Development of gas pressure melting (GPM) method for Ag-sheathed Bi-2212 wires

Effect on void refinement and superconductivity

T. KANAI, N. INOUE
Hitachi Research Laboratory, Hitachi Ltd., 1-1, Omika-cho 7-chome, Hitachi-shi, Ibaraki-ken, 319-12 Japan

A serious problem for Ag-sheathed Bi-2212 wires produced by a partial melt process is an oxygen release which causes effluence of the oxide materials from the Ag sheath and/or formation of voids inside the sheath. To solve it, the oxygen release from the powders should be minimized and any voids should be small and homogeneously distributed. Using formed powders with minimized oxygen content, we investigated melting atmospheric conditions on the properties of the Bi-2212 wires and established a Gas Pressure Melting (GPM) method which is characterized by a higher total gas pressure than the atmospheric pressure. We found that the combined conditions of appropriate oxygen partial pressures of 1.0 to 303.9 kPa and total gas pressure of over 303.9 kPa are very effective for obtaining small voids with a homogeneous dispersion and good superconductivity over a wide melting temperature range. We obtained reproducibly high J_c round wires with J_c of 140 000 A cm^{-2} (0 T) and 40 000 A cm^{-2} (23 T) at 4.2 K. A solenoid coil which has several advantages in its fabrication compared with a pancake coil was successfully fabricated, using a 9 m round wire, based on the findings. The coil generated a maximum magnetic field of 0.7 T.

1. Introduction

The Bi–Sr–Ca–Cu–O system contains two main superconducting phases; i.e. the high-T_c phase (2 2 2 3 phase) with a composition of $Bi_2Sr_2Ca_2Cu_3O_y$ and the low-T_c phase (2 2 1 2 phase) with a composition of $Bi_2Sr_2Ca_1Cu_2O_y$. It has been reported that a good c-axis alignment of the 2 2 1 2 phase can be obtained by a partial melt process in doctor-blade cast tape, which gives a high critical current density, J_c, at 4.2 K [1–3]. The melt process has been applied to Ag-sheathed wires and high J_c values of the order of 10^5 A cm^{-2} have been achieved in short samples [4, 5]. However, using Ag-sheathed wires it has been difficult to produce long wires or magnets with good superconducting properties due to effluence of the oxide materials from the Ag sheath and/or the formation of voids inside the sheath because of oxygen release during the partial melt process. A reduction of the oxygen release can be achieved by (1) using powders, with 0.2 mol % Ag, which are calcined at temperatures closer to the melting point and (2) melting under higher oxygen partial pressure [6]. The properties of Ag-sheathed wires processed as above were investigated by changing the oxygen partial pressure and it was found that formation of the Bi-2 2 1 2 phase under a higher oxygen partial pressure of 101.3 kPa is slower than that under a lower oxygen partial pressure of 20.26 or 50.65 kPa atm; i.e. the cooling rate must be as slow as 0.25 °C min^{-1} to get homogeneity of the intragrain superconductivity, as well as formation of the Bi–2 2 1 2 phase [7]. In addition, J_c has a maximum just above the melting point, however, the J_c values scatter considerably due to the formation and growth of voids.

In the present paper, we discuss the effect of total gas pressure, oxygen concentration and oxygen partial pressure during the partial melt process on the void formation and superconducting properties for Ag-sheathed round wires.

2. Experimental procedure

Commercial powders of 3 N pure Bi_2O_3, SrO, CaO, CuO and Ag_2O were mixed in a normal composition of $Bi_2Sr_2Ca_1Cu_2Ag_{0.2}O_y$ and calcined twice at 810 °C for 10 h, to give powder with a small oxygen release [6]. Silver tubes (6 mm o.d., 4.5 mm i.d.), filled with the powder, were processed by drawing to get 0.7 mm outer diameter wires. The round wire was cut into 3 cm lengths and each sample was partially melted for 10 min under various conditions; i.e. oxygen concentration, $CO_2 = O_2/(O_2 + Ar)$, was changed from 0.034 to 1.0 and total gas pressure, P_{total}, was changed from 101.3 kPa to 1.013 MPa over the temperature range 860–900 °C. Then the samples were cooled down to 815 °C at the rate of 0.25 °C min^{-1}. This rate was selected on the basis of the previous data [7]. The samples were further annealed at 800 °C in Ar–7% O_2 atmosphere for 20 h to adjust the hole concentration for obtaining good superconductivity.

The transport critical current, J_c, of the short wires was measured by a standard four-probe method at 4.2 K with a 1 $\mu V\,cm^{-1}$ criterion. The high magnetic field properties of J_c up to 23 T were measured using the hybrid magnet of the High Field Laboratory at Tohoku University. The intragrain superconducting properties were measured by an a.c. inductive method as a function of temperature in the magnetic field of 0.04 mT using a driving frequency of 100 Hz. The microstructure and the composition of the wires were analysed by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) using a non-standard ZAF method. The void distribution inside the Ag sheath was evaluated using X-ray radiography (voltage: 180 kV, current: 5 mA, target: W). Viscosity of the Bi-2212 material under various melting conditions was qualitatively evaluated by the change in appearance of the pellets (diameter: 5 mm, thickness: 1.0 mm) placed on Ag plates.

