

A phenomenological model on the deformation mechanism of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x} + \text{Ag}_2\text{O}$ composite

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The discovery in 1986 of a ceramic oxide, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, that becomes a superconductor at 77 K is regarded as one of the most important scientific achievements. Efficient processing of this ceramic, into flexible (with strength and toughness) wires, strips and cables, will require that the plasticity of this material be significantly improved so that methods such as extrusion, drawing or rolling can be employed for large-scale production. It has been our conjecture that the successful fabrication of flexible wires will require the development of a metal-superconductor composite and the processing methodology of that composite powder [1].

Researchers in the field [2-6] have long been experimenting on the addition of noble metals like silver to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (also known as the 1-2-3 compound) superconducting ceramics. However, only recently it has been reported [7] that a microcomposite system can be achieved via appropriate powder-processing route, using Ag_2O in combination with the 1-2-3 ingredients, and the sintered billet can be successfully warm-extruded to wires of one-third of its diameter. These wires are flexible and exhibit the Meissner effect without any oxygen-annealing after sintering or after extrusion. This letter discusses in the light of physico-chemical principles, some important aspects that contribute to the success of the above-mentioned processing route.

The processing essentially consists of mixing powders of Ag_2O and 1-2-3 followed by warm compaction at 250°C into 9.5 mm diameter cylindrical billets. After sintering the billets at 880°C, extrusion is performed at 450°C. Different compositions of the powder mix were tested.

The compact exhibits very good "green" strength, and a uniform dense and a well-integrated microstructure (Fig. 1). To achieve this goal, first the powder particle shape and size of the different ingredients were carefully chosen. The 1-2-3 powder, in general, had a non-equiaxed prismatic morphology and a comparatively large size. If packed randomly, an aggregate of these particles will have many interparticle voids. Obviously, much smaller spherical particles of Ag_2O were chosen to fill in these voids readily. Fig. 1 illustrates the size and morphology of the particles.

It should be emphasized that no binder is used during the mixing. It is known [8] that Ag_2O decomposes into metallic silver at 189°C (at $p_{\text{O}_2} = 1$ atm). On this basis it was conjectured that a warm compaction would lead to metallization of the Ag_2O particles on the surface and since this metallization occurs

in situ, under the compaction load (compressive), it might lead to effective interparticle welding. Fig. 2 illustrates how the original Ag_2O particles are joined to form clusters. The continuity of these particles leads to a continuous network in the bulk giving rise to the desirable structural integrity and strength in the "green" state. Furthermore, metallization facilitates plastic flow under the action of the compaction load, and thus improves the integrity by promoting the mechanical bridging and keying action. That metallization indeed took place was confirmed by the X-ray diffraction data obtained from the compacted billets. Density measurement of compacts also points in this direction. The densities of the compacted billets were determined experimentally by the Archimedes method and then compared with the theoretical density of a void-free aggregate of $\text{Ag}_2\text{O} + 1-2-3$ of identical compositions. The results (Table I) are apparently absurd, approaching the theoretical density too closely or even surpassing it! However, it is readily appreciated that the "theoretical density" cannot be dependable because it altogether ignores the metallization phenomenon. Note that compacts with large initial volume fraction of Ag_2O more closely approach the so-called "theoretical density". This observation, evidently, lends credence to the explanation presented. This is also illustrative of the fact that data on "percentage theoretical density" can often be mis-

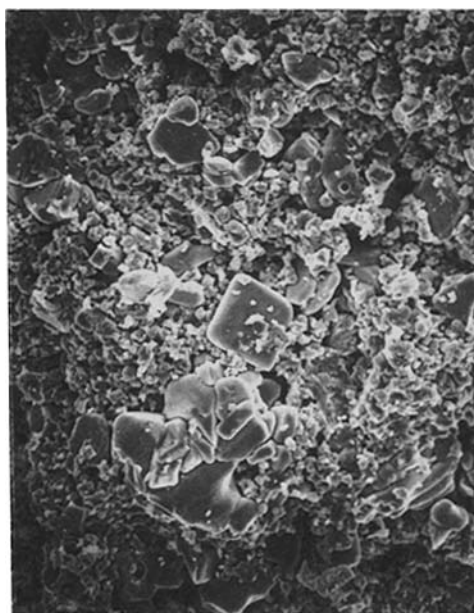


Figure 1 Scanning electron micrograph ($\times 700$) of a compacted billet of starting composition 70 vol % Ag_2O .

