JOURNAL OF MATERIALS SCIENCE 26 (1991) 737–742

Superconducting and mechanical properties of YBCO/Ag composites fabricated at high pressures up to 5.4 GPa

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The YBCO/Ag superconducting composites were fabricated by compressing powders of YBCO and silver mixed at various volume proportions 0 to 100% under pressures of 2.0 and 5.4 GPa and subsequently sintering at 900 °C for 10 h in a flowing oxygen atmosphere. The superconducting transition temperature, particularly T_c ($R = 0$), was found to retain the value above 85 K up to 50 vol % Ag while the normal resistivity at 300 K to reduce below 10 $\mu\Omega$ cm. The highest J_c of 400 A cm^{-2} was attained for the sample containing 20 vol % Ag pressed at 5.4 GPa. The mechanical properties were also improved by the addition of silver: the compressive strength is increased by two to three times and the maximum strain, which is a measure of ductility, reached a value almost four times as large as that in the pure YBCO prepared under the ordinary pressure of 0.5 GPa. The persistence of the superconducting characteristics up to 70 vol % Ag is discussed in terms of the microstructure taken with the scanning electron microscope.

1. Introduction

The high-T_c ceramic superconductors prepared by the ordinary sintering technique are known to be mechanically very brittle and pose difficulties in their practical applications. The reason for the brittleness is mainly the presence of porosity in the ceramics with a limited plastic deformation range. Several attempts have already been made to overcome this difficulty. For example, the ceramic superconducting powders sealed in a silver sheath are drawn into a wire [1] or the mixture of powders of the ceramic superconductor and silver or gold metal is sintered to form a composite material [2–4]. Nishio *et al.* [4] prepared the composite material consisting of powders of $YBa_2Cu_3O_{7-x}$ (YBCO) and pure silver in appropriate proportions and revealed that the superconductivity remained even for a material containing more than 80 vol % Ag and that the mechanical strength against fracture was improved with increasing silver content. They also noted that both the critical current density, J_c, and the mechanical strength increase with increasing pressure applied during fabrication. Their maximum pressure was, however, limited to 1 GPa.

In the present work YBCO/Ag composite superconductors were prepared under pressures of 2.0 and 5.4 GPa at room temperature with subsequent heat-treatment in the oxygen atmosphere. The effect of the pressure on both mechanical and electrical properties of composite materials will be discussed in comparison with the previous data obtained under the pressure below 1 GPa.

2. Experimental procedure

The starting YBCO powders, which are identical to those employed in the previous work [4], were purchased from High Purity Chemetals. The average diameter of the powders was less than 150 μm. The X-ray diffraction lines taken with Cu$K\alpha$ radiation can be indexed in terms of the orthorhombic structure with the lattice constants $a = 0.382$ nm, $b = 0.389$ nm and $c = 1.168$ nm [5]. A bulk sample, prepared by the conventional sintering technique pressed at 0.5 GPa and later sintered at 900 °C under an oxygen atmosphere for 10 h, exhibited superconductivity at $T_c = 91$ K and a width of 3 K.

The YBCO/Ag composite samples were fabricated by mixing silver and YBCO powders in various volume ratios. They were well mixed in an agate mortar. The silver powders employed were 99.9% pure and had 100 μm average diameter. The mixed powders were pressed into cylindrical shapes of 6 mm diameter × 6 mm under the pressure of 2 GPa at 300 K using a piston–cylinder apparatus. The compact was sintered

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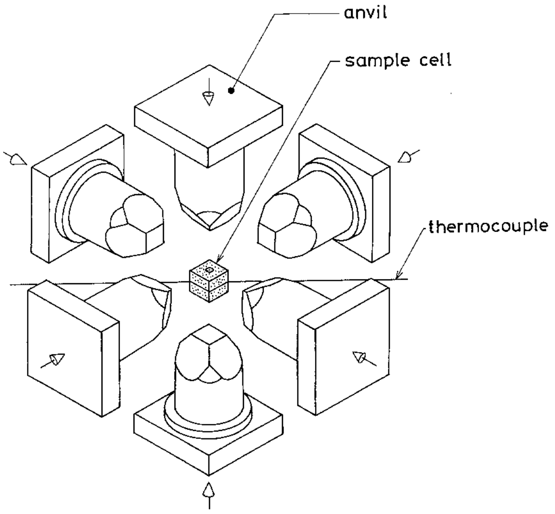

Figure 1 Schematic illustration of cubic high-pressure device. The anvil is made of tungsten carbide.

at 900 °C for 10 h in a flowing oxygen gas atmosphere and then cooled to 300 K at a rate of 3 K $\min^{-1}$.