A solenoid coil was fabricated based on the newly established Gas Pressure Melting (GPM) method. An as-drawing 9-m long Ag-sheathed wire (1.2 mm o.d.) was wound on a stainless steel bobbin to fabricate a solenoid coil (33 mm o.d., 40 mm height). Several voltage terminals were attached to the wire at intervals of 1 m to evaluate the superconductivity characteristics. The coil was partially melted by the GPM method. Critical current, I_c, of the obtained coil was measured at 4.2 K under the criterion of $10^{-13}\,\Omega\,m$.

3. Results

Since the oxygen partial pressure has a large influence on the oxygen release and formation of the Bi-2212 phase during the melt process [6, 7], two factors, total gas pressure, P_{total}, and oxygen partial pressure, P_{O_2}, were changed to see the effect on void formation and superconducting properties.

3.1. Effect of total gas pressure

Fig. 1 shows the effect of total gas pressure, P_{total}, on J_c values. Total gas pressure was changed from 101.3 kPa to 1.013 MPa. (Oxygen partial pressure, P_{O_2}, was varied from 101.3 to 202.6 kPa; however, section 3.3 will show that J_c is insensitive to P_{O_2} in this range.) It was found that the wires which melted under the total gas pressure of 0.61–1.01 MPa have high J_c

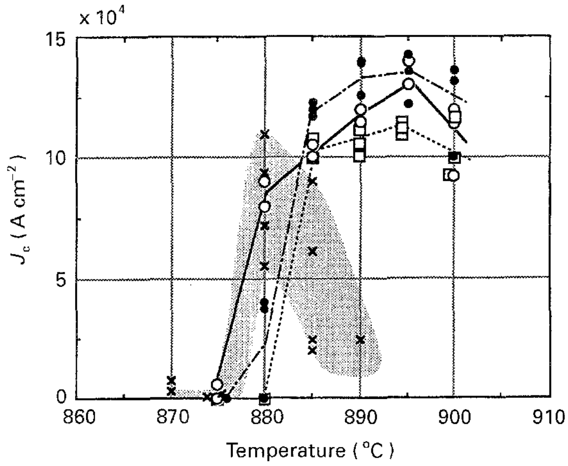

Figure 1 Effect of total gas pressure on J_c of wires processed at oxygen partial pressure of 101.3, 121.56 or 202.6 kPa. P_{total} (kPa) × 101.3, ○ 607.8, □ 1013, ■ 1013; C_{O_2} (kPa) × 101.3 ○ 20.26; □ 10.13, ■ 20.26; P_{O_2} (kPa) × 101.3, ○ 121.56, □ 101.3, ■ 202.6.