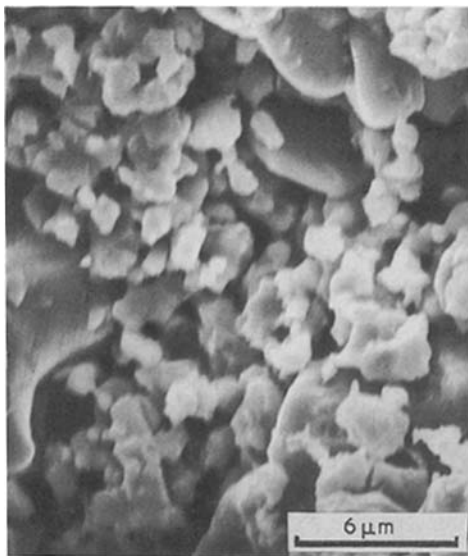


Figure 2 High-magnification ($\times 3500$) scanning electron micrograph of the same specimen as in Fig. 1.

leading unless the microstructure is known for sure quantitatively.

The decomposition of Ag_2O into silver, which began during the compaction, is completed during sintering. X-ray diffraction studies on our sintered billet confirm this. The oxygen released makes up for the oxygen-losing tendency of the 1-2-3 structure and thus effectively maintains the proper oxygen stoichiometry and orthorhombic structure of the superconducting phase. This explains the exhibition of superconducting properties by the extruded wires [7] without any need for post-sintering oxygen annealing. We believe that this decomposition plays an additional important role in significantly improving the densification during the sintering process. These microstructural changes occurring during the sintering process are essentially the key to the achievement of formability of the billet and flexibility of the extruded product. Metallic silver is much denser (specific gravity 10.5) than the monovalent oxide (specific gravity 7.143), the oxide yields 93.1% by weight of silver. These two facts lead to a significant (37%) volume reduction associated with the complete transformation of Ag_2O into silver. It is believed that at some locations inside the bulk the oxygen liberated is readily absorbed by the 1-2-3 structure and the associated volume shrinkage leads to "partial vacuum" developed locally. At other locations the 1-2-3 structure may not already be oxygen deficient and so the oxygen liberated for Ag_2O decomposition may accumulate and cause a local pressure build up. As a result steep

TABLE I Density of compacted billets of various starting composition expressed as a fraction of the theoretical density of void-free aggregates of corresponding compositions

Composition (vol %)		Specific gravity (% theoretical)
Ag_2O	Silver	
50	38.8	96.1
70	59.6	96.2
82	74	100.1

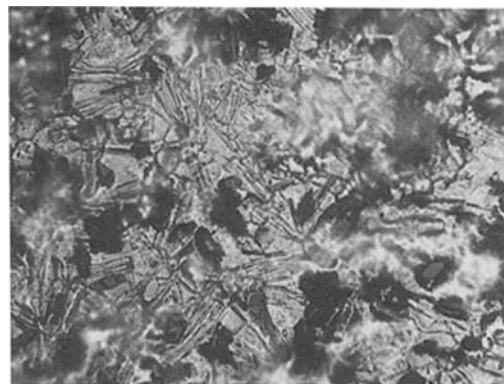


Figure 3 Micrograph ($\times 350$) showing radial dendritic pattern in a sintered billet of starting composition 70 vol % Ag_2O .

pressure gradients may set in locally inside the porous aggregate. In effect the situation tends close to a kind of chemically induced localized "pressure sintering". These pressure gradients might also be enhancing mass transfer by the evaporation-condensation mechanism.

