentially determined by grain boundaries. In a degraded wire sample, a qualitative correlation between the effective upper critical field and the width of the inductive transition was found. This knowledge should allow to overcome the apparent limitation of Jc at high fields (2 x 10⁸ Am⁻² and 3 x 10⁸ A m⁻² at 20 T, 4.2 K and 1.8 K, respectively).

I. INTRODUCTION

For practical applications, PbMo₆S₈ (PMS) is the most interesting compound of the family of Chevrel phases. Although a low temperature superconductor, with a Tc of 15 K, the upper critical field is ~ 51 T at 4.2 K and increases to nearly 59 T at 1.8 K [1], [2]. This physical property allows PbMo₆S₈ to be a candidate for the third generation of superconducting wires for ultra high field magnets in excess of 20 T. A PMS high field insert is particularly suited to work in combination with NbTi and Nb₃Sn coil sections at 2.2 K (1.8 K) because the critical current density can be improved by about 40 % with a reduction of temperature from 4.2 K to 2.2 K (1.8 K). The V-I transition at fields > 20 T can be kept steep, corresponding to n-values in the range of 40 or more [12]. In addition, PMS is nearly isotropic and round monofilament or multifilament wires can be manufactured on an industrial scale [3].

Due to the fact that PMS wires cannot be manufactured in the same manner as NbTi or Nb₃Sn, a powder metallurgical approach was developed by many groups [4]. At present, hot drawing parameters of PMS wires with a Mo barrier are not yet optimized, often leading to the formation of micro cracks (or density variations) running under a 45 ° angle with respect to the wire axis. This situation requires a heat treatment after the wire fabrication in order to sinter the PMS core. Presumably, due to differential thermal expansion (contraction), ordinary annealing, at ambient pressure, is limited to about 800 °C. At higher temperatures, there is no sintering and the critical current density decreases. Hot isostatic pressing (HIP), however, enables to overcome this problem and better sinter conditions can be obtained. A more detailed description of the influence of HIP on superconducting parameters of PMS wires with a Mo barrier is the main objective of this paper.

HIPing of PMS wires was already carried out by several authors [5] - [10].

II. EXPERIMENTAL AND RESULTS

This study was carried out on 0.4 mm (OD) PMS wires with a Mo barrier and a stainless steel (ss) matrix manufactured by Metallwerk Plansee. The area fractions were as follows: 10 % PMS, 22 % Mo and 68 % ss. Pre-reacted PMS powder together with 10 w% of precursor powder (PbS + Mo + MoS₂) were used. The wires were submitted to HIP treatments with argon between 990 °C and 1225 °C for 4 hours at 110 MPa (1.1 kbar). Where appropriate, the same heat treatments were undertaken without applying an isostatic pressure (ambient pressure).

A minimum temperature is required in order to apply the isostatic pressure on the PMS core. This lower limit temperature is not precisely known but is in the range of 800 °C. The upper limit of temperature is given by an interdiffusion between the Mo barrier and the stainless steel matrix. A damage of the barrier may also be introduced during the deformation process, in particular when 100 °C, ordinary annealing, at ambient pressure, is limited to about 800 °C. At higher temperatures, there is no sintering and the critical current density decreases. Hot isostatic pressing (HIP), however, enables to overcome this problem and better sinter conditions can be obtained. A more detailed description of the influence of HIP on superconducting parameters of PMS wires with a Mo barrier is the main objective of this paper.

Critical current density measurements up to 25 T were performed at the High Field Magnet Laboratory and Research Institute for Materials at the University of Nijmegen. For this purpose the straight wire samples were cut to a length of 35 mm (in order to fit perpendicularly to the field direction) and the ends were squeezed with a pair of tongs. After
soldering on the sample holder, two pairs of voltage taps were fixed by silver paint, sensing 2 x 6 mm of the sample length. Jc results for three different heat treatments, representative for two to three samples and both voltage taps, are plotted in Fig. 1. The Jc was defined by the 1 μV cm⁻¹ criterion and taking the PMS cross section, determined by micrographs.

With respect to an ordinary heat treatment at 990 °C (without HIP), there is an improvement of Jc when applying 110 MPa isostatic pressure. A further improvement, in particular at higher fields, can be obtained by increasing the HIP temperature to 1225 °C. The effective upper critical field B* 2, estimated by a Kramer plot, is nearly the same for both HIP temperatures, namely 33.1 T and 33.3 T. The HIP temperature influence on the distribution of the current density, obtained by the calculation of d²V/dI² of the V-I curve of the Jc measurement [15], is plotted in Fig. 2. Note the considerable sharpening at 1225 °C.