The cylindrical sample thus obtained was further pressed at a pressure of 5.4 GPa at 300 K for 3 h after the completion of a series of measurements described below. The hydraulic high-pressure was generated by a cubic high-pressure apparatus with six anvils made of tungsten carbide. A schematic diagram of this is shown in Fig. 1. The pressure scale was calibrated, using as conventional pressure standards the phase transitions of bismuth (I–II) at 2.55 GPa, bismuth (II–III) at 5.67 GPa, tantallum (II–III) at 3.67 GPa and barium (I–II) at 5.5 GPa. The reaction cell containing the calcined composites is made of pyrophyllite of edge length 20 mm. The compressed sample 6 mm diameter × 6 mm in size, was heat-treated at 900 °C in the flowing oxygen gas atmosphere for 10 h. This heat treatment served to reduce the microcracks and the deficient oxygen caused during compression. It is considered that the microcracks are most likely generated because of the lack of uniformity in the pressure distribution. The structure of the composite sample thus obtained was studied using X-ray diffraction with Cu*K*α radiation. The microstructure was examined with the scanning electron microscope in combination with the electron-probe microanalysis.

The following measurements were carried out on the composite samples pressed at 2.0 and 5.4 GPa. The density was measured with the Archimedes method using 99.5% ethanol as a working fluid. The electrical resistivity was measured by the d.c. four-probe method in the temperature range 77 to 300 K. A rectangular sample, 1 mm × 2 mm × 5 mm, was cut from the cylindrical specimen for the resistivity measurements. Silver paste was used for the electrical contacts. The current passing through the longitudinal direction of a sample was adjusted to be less than 1 mA, which is small enough not to affect the determination of the critical temperature, T_c. The critical current density, J_c, was also measured by the d.c. four-probe method at 77 K without applying a magnetic field.

The compressive strength was deduced from the stress–strain curve at 300 K with the strain rate of $6 \times 10^{-4}\,\mathrm{sec}^{-1}$. Here the compressive strength is defined as the maximum stress before cracks develop in the above stress–strain curve. The maximum strain can be also deduced from the measured curve.

3. Results and discussion

3.1. Effects of pressure on the atomic structure and microstructure

Fig. 2a and b show typical X-ray diffraction patterns for the 40 vol % Ag sample pressed at 5.4 GPa before and after the heat treatment described in the preceding section, respectively. Although the relative intensities are slightly different, the X-ray diffraction lines in both cases can be identified in terms of the orthorhombic YBCO phase and pure silver without any other phases involved. The same results were obtained for all other specimens, regardless of the applied pressures and silver contents. It was concluded, therefore, that the high pressure up to 5.4 GPa with the subsequent heat treatment causes no chemical reaction between pure silver and YBCO.

The microstructure was examined for both the as-fractured surface and the surface polished by diamond paste by means of the scanning electron microscope. Fig. 3a and b illustrate the microstructure for fractured surfaces of the pure YBCO pressed at 0.5 and

