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In support and extension of the mechanism of densification, strengthening and deformation behaviour of $YBa_2Cu_3O_{7-x}$–Ag_2O superconducting composites prepared by the powder metallurgy route

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In the evolution of potential shape-forming processes for high-temperature superconducting ceramics, the powder metallurgy route, using $YBa_2Cu_3O_{7-x}$ and Ag_2O powders to fabricate flexible superconducting composite wires by extrusion, occupies a unique status. The processing route is novel, particularly with respect to the strength and deformability of the product at various stages. The extruded wires display a sharp resistive transition upon oxygen annealing. A phenomenological model of the mechanism explaining the microstructural behaviour of this composite had been proposed earlier by the authors. In this communication a processing–microstructure–property correlative approach has been adopted with a view to establishing experimental support for, as well as to effect an extension of, the mechanism of strengthening, densification and deformation behaviour of $YBa_2Cu_3O_{7-x}$–Ag_2O superconducting composites prepared by the powder metallurgy route. The results of mechanical testing and microscopic investigation are used in conjunction to complete the understanding of the mechanism.

1. Introduction

In response to the continued exploration of new application areas, the large family of high-temperature superconductors, having zero resistivity around liquid nitrogen temperature, is drawing ever-increasing attention. In order to achieve the goal of real-life application, however, forming processes have to be developed to effectively shape these materials as desired. The strength and toughness of the materials are, therefore, of principal concern, at least in view of retention of the shape, if not for the shaping process. Considering the inherent brittleness of ceramics, the task of shape-forming becomes extremely difficult, all the more so because the finished product must exhibit high-temperature superconductivity.

Researchers in the field [1–5] have long been experimenting on the use of noble metals, e.g. Ag and Au and their oxides such as Ag_2O added to $YBa_2Cu_3O_{7-x}$ (also known as YBCO), essentially with a view to defeating the difficulties in shape-forming of this superconducting ceramic oxide. The governing idea in common is to externally impose formability on the brittle ceramic by a clever technological use of the ductile metal. However, following a different paradigm of thinking, it has been conjectured [6] that successful fabrication of superconducting wires would require the development of a noble metal–superconductive ceramic microcomposite, and the processing methodology of that composite material. This idea is essentially different from the previous one in the sense that it aims at incorporating strength and deformability within the microstructure of the material, thus developing its own intrinsic formability. In a following publication [7], it was reported that a microcomposite system could be achieved via an appropriate powder processing route using YBCO in combination with Ag_2O. The sintered billet can be successfully warm-extruded to wires of one-third its diameter. The material exhibits a sharp resistive transition at around 90 K upon oxygen annealing. As we shall also find later in this paper, the composite microstructure promises significantly high strength, toughness and deformability. A subsequent communication [8] discussed, in the light of physico-chemical principles, some important aspects underlying the success of the above-mentioned processing route.

In that paper [8], a phenomenological model was forwarded with a view to understanding the mechanism that governs the physico-chemical, mechanical as well as microstructural behaviour of the YBCO–Ag_2O microcomposite. The phenomenon of *in situ* silver generation is postulated to be one of the

0022–2461

principal reasons contributing toward an effective bonding at the interparticle boundaries. The metallized boundaries are proposed to strengthen the material, as well as develop fracture resistance by arresting propagation of microcracks [7]. Briefly stated, the hypothesis [8] regarding the dominant mechanism of sintering claims that densification is essentially attained by localized *in situ* pressure-sintering effects. The decomposition of silver oxide, coupled with the associated volume shrinkage, develop localized pressure gradients within the microstructure. Metallic silver flows along these gradients to fill in the interparticle discontinuities.

The above model, however, was presented with limited experimental support. The evidence was mostly micrographical. Supporting results from relevant mechanical tests were missing. A convincing explanation for the liquefaction of silver below its melting point was wanted. The role of the so-called brittle ceramic phase in the deformation behaviour of the composite as a whole was nowhere explicitly discussed.