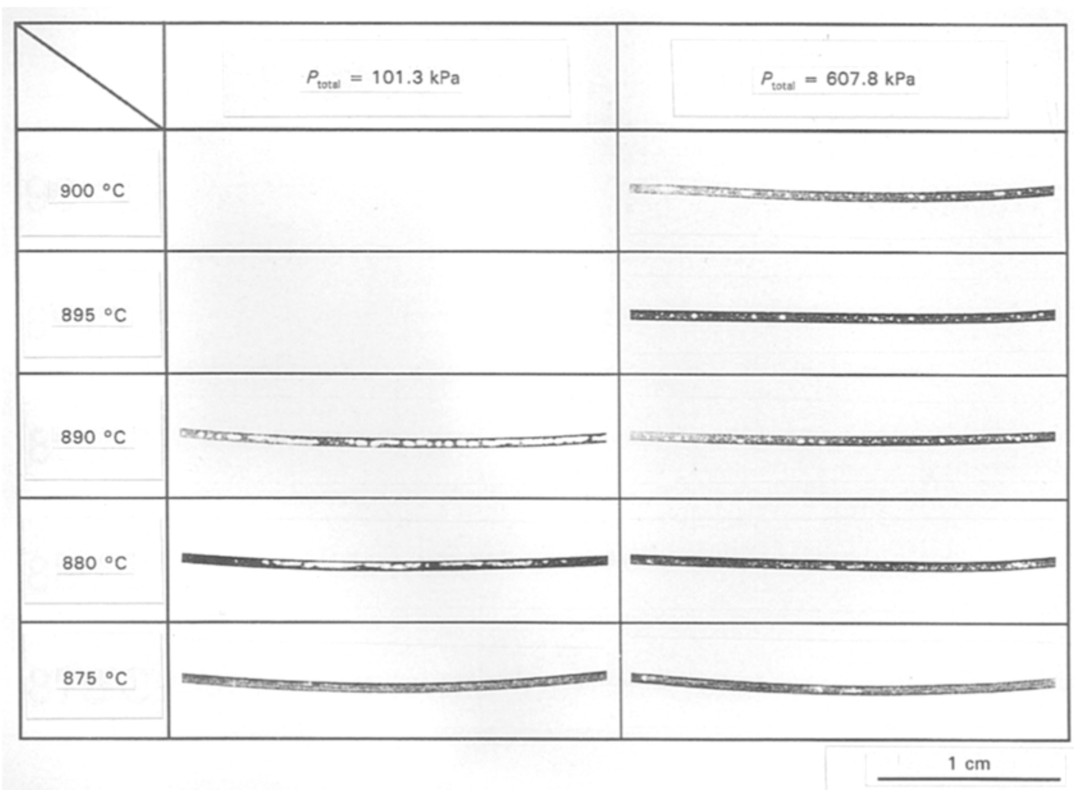

Figure 2 Effect of total gas pressure on void distribution in wires. Wires were processed at oxygen partial pressure of 101.3 or 202.6 kPa. Photos were taken by X-ray radiography.

values beyond 10^5 A cm^{-2} over a wide temperature range from 885 to 900 °C and the J_cs have little scatter. These features are significantly different from those of wires melted under a total gas pressure of 101.3 kPa. These wires have a maximum J_c of 1.1×10^5 A cm^{-2} at 880 °C, but the J_cs are widely scattered and there is a sharp drop above 880 °C. In order to understand the differences, microstructures, void morphology and intragrain properties were investigated.

Fig. 2 shows morphology and distribution of voids inside the sheath as a function of processing temperature. The photos were taken by X-ray radiography. The brighter part inside each wire corresponds to voids which have less absorption of X-rays. Two kinds of wires from Fig. 1 were evaluated; i.e. $P_{total} = 101.3$ kPa and $P_{total} = 607.8$ kPa. The wires processed at P_{total} of 101.3 kPa form continuous voids inside the sheath above the melting temperature of 880 °C. These voids become larger with increasing temperature resulting in voids of several millimetres at 890 °C. The wires melted at P_{total} of 607.8 kPa also form voids, however, they are less than 0.6 mm at the melting temperature of 880–900 °C. The results clearly show that total gas pressure is a very effective way to get finer voids with better homogeneity of their distribution.

Fig. 3 shows the $T_{c\ onset}$ and $T_{c\ end}$ for wires evaluated by the a.c. inductive method. The wires processed at $P_{total} = 607.8$ kPa and $P_{total} = 1.013$ MPa show an almost constant $T_{c\ onset}$ and $T_{c\ end}$ of 94 K and 85 K over the melting temperature of 880 °C. On the other hand, the wires melted at $P_{total} = 101.3$ kPa show a maximum $T_{c\,onset}$ of 93 K and T_c end of 82 K at 885 °C, which are almost the same as the wires melted at $P_{total} = 607.8$ kPa and $P_{total} = 1.013$ MPa. However, the wire melted at 890 °C shows a significant drop of both $T_{c\,onset}$ and $T_{c\,end}$ [7]. This means that the wires processed at $P_{total} = 607.8$ kPa and 1.013 MPa has no degradation of the intragrain superconductivity over a wide melting temperature range from 885 to 900 °C, unlike the wires processed at P_{total} of 101.3 kPa. This understanding is also supported by SEM microstructure analysis. All wires processed under the higher total gas pressures of 607.8 kPa and 1.013 MPa consist of Bi-2212, (Sr, Ca)$Cu_{1.6}O_x$ (close to "14:24 phase"), SrO and Ag, regardless of the melting temperature. No additional phases form even at the highest processing temperature of 900 °C unlike the wire processed at $P_{total} = 101.3$ kPa.

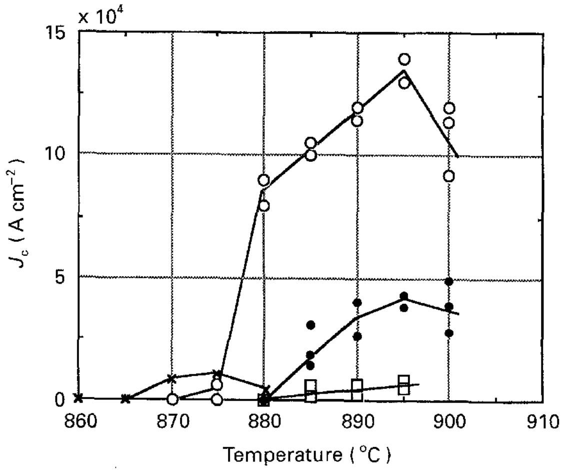

Figure 4 Effect of oxygen partial pressure on J_c of the wires processed under constant total gas pressure of 607.8 kPa. P_{O_2} (kPa) □ 20.26, ● 60.78, ○ 121.56, × 607.8; C_{O_2} (kPa) □ 3.44, ● 10.13, ○ 20.26, × 101.3.