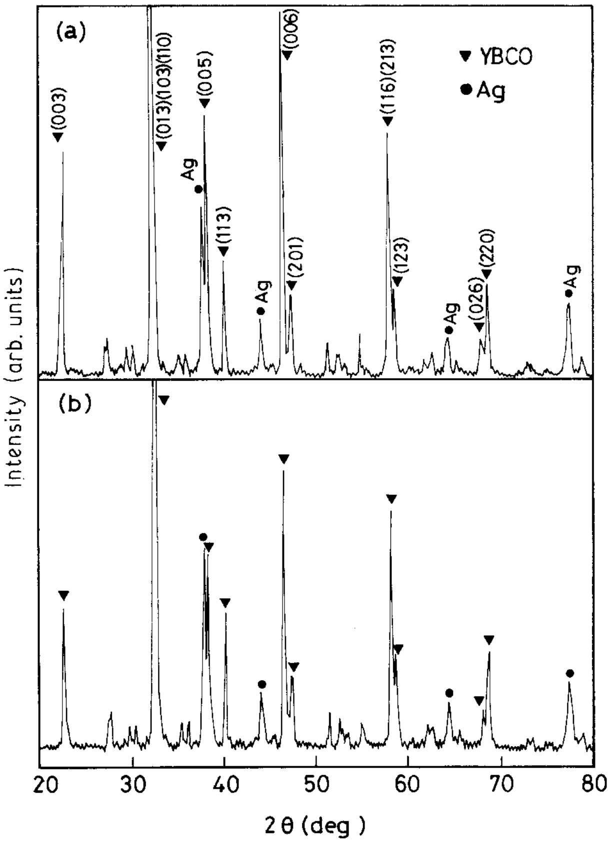

Figure 2 X-ray diffraction spectra for the sample containing 40 vol % Ag pressed at 5.4 GPa (a) without and (b) with the heat treatment at 900 °C for 10 h in the flowing oxygen atmosphere. Silver is found to remain intact after the heat treatment. (▼) YBCO, (●) Silver.