In this communication a processing–microstructure–property correlative approach has been adopted with a view to establishing experimental support for, as well as to effect an extension of, the mechanism of strengthening, densification and deformation behaviour of $YBa_2Cu_3O_{7-x}$–Ag_2O superconducting composites prepared by the powder metallurgy route. Mechanical testing has been performed on the material, at various stages of fabrication, to verify the predictions and implications of the model. In view of the fact that both the processes of compaction and extrusion are essentially compressive in nature, a compression test has been performed on the material at various stages to characterize its mechanical behaviour. Additional micrographic investigations have been undertaken in search of more direct microstructural evidence. The micromechanism explaining the drop in the liquidus temperature of the metallic phase below the melting point of silver has been revealed, and confirmative evidence provided. Transmission electron microscopic studies have revealed the role played by the superconducting ceramic phase during deformation-processing of the composite microstructure. Following predictions implicit in the elaborate model developed here, preliminary experiments on the hot extrusion of powder compacts without any sintering step have shown promising results. Finally, we note that the experimental evidence for our model has been obtained from a specific material, namely the YBCO–Ag_2O microcomposite. However, we know that there exist many other superconducting ceramic oxides of the same generic nature as YBCO. It may not be too ambitious to expect that essentially a similar mechanism would govern the microstructural behaviour, should similar composites with these other ceramics be prepared.

2. Experimental procedure

Preparation of the composite started with thoroughly mixing superconductive $YBa_2Cu_3O_{7-x}$ powder with the desired amount of Ag_2O powder, giving a 50 vol % composition. The average particle size of the powders was in the 5–10 μm range. The powder mix was then warm-compacted, mostly at 250 °C, into 9.2 mm diameter billets of approximately 20 mm length. The compacted billets were usually sintered in air at 880 °C followed by furnace cooling. Subsequently the billets were extruded [7] at 450 °C into 3.2 mm diameter wires, maintaining a single-step extrusion ratio of 9:1. Room-temperature compression tests were performed on specimens prepared from compacted as well as sintered billets, maintaining a diameter to height ratio of 1:3.

3. Results and discussion

With a view to understanding the micromechanism of strengthening of YBCO–Ag_2O powder compacts, it had been "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 compaction load (compressive), it might lead to effective interparticle welding" [7]. This postulate was essentially founded on the fact that thermodynamically Ag_2O decomposes into metallic silver at 189 °C (at $p_{O_2} = 1$ atm). In order to have direct experimental verification, two different types of compression test specimens were prepared from a batch of powder having a composition of 50 vol % Ag_2O. One variety was compacted at 175 °C and the other at 250 °C, keeping all other parameters of the compaction process unchanged. The results of compression tests conducted on them are shown in Fig. 1. It is interesting to note that although the variation in compaction temperature was scarcely adequate to effect a significant change in the compaction process kinetics, yet the ultimate strength (as well as total strain) of the specimen compacted at 250 °C was very nearly twice that of the specimen compacted at 175 °C. In addition, microscopic investigation of the specimen compacted at 250 °C reveals incipient formation of metallic silver (glistening white specks) as shown in Fig. 2, while no

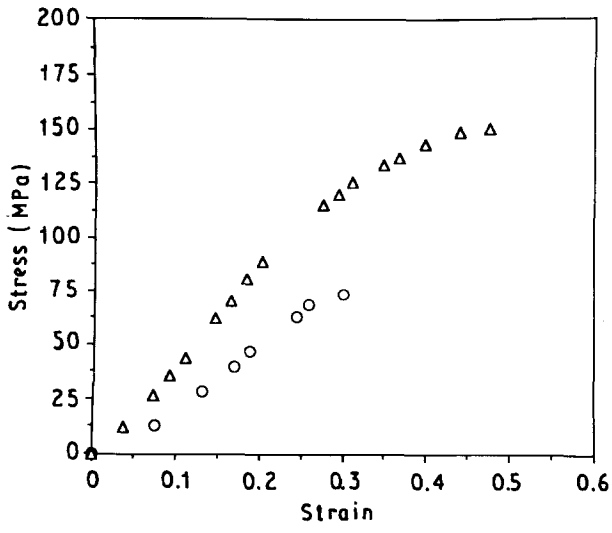

Figure 1 Comparison of compression test results from specimens compacted at different temperatures: (○) 175 °C, (△) 250 °C.