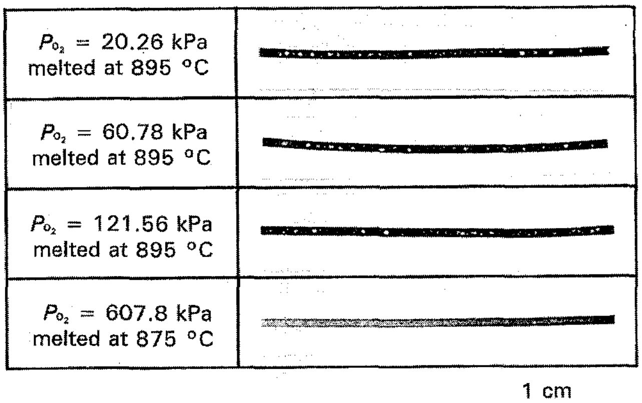

Figure 5 Effect of oxygen partial pressure on void distribution. Wires were melted under constant total gas pressure of 607.8 kPa.

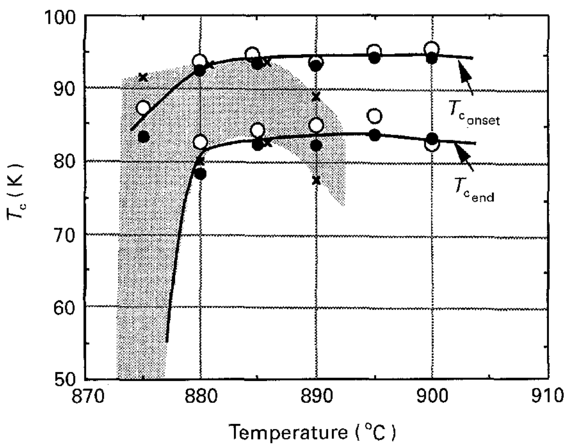

Figure 3 T_cs of the wires processed under different total gas pressures (●) and temperatures. Oxygen partial pressure was 101.3 (×), 121.56 (○) 202.6 (●) kPa. T_cs were evaluated by the a.c. inductive method. See [7] for details.

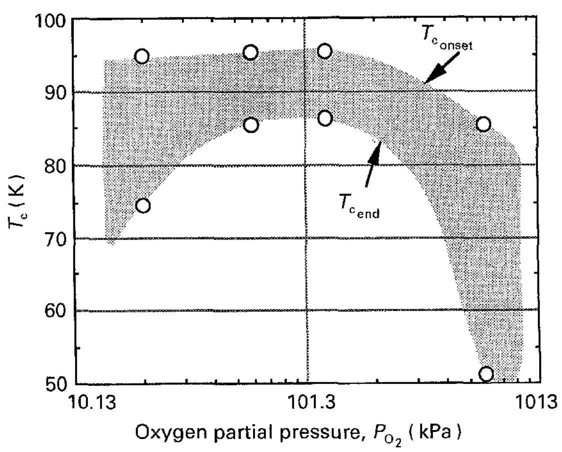

Figure 6 T_cs of the wires melted under different oxygen partial pressures. Total gas pressure was kept constant at 607.8 kPa.

Therefore, the reasons why the wires melted at P_{total} of 607.8 kPa and 1.013 MPa show reproducibly high J_c values are the refinement and homogeneity of the voids and no degradation of the superconductivity. These points are in striking contrast to the wires melted at P_{total} of 101.3 kPa.

3.2. Effect of oxygen partial pressure

Fig. 4 shows the effect of oxygen partial pressure on J_c values at a constant total gas pressure of 607.8 kPa. The maximum J_cs which appear at 895 °C increase with increasing oxygen partial pressure from $P_{O_2} = 20.26$–121.56 kPa and have a value of 1.4×10^5 A cm^{-2} at $P_{O_2} = 121.56$ kPa. However, further increases in P_{O_2} up to 607.8 kPa atm are marked by a big decrease in J_c.

Fig. 5 shows the void distribution of the wires melted under different atmospheres at the temperatures which give the maximum J_cs. Regardless of the melting atmospheres, all wires have almost the same void size of under 0.3 mm, and voids are distributed homogeneously.

Fig. 6 shows the dependency of the oxygen partial pressure on the $T_{c\,onset}$ and $T_{c\,end}$ of the wires as estimated from the inductance change. The $T_{c\,onset}$ is about 95 K for oxygen partial pressures of 20.26–121.56 kPa, while at the oxygen partial pressure