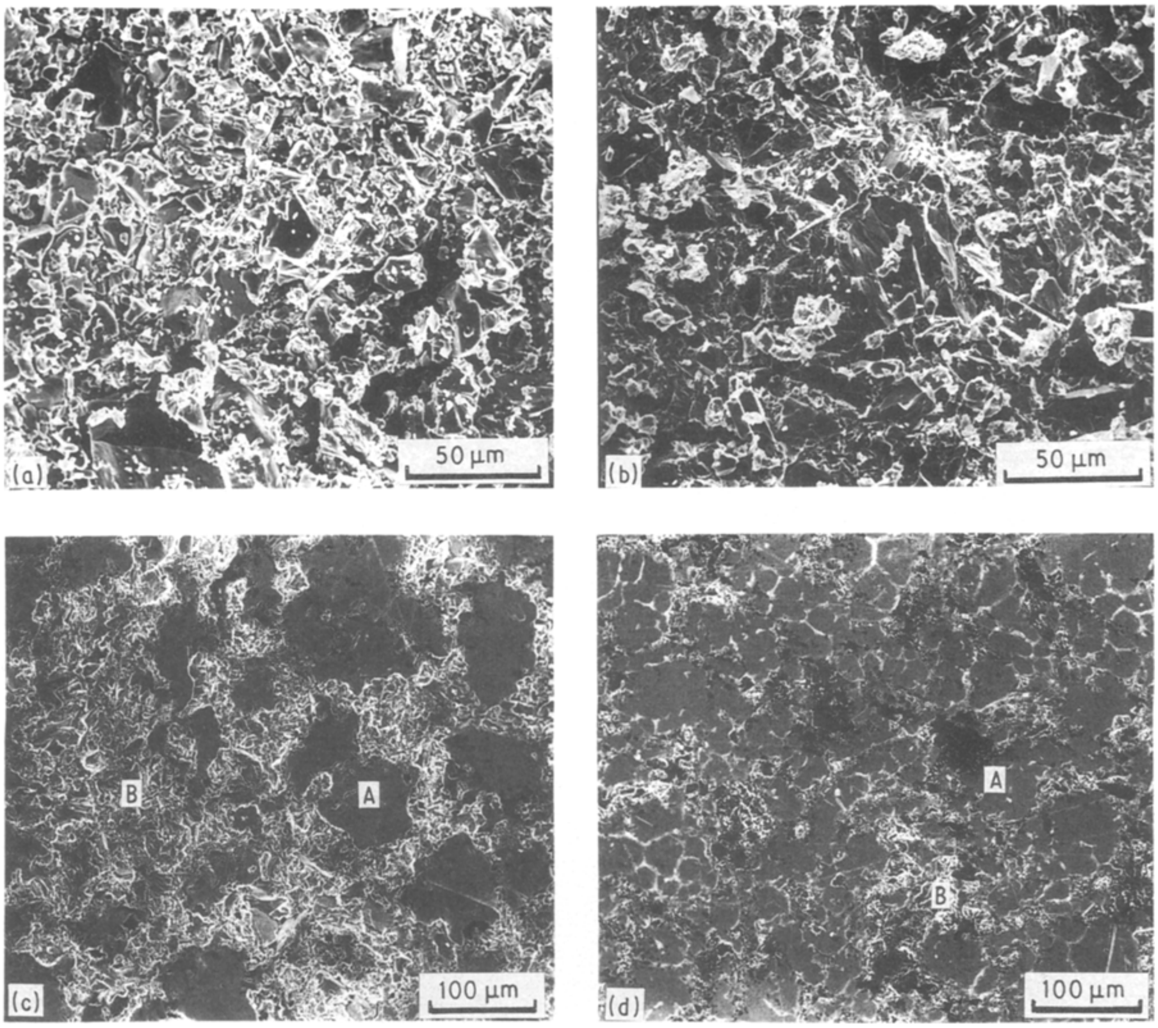

Figure 3 Scanning electron micrographs of (a) the fractured surface of pure YBCO prepared under the pressure of 0.5 GPa, (b) the fractured surface of pure YBCO prepared under the pressure of 5.4 GPa, (c) the polished surface of the 20 vol % Ag sample (pressed at 5.4 GPa), and (d) the polished surface of the 70 vol % Ag sample (pressed at 2.0 GPa). A, silver particles; B, YBCO.

5.4 GPa, respectively. As is clearly seen, the porosity is substantially reduced for the sample pressed at 5.4 GPa. The presence of silver particles for the sample containing silver was found to be hardly visible when the micrograph was taken on the fractured surface. Hence, the polished surface was studied. Fig. 3c and d show micrographs of the 20 (pressed at 5.4 GPa) and 70 vol % Ag (pressed at 2.0 GPa) samples, respectively. It is noted that the silver particles remain intact and maintain the same size as that of the starting powders, whereas YBCO particles become much finer than the original ones and are distributed uniformly around a large silver particle. It was realized that this feature is apparently independent of the pressure applied (see also Fig. 6 in [4]) and that the YBCO powders are ground into finer particles and form more or less bimodal distribution in particle size: one 20 to 30 µm and the other less than 5 µm. Fig. 3d also indicates that the superconducting network is still maintained without serious disruption even in the sample containing 70 vol % Ag. The formation of this unique structural morphology should be responsible for the manifestation of unique superconducting and mechanical properties, which will be discussed below.

The ratio of the measured density d, to the ideal one for the composite samples is plotted in Fig. 4. Here the ideal density, d_0, was simply calculated by taking a weighted mean of the crystallographic densities of pure silver ($d = 10.5\ \mathrm{g\,cm^{-3}}$) and YBCO ($d = 6.3\ \mathrm{g\,cm^{-3}}$). It can be seen that the ratio reaches almost unity or 100% for the sample pressed at 5.4 GPa but the deviation becomes noticeable in the silver-rich region. It is realized that the pressure as high as 5.4 GPa can produce an almost ideally packed composite sample. The reason for the decrease in the ratio for silver-rich samples is not clear at this stage. It may be caused by the expansion of the air captured between the neighbouring silver particles, where the chances of direct contact without being coated with fine YBCO particles increase as the silver content increases. In the previous experiment [4], the density was simply determined by measuring its dimensions. To allow a direct comparison with the present work, the density for the previous samples was remeasured with the Archimedes method and the ratio of the density was deduced in the same manner. Their values are incorporated in Fig. 4. It is clear that the sample pressed at 1 GPa is still quite porous.