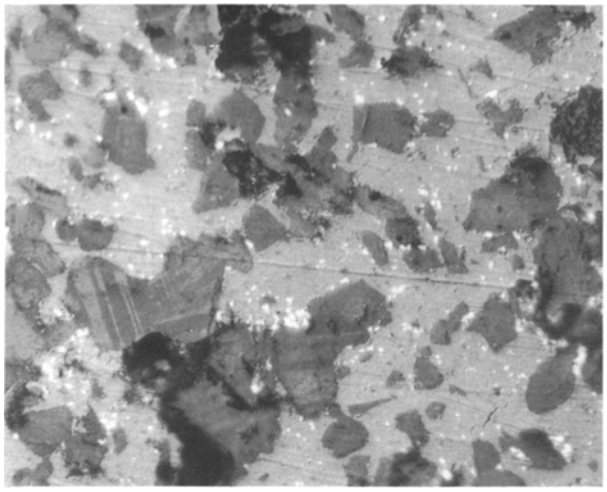

Figure 2 Optical micrograph (× 1000) of a specimen after warm compaction at 250 °C.

trace of such metallization was observed in the specimen compacted at 175 °C. Together, these two observations testify strongly in favour of the hypothesis.

In accord with our model of densification of the YBCO–Ag_2O composite [8], the results of microscopic investigation reported here, as well as earlier [7, 8], lead us to postulate that the metal–ceramic (Ag–YBCO) interphase interface is relatively stronger, defect-free and resistant to fracture propagation as compared with the interceramic YBCO–particle interface. However, in order to make an assertion, the requirement for confirmative evidence from at least one direct mechanical test cannot be compromised. In view of this, compression tests were performed on otherwise similar sintered specimens of three different microstructural fineness (Fig. 3). It is readily appreciated that the finer the distribution of the two different phases in a duplex microstructure, the larger is the area fraction, as well as the actual area, of the interphase interface in comparison with that of the interceramic–particle interface. Note that if deformability was primarily governed by the bulk of the ductile metallic phase, then all three specimens would have behaved similarly because they had identical chemical composition, and hence the same volume fraction of the metallic phase. In the light of the above, the results of the compression test as shown in Fig. 4 stand in verification of the postulate. The better fracture resistance and hence higher energy-absorption capacity of the finer microstructures, having a larger interphase interface area, is manifested in their ability to undergo a larger plastic deformation prior to failure. Note that a 50 vol % Ag_2O–YBCO powder mix yields a 40 vol % Ag–YBCO composite billet upon sintering. Comparison with the compression test results of previous workers [9] on similar specimens, as shown in Fig. 5, indicates that these microcomposites, particularly the ones with a uniform and fine microstructural distribution such as type A (Fig. 3), have attained a superior level of mechanical properties, especially deformability.

From a general knowledge of the micromechanism of failure of a polycrystalline aggregate, it may be said