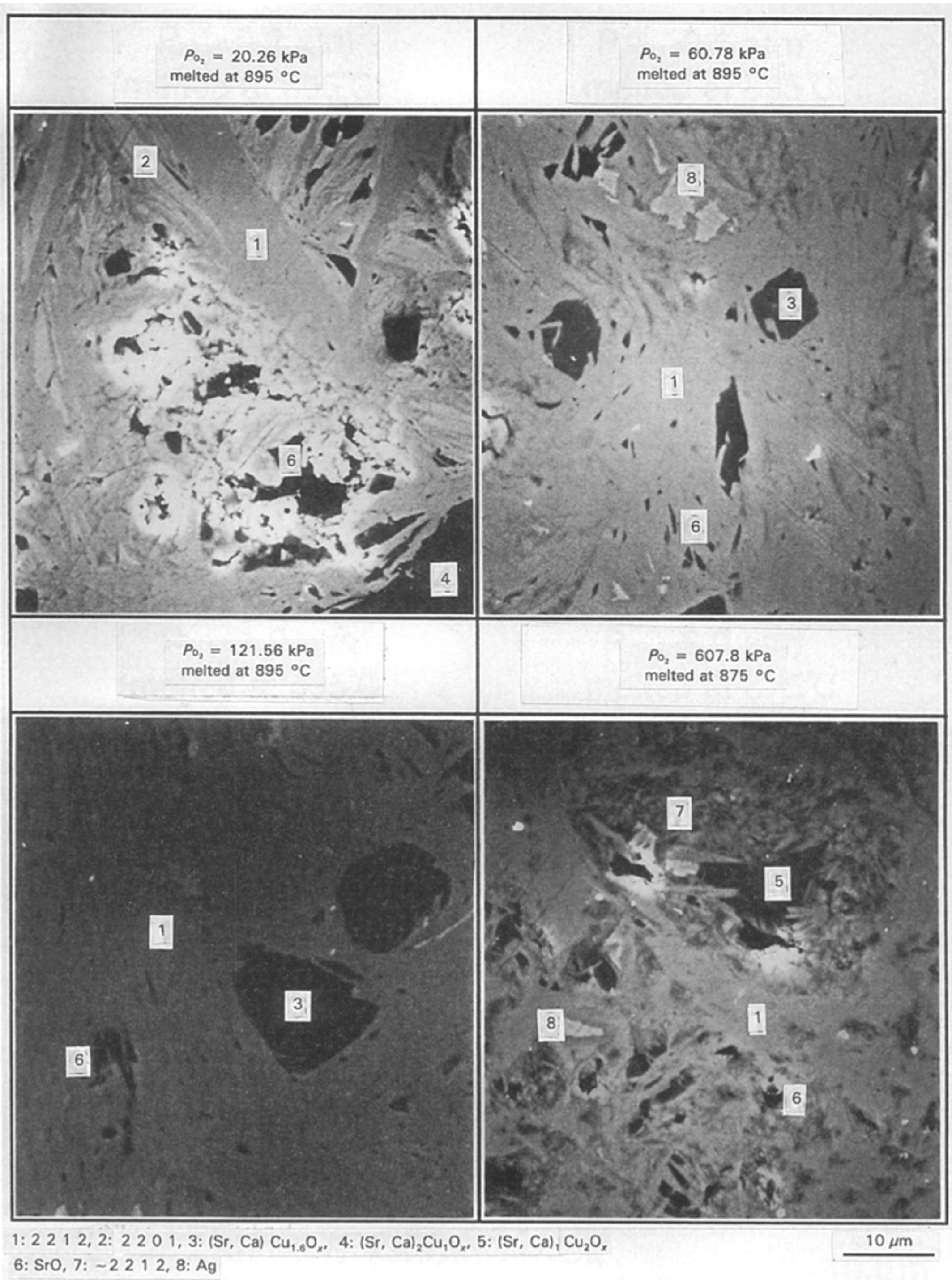

Figure 7 SEMs of the wires melted under different oxygen partial pressures. Total gas pressure was kept constant at 607.8 kPa.

of 607.8 kPa the $T_{c\ onset}$ drops slightly to 85 K. On the other hand, the $T_{c\ end}$ is lowered significantly for the lowest and highest P_{O_2} conditions of 20.26 and 607.8 kPa. This means that some of the intragrain superconducting properties are severely degraded by the melting conditions and the samples are a mix of good and poor superconductivities. However, the wires melted at P_{O_2} of 60.78–121.56 kPa have $T_{c\ end}$ of 86–87 K; i.e. there is no degradation with a sharp superconducting transition of about 10 K.

Fig. 7 shows the microstructures of wires melted under different oxygen partial pressures. The wires melted at P_{O_2} of 60.78–121.56 kPa mainly consist of the superconducting Bi-2212 phase with other foreign phases of $(Sr, Ca)_{1.6}O_x$, SrO and Ag. However, in the wire melted at $P_{O_2} = 20.26$ kPa the foreign phases were $(Sr, Ca)_2CuO_x$, SrO and the additional Bi-2201 phase which grows between Bi-2212 grains. In the wire melted at the highest P_{O_2} of 607.8 kPa, foreign phases of $(Sr, Ca)Cu_2O_x$, SrO and an additional "number 7" phase, having a composition close to that of Bi-2212 based on EDS analysis, but which is not the same judging from the photo contrast. These additional phases which cause the low $T_{c\ end}$ are characteristic of the low J_c wires.

Therefore, the low J_c of the wires melted at the extreme conditions of the $P_{O_2} = 20.26$ or 607.8 kPa (total gas pressure of 607.8 kPa) is not attributed to the void formation, but degradation of the intragrain superconductivity.