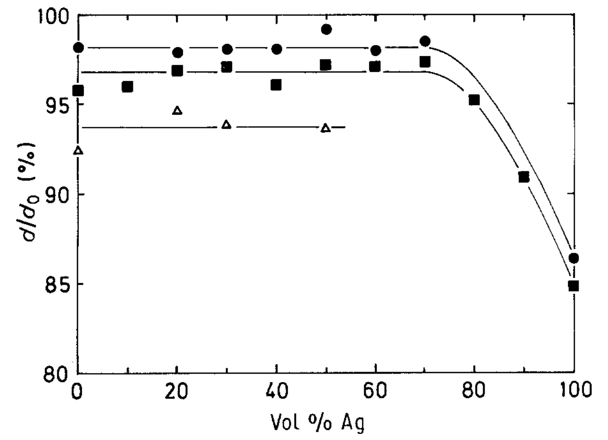

Figure 4 The ratio of the measured density, d, to the crystallographic density, d_0, as a function of silver content for various YBCO/Ag composites prepared under different pressures: (△) 1.0 GPa, (■) 2.0 GPa and (●) 5.4 GPa. The density of the previous samples prepared under the pressure of 1.0 GPa [4] was measured and plotted to allow a direct comparison with the present data.

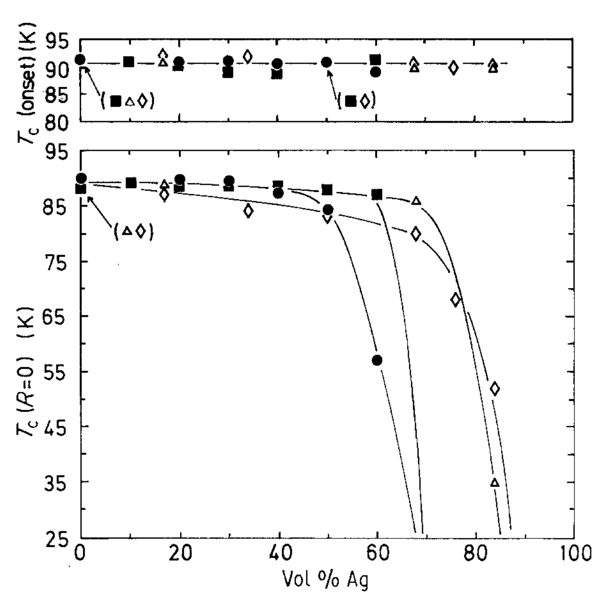

Figure 6 Superconducting transition temperatures T_c (onset) and T_c ($R = 0$) as a function of silver content for the YBCO/Ag composite samples prepared under various pressures: (◇) 0.4 GPa, (△) 1.0 GPa, (■) 2.0 GPa and (●) 5.4 GPa. The data for the samples at 0.4 and 1.0 GPa were reported previously [4].

3.2. Effect of pressure on the superconducting properties

Fig. 5 shows the temperature dependence of the normalized electrical resistivity for the 20 vol % Ag samples subjected to two different treatments. The as-pressed sample at 5.4 GPa exhibits a rather broad superconducting transition and its resistivity completely disappears at about 80 K. A sharp transition is recovered, once the sample is heat treated at 900 °C for 10 h in the flowing oxygen gas atmosphere. This may be thought of as arising from the restoration of the weak-links of the electrical contact between the YBCO particles [6] and/or the recovery of the oxygen deficiency caused by a high-pressure treatment [7].

The critical temperature T_c (onset) and T_c ($R = 0$) for the samples pressed at 5.4 and 2.0 GPa followed by the subsequent heat treatment at 900 °C are plotted in Fig. 6 as a function of silver content. Included are the previous data for the samples prepared under pressures of 0.4 and 1 GPa [4]. T_c (onset) is found to maintain a value of 90 to 91 K, irrespective of the silver content and pressures employed. In contrast, T_c ($R = 0$) gradually decreases with increasing silver content but its decrease is not serious, as long as the silver content is below 50 vol %. A critical silver content, at which a drastic decrease in T_c ($R = 0$) occurs, is lowered on increasing the pressure employed. Hence, the sample containing more than 50 vol % Ag pressed at 5.4 GPa possesses a rather broad superconducting transition temperature. This indicates that the present heat treatment is still insufficient for the silver-rich samples pressed at 5.4 GPa to recover satisfactory superconducting characteristics.

