# Studies on Superplastically Deformed 123/Ag Composites

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*Abstract*---**Composites containing 25 vol% Ag were compressed at room temperature to over 110% at 850°C in air. Measurement of the strain rate sensitivity yielded a value of 0.5, characteristic of superplastic deformation. As deformed materials had sub-micron grain size and significant c-axis texture parallel to the pressing direction. TEM examination showed that the grains were highly defected and that the grain boundaries were clean. The $T_c$ was however low with an onset of 50K and a width of ~10K. Annealing studies were carried out with an aim to "fully oxygenate" the material and anneal out a *minimal* number of defects to obtain higher transition temperatures, at the same time retaining a significant defect density for enhanced flux-pinning. Magnetization measurements were performed after most anneals in order to evaluate intragranular and intergranular properties. Results indicate the presence of unusually high $J_c$'s at low temperatures after the final anneal ($T_c$ onset ~90°K). The observations may be explained by highly superior intragranular properties coupled with increased local current loop size.**

## I. INTRODUCTION

$YBa_2Cu_3O_X$ (123) appears to be the material of choice for high temperature (77K) applications. In view of this several non-conventional techniques are being explored/evaluated to process polycrystalline 123. Since 123 is known to be quite brittle, near net shaping of the material would be highly desirable. Here we report on the microstructure and superconducting properties of samples obtained by superplastic deformation of 123/25vol%Ag.

## II. EXPERIMENTAL

Commercial grade 123 powders were ground to sub-micron size, mixed with 25 vol%Ag and pressed uniaxially and isostatically under a pressure of 345MPa. The compacts were sintered at 875°C for 6hrs in air and annealed at 500°C for 24hrs in flowing oxygen. The sintered blocks (with densities greater than 95% of the theoretical density) were cut and ground into rectangular bars. The machined samples were tested in a split-type furnace attached to an Instron testing unit. The samples were preheated at a rate of 10°C/min and held for 1.5 hrs at the assigned test temperature before loading. They were then deformed under compression at temperatures of 750, 775, 800, 825, 850°C at a constant strain rate ranging from $1.0x10^{-5}$/sec to $5x10^{-4}$/sec. The strain rate was changed during the test to determine the stress exponent. Microstructures of the samples were examined using optical microscopy, scanning and transmission electron microscopy. Magnetic susceptibility and DC Magnetization measurements were performed using a Lake Shore Susceptometer. In addition, DC Magnetic susceptibility was measured using a SQUID Magnetometer.

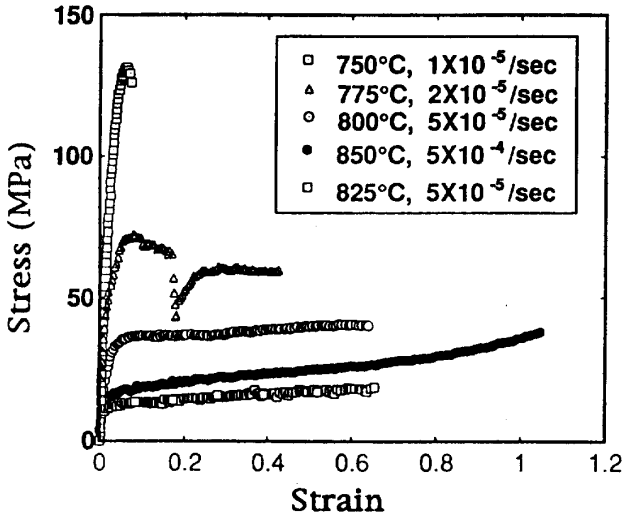


Fig. 1. High temperature deformation behavior of 123-25vol% Ag composites: stress-strain curves for compression at various temperatures and strain rates are shown.

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TABLE I

| Temperature (K) | Field (T) | $J_C$(Parallel) A/cm$^2$ | $J_C$(Perpendicular) A/cm$^2$ | $J_C$(Para.)/$J_C$(Perp.) |
|---|---|---|---|---|
| | | | | |
| 5K | 0 | $8 \times 10^5$ | $2 \times 10^5$ | 4 |
| | 2 | $2 \times 10^5$ | $7 \times 10^4$ | 2.8 |
| 20K | 0 | $3 \times 10^5$ | $9 \times 10^4$ | 3.3 |
| | 2 | $5 \times 10^4$ | $1 \times 10^4$ | 5 |
| 60K | 0 | $5 \times 10^4$ | $1.5 \times 10^4$ | 3.3 |
| | 2 | $3 \times 10^5$ | $1 \times 10^3$ | 3 |

## III. RESULTS & DISCUSSION

All tested samples, except for those at 750°C, showed large plastic deformation. The deformation curves are shown in Fig.1 [1]. At 750°C and $1.0 \times 10^{-4}$/sec, the sample fractured after 5% strain. At 775°C or higher, however, the sample deformed plastically up to 25-110%. Under plastic deformation, the strain rate $d\varepsilon/dt$, and the flow stress,$\sigma$, are related by the expression $d\varepsilon/dt = A \sigma^n \exp(-Q/RT)$, where, A is a constant, n is the stress rate exponent, Q is the activation energy for deformation, R is the gas constant and T is the temperature in Kelvin. The value of n was determined to be 1.8 at 850°C. The strain rate sensitivity at 850°C was determined to be ~0.57. This value lies in the range of 0.3-1.0 for most superplastic materials. The strain rate sensitivity is close to that predicted by the grain boundary sliding model for superplastic behavior and hence grain boundary sliding is thought to be the dominant deformation mechanism.