3.3. Characteristics of wires produced by the Gas Pressure Melting (GPM) method

Fig. 8 summarizes average J_c values at 4.2 K for two to five wires melted at optimized temperatures under different conditions (oxygen concentration and total gas pressure). For each set of atmospheric conditions, wires were melted at temperatures from 860 to 900 °C at intervals of 5 °C. Higher J_c values over 10^5 A cm^{-2} at 4.2 K are obtained in the shaded region between the

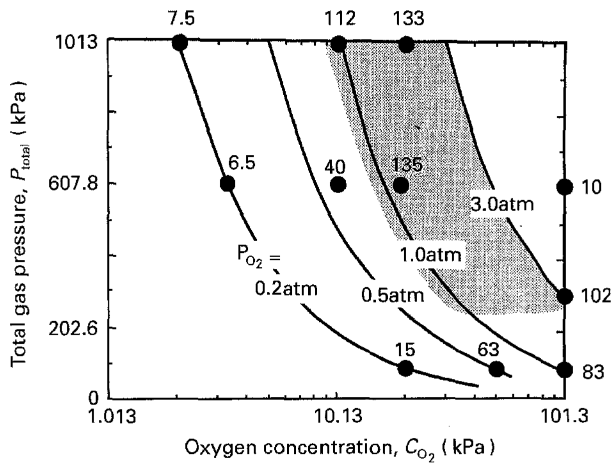

Figure 8 Average J_c values of two to five wires melted at optimized temperatures under various total gas pressures and oxygen concentrations and at 4.2 K, 0/T. The melting temperatures were changed from 860 to 900 °C at intervals of 5 °C. The unit of J_cs is kA cm^{-2}. The shaded region is preferable for obtaining reproducible high J_c wires.

P_{O_2} lines of 101.3–303.9 kPa and over the total pressure of 303.9 kPa, which are the preferable conditions for the GPM method. In particular the wires melted at C_{O_2} of 20.26 kPa P_{total} of 607.8 kPa (hence P_{O_2} = 121.56 kPa) or C_{O_2} of 20.26 and P_{total} of 1.013 MPa (hence P_{O_2} = 202.6 kPa) show J_c values as high as 1.3×10^5 A cm^{-2} at 4.2 K.

Fig. 9 shows the J_c-B properties at measurement temperatures from 4.2 to 60 K for the optimized wire melted at C_{O_2} of 20.26 and P_{total} of 607.8 kPa at 895 °C. At 4.2 K, the J_c (1.4×10^5 A cm^{-2}) at 0 T is about three times larger than J_c (4×10^4 A cm^{-2}) at 23 T. Even at 20 K the wire carries J_c of 1×10^4 A cm^{-2} at 7 T. Over 20 K, J_c drops rapidly with an increase in the magnetic field.

The reason why the GPM method is suitable for obtaining reproducibly high J_c Bi-2212 wires by a partial melt process is summarized schematically in Fig. 10. There are two factors which affect the superconducting properties: one is the oxygen partial pressure and the other is the total gas pressure. Increasing oxygen partial pressure decreases the oxygen degasification under the melting conditions [6] and an appropriate oxygen partial pressure in the range

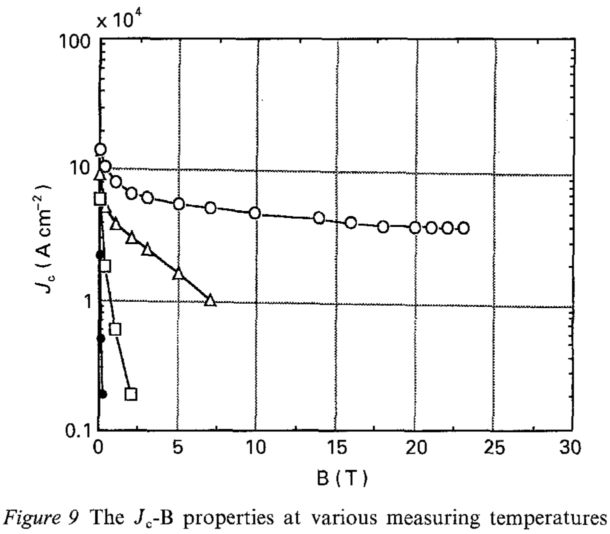

Figure 9 The J_c-B properties at various measuring temperatures from 4.2 to 60 K for wires melted under oxygen concentration of 20.26 and P_{total} of 607.8 kPa at 895 °C. ○ 4.2 K; △ 20 K; □ 40 K; ● 60 K.

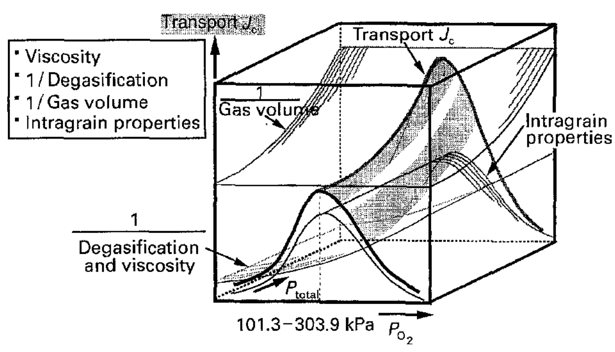

Figure 10 Schematic showing characteristics of wires produced by the GPM method. Transport J_c is proportional to the inverse of degasification, the intragrain properties, the viscosity and the inverse of gas volume. Appropriate oxygen partial pressure and higher total gas pressure (over 303.9 kPa) are essential for obtaining high J_c wires.