A critical current density, J_c, measured at 77 K is plotted in Fig. 7 as a function of silver content. The value of J_c is evaluated using the effective cross-section of YBCO. In other words, silver is naturally

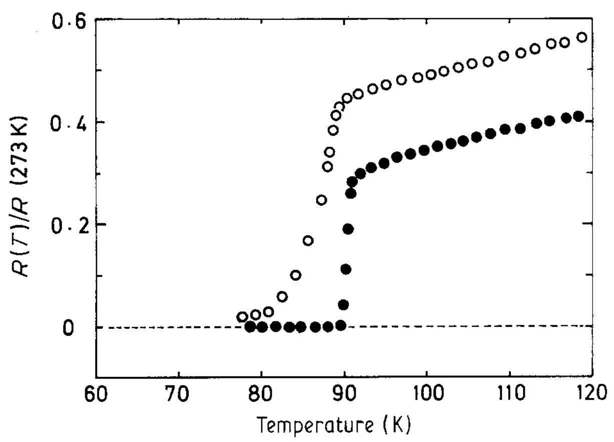

Figure 5 Temperature dependence of the electrical resistivity for the 20 vol % Ag sample prepared under the pressure of 5.4 GPa (○) without and (●) with heat treatment at 900 °C for 10 h in a flowing-oxygen atmosphere. The electrical resistivity is normalized with respect to the value at 273 K.

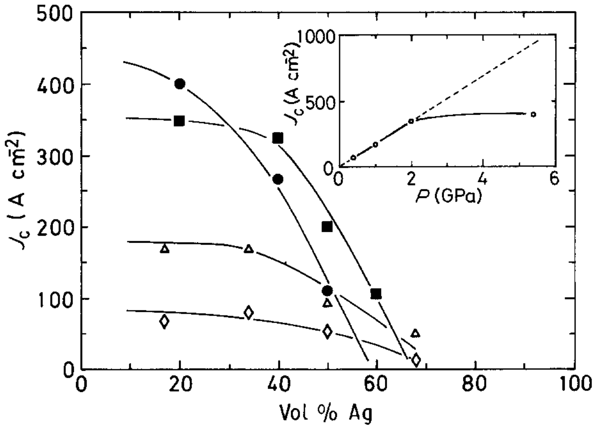

Figure 7 Critical current density, J_c, as a function of silver content for the YBCO/Ag composite samples prepared under various pressures: (◇) 0.4 GPa, (△) 1.0 GPa, (■) 2.0 GPa and (●) 5.4 GPa. The data for the samples at 0.4 and 1.0 GPa were reported previously [4]. An inset shows the dependence of J_c on the pressure for the 20 vol % Ag sample. A dashed line is drawn through the first three data points.

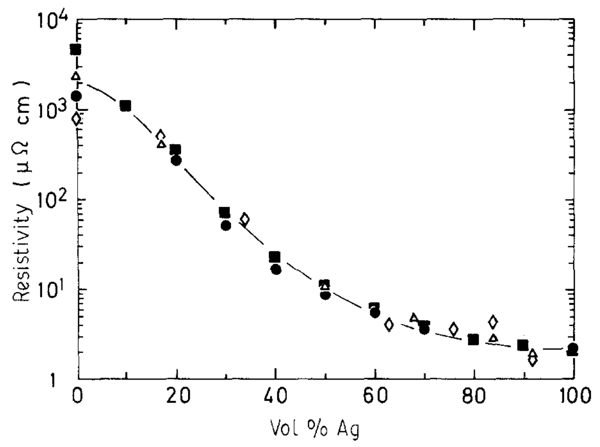

Figure 8 Electrical resistivity at 300 K for the YBCO/Ag composite samples prepared under various pressures: (◇) 0.4 GPa, (△) 1.0 GPa, (■) 2.0 GPa and (●) 5.4 GPa. The data for the samples at 0.4 and 1.0 GPa were reported previously [4].