SEM examination of the as-deformed and an undeformed control sample indicated that after deformation significant c-axis texture is produced parallel to the pressing direction. The morphology of the silver phase within the deformed sample appears to vary as a function of position or local stress, with smaller size and higher aspect ratio near the center. However, no preferential orientation of Ag was observed. TEM examination indicated no Ag coating on 123 grains boundaries in the as-deformed sample indicating that the deformation behavior was characteristic of 123. All grain boundaries examined were clean in the sense that no secondary phases were present. Magnetic susceptibility measurements on the as-deformed sample indicated a $T_c$ onset of ~50K with a transition width of ~40K. TEM examination also showed that all grains in the deformed sample were highly defected and a very high density of stacking faults was present. Fig.2 shows a typical TEM micrograph. While grain boundary sliding is likely to be the dominant deformation mechanism, the high density of defects within the grains suggests some contribution from intragranular mechanisms.

Since the deformed sample had a high density of defects and since the grain boundaries were particularly clean and sharp, there exists potential for such materials to exhibit unique superconducting properties under conditions of optimal defect densities and oxygen concentration. To explore this possibility, a series of low temperature heat treatments in oxygen was conducted with a view to "fully oxygenate" the sample. Typical "oxygenation" treatments was 600°C, 5hrs, 500°C, 5hrs and 400°C, 5hrs in flowing oxygen. This raised the $T_c$ onset to ~70K, and the $T_c$ width to ~30K. Subsequent low temperature heat treatments were unsuccessful in raising $T_c$. The "$T_c$" appeared to have stabilized at ~70K. There exists the possibility that this may have been caused by low energy defect configurations within the grains.

In order to anneal out some defects and/or to modify the existing defect distribution, several successive high temperature treatments were conducted. Heat treatment temperatures were chosen to ensure that no bulk melting of either the silver or 123 occurred. Initially treatments were done in air between 800°C and 920°C for 2hrs. However, the $T_c$ did not rise to 90K. Further high temperature treatments were done at 920°C in 2% oxygen. The annealing time at high temperature was kept low (2hrs) with a view to minimize grain growth. After several treatments, this set of heat treatments was successful in raising the $T_c$ onset to ~90K. However the transition was still quite broad with a width of ~30K. From this point on magnetization data as a function of temperature and field were acquired as a function of successive heat treatments. The $J_c$ was calculated from magnetization hysteresis using Bean's critical state model. Assuming that the size of the circulating loop equaled the sample dimensions, a value of ~$10^5$A/cm$^2$ was obtained at 5K and zero field and a value of ~$3 \times 10^4$ A/cm$^2$ at 5 K and 2T ( the field was applied perpendicular to the pressing direction). Further high temperature treatments resulted in sharper transitions (~20K width), with a slight increase in $J_c$. This was followed by extended low temperature oxygen anneals in order to further sharpen the transition. Initial, low temperature oxygenation had no effect on the transition

Fig. 2. Typical TEM image of deformed 123 with very high defect density within the grains.

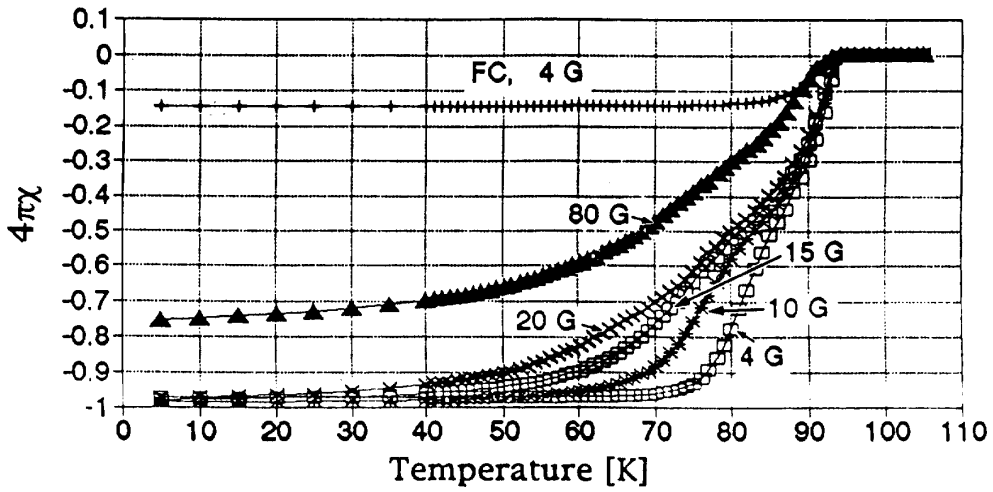


Fig. 3. DC magnetic susceptibility data for the deformed and annealed sample. FC, 4G: sample cooled to 5K in a 4G field. For ZFC curves (4G-80G): sample cooled to 5K in zero field, the field applied and sample warmed to $T>T_c$.

and further treatment resulted in a "step" or "knee" in the magnetic susceptibility at ~84K, with no significant change in the transition width and had little effect on $J_c$.