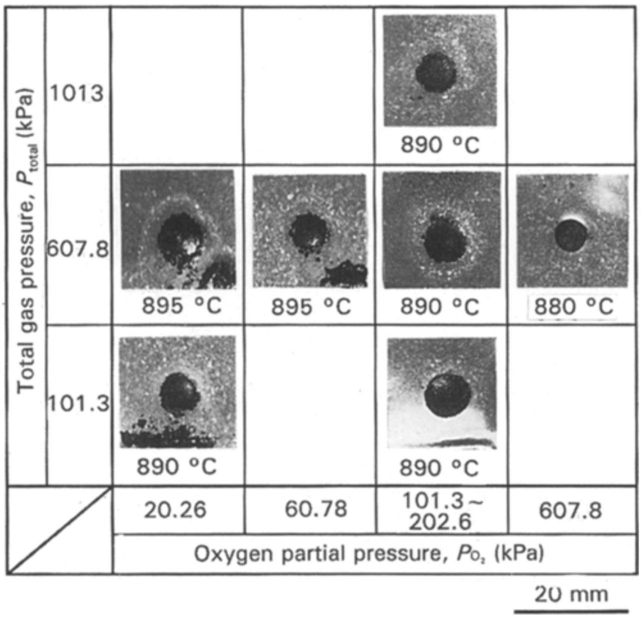

Figure 11 The appearance of pellets on Ag plates processed 10 °C higher than the melting point for each set of atmospheric conditions.

101.3–303.9 kPa gives good intragrain properties as mentioned above. The oxygen partial pressure also affects the viscosity of the Bi-2212 material at the melting conditions. Fig. 11 shows the appearance of pellets on an Ag plate processed at temperatures 10 °C higher than the melting point for each set of atmospheric conditions. The melting point is assumed to be the lowest melting temperature for which J_c of the order of $10^4\ \mathrm{A\,cm^{-2}}$ was observed. It is clear that the pellets melted at lower oxygen partial pressure get out of shape more than those melted at higher oxygen partial pressure, regardless of the total gas pressure, which means that the viscosity of the Bi-2212 material under lower oxygen partial pressure is lower than that under higher oxygen partial pressure. Higher viscosity is advantageous in suppressing void growth. On the other hand, increasing the total gas pressure causes reduction of the gas volume at the melt process, which is inversely proportional to the total gas pressure. Therefore, the higher transport J_c is obtained in the case of higher values of 1/degasification, 1/gas volume, viscosity and intragrain properties as shown in Fig. 10.

The GPM method allows refinement and homogeneous distribution of voids by reducing degasification and gas volume and increasing viscosity while optimizing superconducting properties by controlling oxygen partial pressure. This results in reproducibly high J_c wires by the partial melt process.

3.4. Performance of the solenoid coil fabricated by the GPM method

A Bi-2212 solenoid coil was fabricated based on the GPM method. Table I shows the parameters for the coil. A 9 m wire was insulated using braided Al_2O_3 fibres and wound on a stainless steel bobbin coated with Al_2O_3. The final coil had a 33-mm outer diameter and 40-mm height. The coil was melted at 890 °C for 10 min at $C_{O_2} = 20.26$ and $P_{total} = 607.8$ kPa and cooled down to 815 °C at the rate of $0.25\ °\mathrm{C\,min^{-1}}$ and furnace cooled to room temperature. This was followed by Ar–7% O_2 annealing at 800 °C for 20 h. The fabricated solenoid coil is shown in Fig. 12.

TABLE I Parameters for the Bi-2212 solenoid coil

Wire length/diameter	9 m/1.2 mm
Inner/outer diameters of bobbin	14 mm/33 mm
Coil height	40 mm
Number of turns	126
Insulator	Al_2O_3 braided fibres