assumed to have nothing to do with the superconducting path. The data for pure YBCO turned out to be less reproducible because of the unavoidable joule heating at the silver paste junctions and, hence, are omitted in the present discussion. As is seen from Fig. 7, the value of J_c decreases monotonically with increasing silver content. Moreover, the higher the applied pressure, the more significant is the reduction rate of J_c. The maximum J_c of 400 A cm^{-2} is attained for the 20 vol % Ag sample pressed at 5.4 GPa. In the inset to Fig. 7, the J_c value for the 20 vol % Ag sample is plotted against the applied pressure. The value of J_c obtained at 5.4 GPa is found to be substantially smaller than the value of 1000 A cm^{-2} expected from the extrapolation. Further refinement in the heat-treatment mode coupled with the more detailed microstructural analysis is certainly needed to raise J_c with the hope that it would eventually approach the extrapolated value. It may be worthwhile mentioning here that the pulse current four-probe method for the YBCO sample pressed at 5.4 GPa recently recorded a J_c value of 1650 A cm^{-2} at 77 K [6].

The room-temperature resistivity for the composite samples pressed at 5.4 and 2.0 GPa is shown in Fig. 8 as a function of the silver content. The previous data are also included [4]. The resistivity decreases monotonically and reaches the same order of magnitude as that of pure silver, once the silver content exceeds 60 vol %. This suggests that the direct contact between the silver particles becomes dominant and the metallic path is formed around this concentration range. More surprisingly, the pressure dependence is less significant on this logarithmic scale. This suggests that the room-temperature resistivity is dominated by the distribution of silver particles and is insensitive to the detailed microstructure of the YBCO networks in sharp contrast to the superconducting properties such as J_c and T_c ($R = 0$).

3.3. Effect of pressure on the mechanical properties

The stress-strain curve was measured under the compressive mode for various YBCO/Ag composite samples. Typical results for the samples containing 30 and 50 vol % Ag are shown in Fig. 9. Obviously, the stress for the YBCO sample initially increases linearly with increasing strain and suddenly drops at the initiation of the cracks, indicating the absence of the plastic deformation. In contrast, the plastic region appears and becomes more prominent with increasing silver content, as is evident from the deviation from the linear relation at the higher strain region.

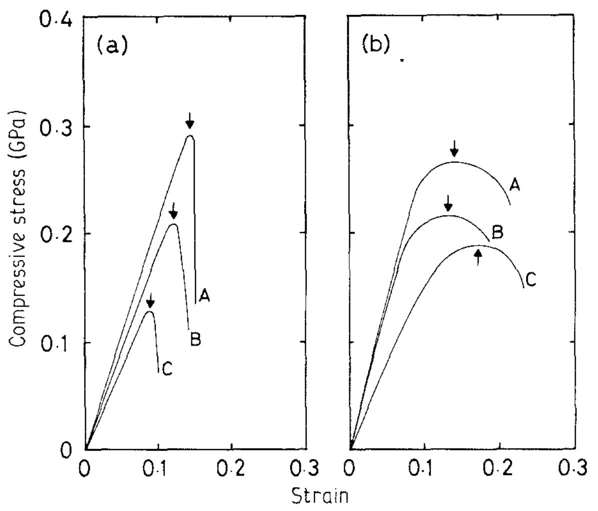

Figure 9 Compressive stress–strain curves for (a) the 30 vol % Ag and (b) 50 vol % Ag samples prepared under various pressures. Applied pressures: A, 5.4; B, 2.0; C, 1.0 GPa. Arrows indicate the position at which the compressive strength and the maximum strain are deduced.

The compressive strength and the maximum strain, derived from the strain–stress curve in Fig. 9, are plotted in Figs 10 and 11, respectively as a function of silver content for samples prepared under different pressures. First of all, it is noted that both compressive strength and the maximum strain increase generally with increasing silver content, indicating that the addition of silver to YBCO improves the mechanical properties. For instance, the compressive strength of the composite containing 50 vol % Ag pressed at 5.4 GPa, which maintains the T_c ($R = 0$) of 85 K, reaches 0.25 GPa or a value about 2.5 times higher than that for the pure YBCO pressed at the ordinary pressure of 0.5 GPa.