The inductively measured critical temperatures of the same PMS wires subject to the above mentioned heat treatments is shown in Fig. 3. The Tc-onset for the 990 °C annealing is at 12.4 K, independent if HIP is applied or not. An important difference can be seen in the width of the transitions. Under isostatic pressure the latter can be reduced considerably. An increase of the HIP temperature to 1225 °C can also shift the onset up to 14.2 K with a completed transition at 13 K. The hatched area in Fig. 3 indicates the variation of the inductive transition over 4 cm of the length of the wire (the length of the detection coil is 5 mm). This scatter can also be observed in the 990°C HIP treatment but only the transition width varies and the Tc onset stays constant. The wire treated at 990 °C without HIP did not show any variation of the Tc transition over the considered length (4 cm).

The critical current density of the HIPed wire at 1225 °C was re-measured six weeks later and a degradation of Jc at fields > 10 T was observed (Fig. 4). Simultaneously, the effective upper critical field (estimated by a Kramer plot) was reduced from 33.3 T to 30.0 T. The understanding of such a behavior is important, because measures can be taken against the low B* 2 and, consequently, of the anomalous fall off of Jc above 15 T. In Fig. 5 the distribution of the critical current density after degradation is plotted. Note the appearance of a double peak. By analyzing the field dependence of these peaks, again by a Kramer plot, one obtains an upper critical field of the left hand peak of 31.4 T and of 46.4 T for the right hand peak. As it is shown in Ref. [12], the lower value may be attributed to the effective upper critical field of grain boundaries and the higher value to the

Fig. 1. Critical current density vs. transverse magnetic field for three different heat treatments. The after Kramer extrapolated effective B* 2 is 33.1 T and 33.3 T for the HIPed wire samples at 990 °C and 1225 °C, respectively. The dashed curve was calculated with a scaling law, supposing an optimized B* 2 of 51 T at 4.2 K [12].

Fig. 2. The distribution of the current density for two different HIP temperatures.

Fig. 3. Normalized ac susceptibility vs. temperature for three different heat treatments. HIPing at 990 °C acts preferentially on the width of the transition. HIPing at 1225 °C results in addition to an improvement of the Tc-onset. The hatched area indicates Tc variations over the wire length of 4 cm.
Fig. 4. Critical current density vs. transverse applied field of a HIP treated wire at 1225 °C for 4 hours and at 110 MPa. The same wire was re-measured 6 weeks later, showing degradation at high fields. The degradation is presumably caused by the relaxation of thermally induced strain on the PMS core.

$B_c^2$ of grains.

In order to better understand the degradation, the $T_c$ was re-measured after degradation and the result is shown in Fig. 6. The hatched area presents the measurement before degradation and over a wire length of 4 cm. In the worst case, the transition starts at 10 K. The transition after degradation was measured exactly at the two positions of the voltage taps of the $J_c$ experiment and begins at ~8 K.

III. DISCUSSION

H. Yamasaki et al. [9] already reported that the connectivity between PMS grains can be improved by a HIP treatment, resulting in an increase of $J_c$. Comparing the 990 °C data (Fig. 1), we made the same observation at fields $< 10$ T. However, a higher HIP temperature, e.g. 1225 °C, gives a further improvement of $J_c$ in fields above 8 T, although the estimated $B_c^2$ is approximately the same for HIPping at 990 °C and 1225 °C. This behavior can be explained by analyzing the pinning force vs. reduced field [12]. HIPping at 990 °C yields a maximum pinning force at a reduced field of $b \approx 0.2$ which is an indication for grain boundary pinning, such as in Nb$_3$Sn. At 1225 °C the maximum of the pinning force is shifted to $b \approx 0.4$, indicating that intra grain pinning becomes dominate [16].