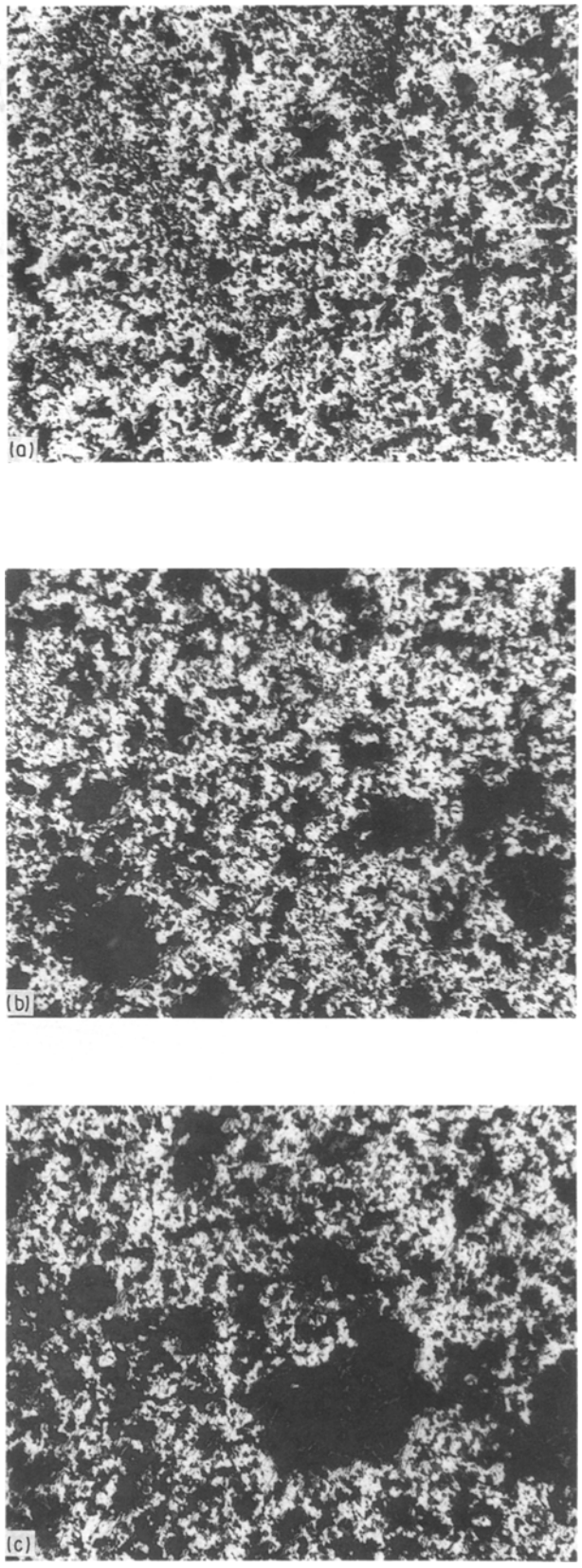

Figure 3 Optical micrographs (× 100) of sintered specimens showing variation in microstructural fineness: (a) type A, (b) type B and (c) type C.

that the ultimate strength of a specimen is somewhat inversely related to the size of the largest flaw in its microstructure. At around the ultimate strength level, the applied load works to initiate and propagate microcracks forming at these larger flaws. It is obvious that in powder aggregates the larger among the microstructural flaws are almost invariably located in the

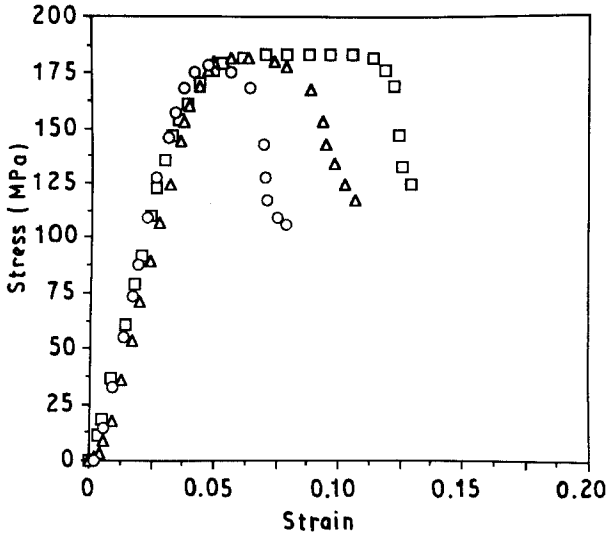

Figure 4 Compression test results from sintered specimens of types (□) A, (△) B and (○) C having different microstructural fineness.