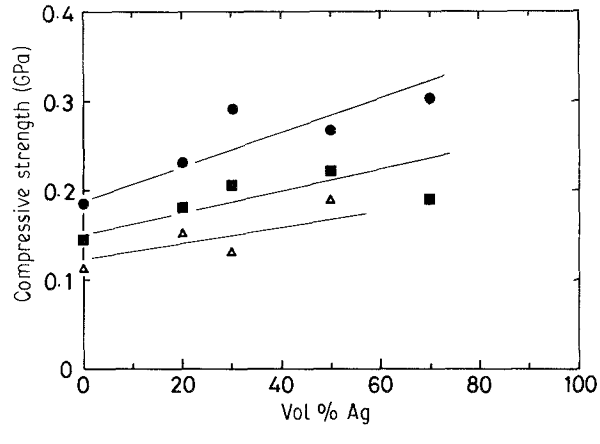

Figure 10 Compressive strength as a function of silver content for the YBCO/Ag composite samples prepared under various pressures: (△) 1.0 GPa, (■) 2.0 GPa and (●) 5.4 GPa.

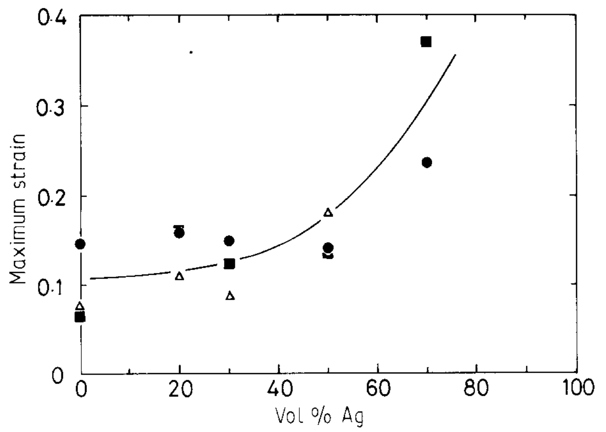

Figure 11 Maximum strain as a function of silver content for the YBCO/Ag composite samples prepared under various pressures: (△) 1.0 GPa, (■) 2.0 GPa and (●) 5.4 GPa.

Judging from the achievement of a nearly perfect packing density under the pressure of 5.4 GPa, it is believed that further enhancement in the compressive strength may not be easily expected. Indeed, the observation of the fractured surface by the scanning electron microscope indicates that the fracture predominantly occurs along the YBCO networks. Hence, a substantial improvement in the mechanical properties may not be feasible, unless the YBCO network itself is strengthened. Finally, it may be noted that, although the compressive strength can be increased with increasing applied pressure, the maximum strain is apparently independent of the pressure within the accuracy of the data points. This suggests that the maximum strain, which is a measure of ductility, depends more strongly on the mechanical properties of silver particles, which are certainly less affected by the pressure applied.

4. Conclusion

Superconducting and mechanical properties for YBCO/Ag composite materials have been studied with a particular attention on the pressure applied upon the compression of powdered YBCO and silver. The pressure was varied up to 5.4 GPa. It was found that the density for the composite containing up to 60 vol % Ag reached an almost crystallographic value, when pressed at 5.4 GPa. For the samples pressed at 5.4 GPa, the superconducting transition temperature T_c ($R = 0$) above 85 K was preserved up to 50 vol % Ag, while the normal resistivity at 300 K is suppressed below 10 $\mu\Omega$ cm. The maximum J_c of 400 A cm^{-2} was observed for the 20 vol % Ag sample. The mechanical properties characterized by the compressive strength and the maximum strain were also found to be improved two to three times, relative to that for the pure YBCO prepared under the ordinary pressure of less than 1 GPa.

Acknowledgements

The authors thank Dr N. Kawahara, Nippondenso Co. Ltd, for fruitful discussions, Dr K. Kuroda and Mr F. Ogasawara, Nagoya University, for their help in handling the scanning electron microscope, and Mr Y. Masanaka, Nagoya University, for machining the composite samples.

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Received 26 September 1989
and accepted 1 February 1990