Next, a smaller piece was cut from the original sample for further magnetization measurements to determine if any anisotropy was present in the sample for applied fields parallel or perpendicular to the pressing direction. Results obtained using the entire sample dimensions to calculate the $J_c$ are listed in Table 1.

These $J_c$ values and the anisotropy in $J_c$ for fields parallel and perpendicular to the pressing direction are similar to those obtained for melt-processed 123 [2,3].

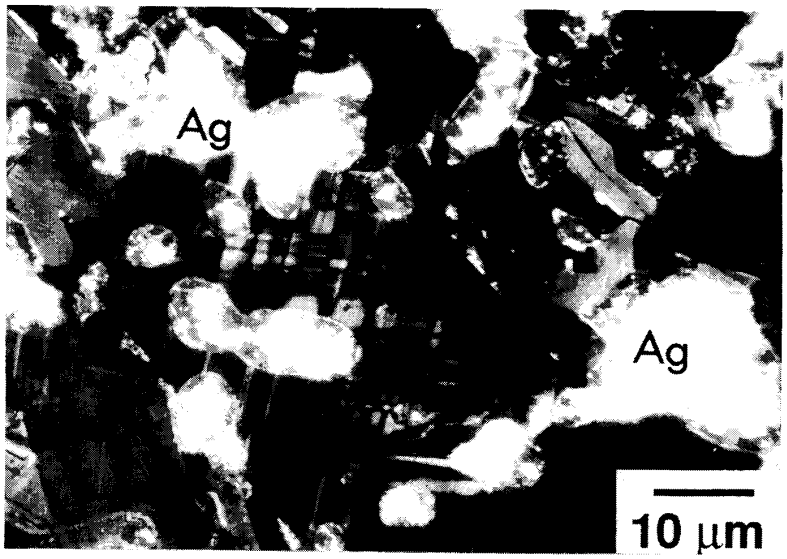


Fig. 4. Microstructure of the sample after the final anneal. Average grain size ~ 30μm.

Since high $J_C$'s were obtained assuming the sample dimensions as the size of the circulating loop, it was of great interest to study the intergrain properties. DC magnetic susceptibility studies were conducted to establish the nature of inter-grain connectivity. ZFC (zero field cooled) measurements in small magnetizing fields in the range of 0-20G, indicated the presence of "steps" or "knees", which had a strong dependence on the applied magnetic field. Increasing applied fields caused the position of the knee to move rapidly downward in temperature (see Fig.3). This behavior is a characteristic signature of "weak links" or poor inter-grain connectivity. However, since extremely high-$J_C$ values are obtained using sample dimensions, it is possible that only a fraction of the grains are weak-linked. Optical microscopy indicated that after the final heat treatment significant grain growth had occurred (see Fig.4) and the grains were almost equiaxed. The average grain size was estimated to be ~30μm (compared to ~1μm starting grain size). Assuming this grain size for calculation of $J_C$, values higher by a factor of 30 than those listed above are obtained. The microstructure of the annealed sample indicated that a large portion of the readily apparent deformation induced texture was lost during recrystallization and grain growth. However, no x-ray pole figure measurements were done. It is likely that the measured $J_C$ values may be explained by a combination of increased intergranular $J_C$ as well as the presence of some strongly coupled grain boundaries, yielding effective current loops larger than the average grain size. Should a complicated percolative current path exist in the material, then the effective current loop size is difficult to determine accurately. Further TEM examination of the sample in its present state are required reveal the nature, density and distribution of pinning centers within the grains.

## IV. SUMMARY

Superplastic deformation was performed on 123/25vol%Ag composites. The as-deformed material is highly defected and has a reduced $T_C$. It is not possible to increase the $T_C$ of the deformed samples by low temperature annealing alone. High temperature treatments were found to be necessary to anneal out some of the defects. A series of heat treatments were performed on a deformed 75%123-25%Ag sample with the aim of optimizing superconducting properties. The $T_C$ and $J_C$ (magnetization) were measured at each stage. After the final annealing, the $T_C$ was raised to 90K, however the transition was still broad (~20K). Nevertheless, magnetization measurements indicate the presence of unusually high critical currents at low temperatures. These observations may be explained by highly superior intragranular properties coupled with increased local loop size(i.e. fraction of neighboring grains that are strongly linked is increased).

## REFERENCES

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