As mentioned before, the high field behavior of $J_c$ depends strongly of the effective upper critical field. In this paper, as well as in other literature, the reported values of $B_c^2$ are below those measured by specific heat [2], [14]. Such an observation, together with an estimated intra grain $J_c$ of one order of magnitude higher then the inter grain $J_c$, indicates a granular behavior [11], [13], [19]. In Ref. [11] $B_c^2$ of PMS is discussed in more detail and it has been shown that, due to a subtle transition between a clean and dirty limit behavior, $B_c^2(0)$ is nearly constant for a $T_c$ onset between roughly 11.5 K and 14.5 K. We fitted these data [2], [11], [14] and observed a maximum of $B_c^2(0)$ at a $T_c$ onset of 13 K which is 63.3 T in the clean limit and 60.3 T in the dirty limit approximation. The maximum of $B_c^2$ at practical temperatures is as follows: $B_c^2(1.8K) = 58.7$ T and $B_c^2(4.2K) = 51.1$ T. The corresponding $T_c$ onset temperature is slightly shifted to 13.1 K and 13.3 K at 1.8 K and 4.2 K, respectively.

It is now interesting to see the influence of HIPping on the critical temperature. It seems that HIP at low temperatures (990 °C) acts preferentially on the width of the transition, reducing the low $T_c$ tail. At higher temperatures (1225 °C) the $T_c$ onset is also shifted to higher values. There are several factors influencing $T_c$ and its transition width of the ac-susceptibility [11]. The observed behavior may be explained.

Fig. 5. The distribution of the critical current density after degradation. By analyzing the field dependence of the peaks one can attribute the left hand peak to grain boundaries and the right hand peak to grains [12].
by a chemically inhomogenous state before HIPing. The PMS powder applied in the wire was synthesized in a quartz ampoule at 1050 °C [12]. The onset of \( T_c \) was situated at 13.2 K with a transition width going to 7 K. Synthesis in quartz ampoules introduces easily oxygen contamination, resulting in a reduction of \( T_c \), and 1050 °C is too low for this type of synthesis in order to get homogenous PMS [11]. The presence of 10 w% of precursor powder (PbS, MoS\(_2\) and Mo) may also contribute to a chemically non homogenous situation. The variation of \( T_c \) as a function of the wire length can be explained by this, but can also be an indication that the HIP process is not yet optimized. Nevertheless, the tendency for a reduction of the transition width, together with a shift of the \( T_c \) onset to higher temperatures by applying HIP is very encouraging for a PMS wire technology based on a molybdenum barrier. In the case of a niobium barrier, one observes exactly the opposite, even without HIP. The heat treatment after wire manufacturing causes a broadening of the \( T_c \) transition and the \( T_c \) onset decreases due to the reactivity of Nb with respect to PMS [20], [21]. For instance at 900 °C, after already 30 minutes of annealing, this broadening occurs, indicating that lower temperatures are necessary in order to overcome this problem [21].

Generally speaking, in the case where the \( T_c \) transition, goes below approximately 13 K (maximum of \( B_{c1} \)), the upper critical field is reduced. This is supported by the observation of an increased \( T_c \) transition width in a degraded wire sample as shown in Fig. 6. At present, mainly due to the inhomogenous nature of the wire, this is only a qualitative correlation. It is worth to mention that in long length PMS wires no time dependent effects of \( J_c \) are known. Degradation of \( J_c \) is only observed in short wire samples. The most probable reason is that the thermally induced stress is reduced over the ends of the wire, putting the superconductor eventually under tensile stress. Because the effective upper critical field is reduced, which is also the case by applying an uniaxial strain on PMS wires [17], [18], this explanation seems to be reasonable.

As shown in Fig. 2, the distribution of the current density is much smaller at 1225 °C as at 990 °C. At 1225°C the fraction of the wire generating 1 \( \mu \)VCm\(^{-1} \) is in the order of 0.2 % [12]. Because similarly low values were observed in badly heat treated Nb3Sn wires [15], it is supposed that the HIP treatment can be improved. In commercial superconducting wires this value can go up to 20 % to 30 % [15].

In conclusion, the better knowledge of the degraded state enables us to understand why critical current densities of PMS wires in literature seem to be limited to about 2\( \times 10^8 \) Am\(^{-2} \) at 20 T and 4.2 K. It is imperative that the superconducting transition does not go below approximately 13 K, where the optimum of the upper critical field is expected [2], [11], [14]. In the case of a PMS wire with a niobium barrier, this a particular difficult task. In PMS wires with a molybdenum barrier, the availability of high quality PMS powder [11], together with optimized HIP conditions (or hot deformation parameters), should allow a considerable improvement of the (effective) upper critical field, and consequently, of \( J_c \) at high fields.

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