However, it is more interesting to note that the sintering temperature (880°C) is very close to the melting point of pure silver (962°C), and the metal will be almost in a "fluid" state at such a high homologous temperature. Furthermore, the presence of oxides may bring down the effective liquidus temperature, and chemical reaction among the constituents may form a liquid phase. The radial dendritic pattern in the sintered microstructure (Fig. 3) indeed testifies in favour of liquefaction during sintering. Because of the localized pressure gradient, therefore, the "fluid" material is effectively sucked inwards to fill the voids and capillaries. The result is a strong and tough composite billet having a dense non-porous microstructure. Complete conversion of Ag_2O to silver in an ideally compacted billet, originally prepared with 70 vol % Ag_2O , should cause a theoretical volume shrinkage of 25%. The experimental observation of approximately 17% shrinkage appears to be in agreement. However, a numerical comparison in order to substantiate this simple, physical, qualitative model of densification is not very dependable, since the sintering process of the Ag_2O +

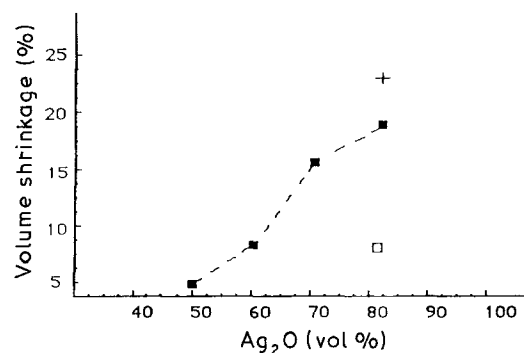


Figure 4 Effect of starting composition and compaction load on volume shrinkage of the billet during sintering. (■) 2400 lb (1090 kg) compaction load, $\text{Ag}_2\text{O}/1-2-3$ mix; (□) 2400 lb compaction load, silver/1-2-3 mix; (+) 1600 lb (726 kg) compaction load, $\text{Ag}_2\text{O}/1-2-3$ mix.

1-2-3 mix is extremely complicated and little characterized. Instead, it is more meaningful to examine the trend in the variation of the volume shrinkage during sintering for various compositions of the starting mixture (Fig. 4). A larger starting Ag_2O fraction consistently shows a higher volume shrinkage, being always in agreement with the model. The significantly low shrinkage of the specimen prepared by mixing 1-2-3 and silver (instead of Ag_2O) powders lends further credence to the proposed micromechanism of densification. The effectiveness of this mechanism of densification is highlighted by the unusually high shrinkage associated with a billet that had an unusually low initial density due to a low compaction load. However, the high volume shrinkage compensated for the low initial density. The sintering operation yielding a billet as dense as those compacted under a higher load. This has a significant implication of detaching the criticality from the compaction step of the processing route. The sintering process is relatively insensitive to the compact density, and the same high sintered density could be achieved from a compact that was sufficiently dense only to withstand handling stresses.

The phenomenon of *in situ* silver generation is also postulated to be one of the principal reasons contributing towards a strong bonding between the 1-2-3 dispersoids and the silver matrix. It is, indeed, more likely that a much more vigorous chemical interaction may result between 1-2-3 powder and the nascent silver than would have resulted if the silver had not been nascent. Fig. 5 shows an optical micrograph of the cross-section from an extruded wire of 70 vol % starting composition. The dark and out-of-focus foreground was originally a colony of the 1-2-3 phase. During microstructure preparation, pieces have been chipped off this brittle ceramic colony by the action of the grinding stresses. Eventually a cavity/depression is created in this region. The micrograph clearly shows two "chunks" bonded to the silver matrix (bright) and hanging over the larger depression. Features like this were very common in all of the extruded specimens, and essentially testify in favour of the strength of the 1-2-3/silver interface. The ceramic-metal interface is sufficiently strong not to give way under the grinding stresses that were sufficiently large to cause fracture and disintegration of the ceramic phase. Scanning