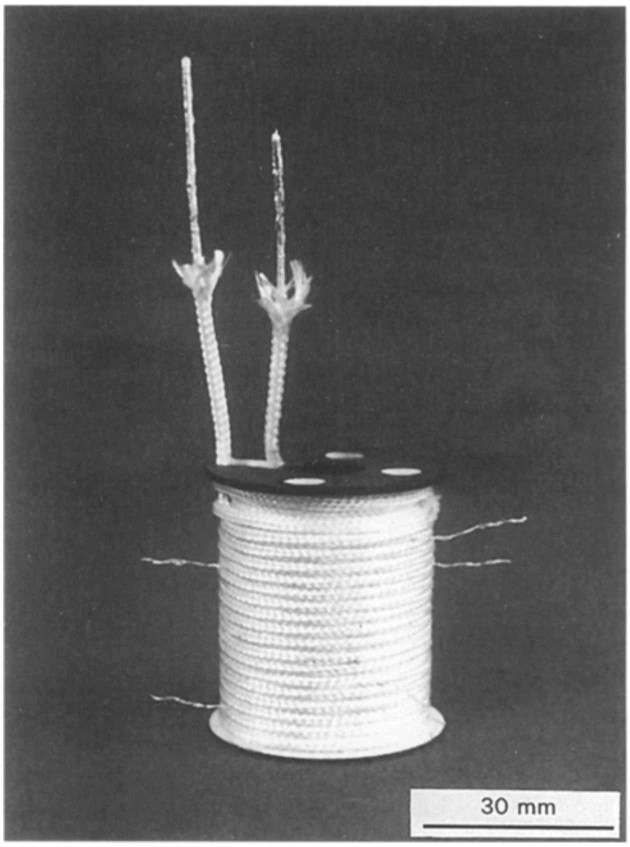

Figure 12 Photograph of a solenoid coil fabricated by the GPM method.

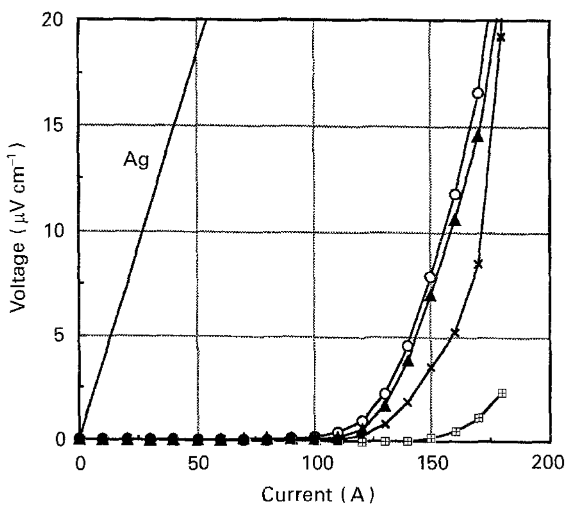

Figure 13 V–I curves for representative regions of the solenoid coil. ○ inside; ▲ centre; ⊞ outside; × whole length.

Fig. 13 shows the V–I curves for representative regions, i.e. inside, centre and outside portions of a 1-m length of the coil. Critical current, I_c, differs in the regions; i.e. I_c decreases in the order of outside, centre and inside. This is reasonable, taking into account the self magnetic field of the coil. I_c of the coil is 120 A under the criterion of $10^{-13}\ \Omega\,m$ and quenched current reaches 185 A. The coil successfully generates B_{max} of 0.7 T at the quenched current and 0.45 T at the critical current.

4. Conclusions

Oxygen partial pressure and total gas pressure during melt process significantly affect void formation and superconducting properties for Ag-sheathed wires. Oxygen partial pressures of 101.3–303.9 kPa and total gas pressures over 303.9 kPa are prerequisites for getting good intragrain superconducting properties and void refinement inside the sheath, which allows fabrication of reproducibly high J_c wires by the partial melt process. Using the established GPM method, J_cs of 140 000 A cm^{-2} (0 T) and 40 000 A cm^{-2} (23 T) at 4.2 K were obtained in a short wound wire. Fabrication of a solenoid coil, which has a lot of advantages compared with fabrication of a pancake coil was carried out using a 9-m round wire. It generated the maximum field of 0.7 T.

Acknowledgements

The authors would like to thank Professor K. Watanabe of the Institute for Materials Research of Tohoku University for allowing them to use the hybrid magnet of the High Field Laboratory for Superconducting Materials.

References

1. J. KASE, K. TOGANO, H. KUMAKURA, D. R. DIETDERICH, N. IRISAWA, T. MORIMOTO and H. MAEDA, *Jpn. J. Appl. Phys.* **29** (1990) L1096.
2. J. SHIMOYAMA, J. KASE, T. MORIMOTO, H. KITAGUCHI, H. KUMAKURA, K. TOGANO and H. MAEDA, *ibid.* **31** (1992) L1167.
3. J. SHIMOYAMA, N. TOMITA, T. MORIMOTO, H. KITAGUCHI, H. KUMAKURA, K. TOGANO, H. MAEDA, K. NOMURA, and M. SEIDO, *ibid.* **31** (1992) L1328.
4. H. KRAUTH, K. HEINE and J. TENBRINK, in High-Temperature Superconductors, Proceedings ICMC'90, Garmisch-Partenkirchen, FRG, May, 1990 (Informationsgesellschaft mbH, Oberursel, 1991) p. 29.
5. T. ASANO, Y. TANAKA, M. FUKUTOMI and H. MAEDA, *Jpn. J. Appl. Phys.* **29** (1990) L1066.
6. T. KANAI and T. KAMO, *Supercond. Sci. Technol.* **6** (1993) 510.
7. T. KANAI, N. INOUE and T. KAMO, *J. Mater. Res.* **9** (1994) 1363.

Received 23 February
and accepted 14 November 1994