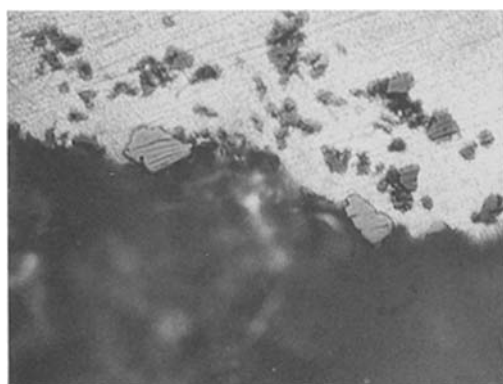


Figure 5 Optical micrograph ($\times 350$) from the cross-section of an extruded wire of starting composition 70 vol % Ag_2O .

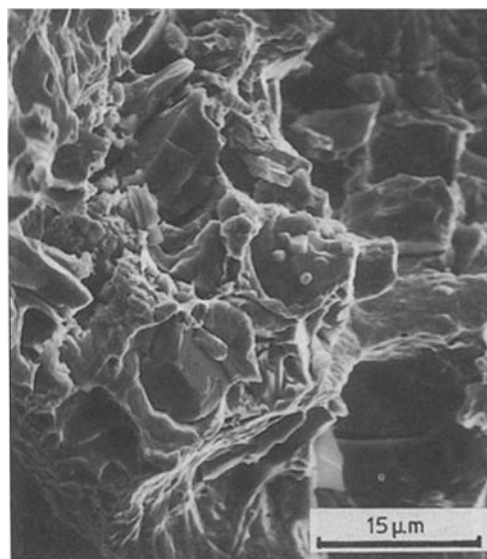


Figure 6 Scanning electron micrograph ($\times 1400$) of the fractured cross-section of an extruded wire of starting composition 70 vol % Ag_2O .

electron fractographs (Fig. 6) also reveal that the ceramic particles (dark regions) are strongly bonded to a ductile metallic matrix. It is noteworthy that no interface failure or cavitation was observed in the extruded wire.

Starting from a mixture of two oxides, the processing route eventually leads to a sintered billet that is essentially a metal-ceramic microcomposite. The microstructure consists of hard and brittle particles of the 1-2-3 ceramic phase dispersed in a ductile matrix of metallic silver. Needless to say, almost the entire plastic strain during the extrusion is taken by the ductile matrix. During large deformation of this kind of duplex microstructure, the dispersoid-matrix interface may tend to cavitate, leading to internal failures. A slow rate of deformation at an elevated temperature is known to minimize that problem. Essentially this has provided the guidelines for selecting a very slow extrusion strain rate of 10^{-4}sec^{-1} at an elevated temperature (450°C), which has eventually led to successful extrusion.

Finally, it is pointed out that the directional material flow involved in extrusion causes a preferential alignment pattern of the dispersoids along the

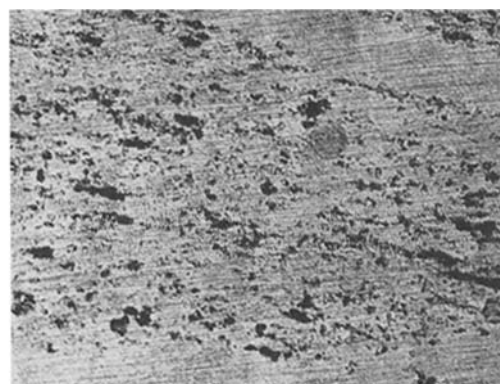


Figure 7 Optical micrograph ($\times 112$) of the longitudinal section of an extruded wire of starting composition 70 vol % Ag_2O .

axial direction. An optical micrograph of the longitudinal section from an extruded wire (Fig. 7) displays clear indication of such "fibring" of the 1-2-3 phase along the axial direction. If properly controlled, such mechanical fibring may have a significant influence on the electrical and magnetic properties of the superconducting wire.

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