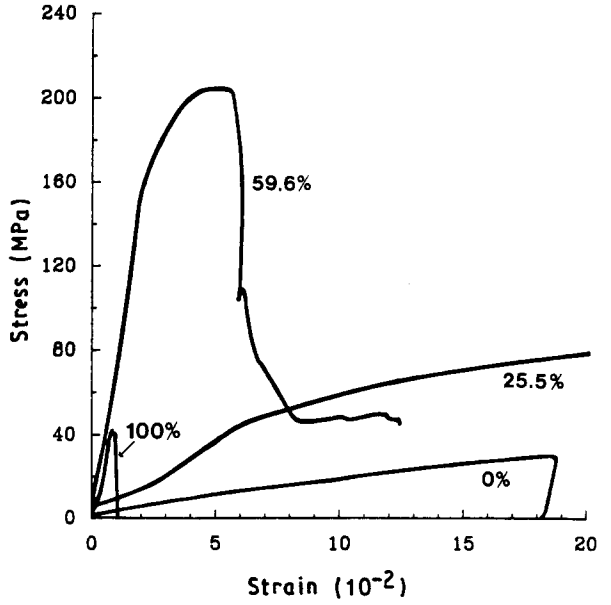

Figure 5 Results of compression tests performed on YBCO–Ag composites by Garland *et al.* [9]. For a comparison with the mechanical behaviour of our composites in Fig. 4, note the behaviour of the composite having a 59.6% volume fraction of YBCO, as indicated on the graph.

interparticle regions. In the context of the composite concerned, therefore, the ultimate strength level would in practice be maximized if the interparticle boundaries all over the microstructure were practically welded. Note that, contrary to the effect on deformation behaviour, the relative area fraction, as well as actual areas, of the intraphase and interphase boundaries are of little importance here. When subjected to the same prolonged, high-temperature sintering treatment, it is reasonable to expect that interparticle bonding would be practically complete in all three microstructures (Fig. 3). In the light of the above, therefore, all three are expected to display essentially the same level of ultimate strength. That is indeed what we see in the experimental results (Fig. 4).

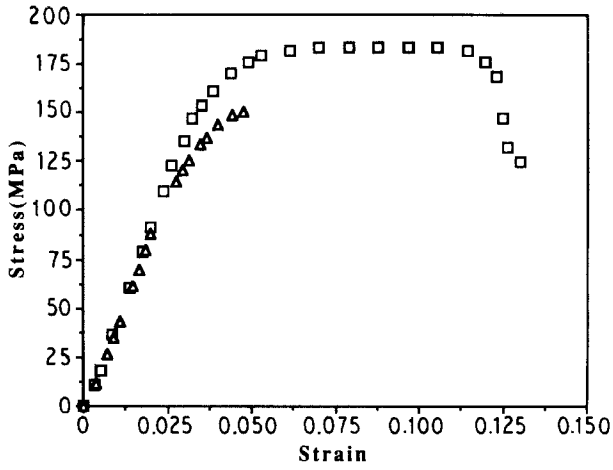

Figure 6 Comparison of compression test results obtained from (□) a sintered specimen with the finest microstructure (type A) and (△) a specimen warm-compacted at 250 °C.

It is understandable that the inherent weakness of "unsintered" powder aggregates essentially reflects not the weakness of individual powder particles, but the weakness of the bonding at the particle boundaries. Bearing that in mind we note, in Fig. 2, that most of the silver germinates preferentially at the particle boundaries. This formation of nascent silver promises to overcome the weakness effectively. Fig. 6 compares the compression test response of a specimen compacted at 250 °C with that of the sintered specimen displaying the "best" mechanical behaviour, namely type A. The two specimens had an identical starting composition. We note that the ultimate strength of the warm-compacted specimen is quite comparable with that of the sintered specimen. It is reasonable to conclude now that metallization at the interparticle boundaries, and not the bulk of the metallic phase in the microstructure, is primarily responsible for development of the strength. This observation also demonstrates that, contrary to common belief, it is possible to impart considerable strength to powder aggregates without resorting to any prolonged, high-temperature sintering treatment. However, it should not be overlooked that the deformation prior to fracture is significantly smaller in the warm-compacted specimen. In search of an explanation, the first impulse would, perhaps, be to argue that the absence of any significant amount of bulk, ductile metallic phase is solely responsible for its poor deformation characteristics. However, this argument loses much of its strength when viewed in the light of the discussion of our observations in Fig. 4. Note that we have reasons [7, 8] to believe that the deformation characteristics prior to fracture of this composite material are largely governed by the microstructural resistance to microcrack propagation offered by well-developed metallized interphase boundaries. The results of microscopic investigation (e.g. Fig. 2) indicate that in a warm-compacted billet the process of metallization at the boundaries has been initiated, and is in progress, but is yet to be complete and well-developed throughout the entire microstructure. In view of that it may not be extravagant to claim that the poor deformation characteristics of the warm-compacted billet can be

attributed, at least partially, to the lack of well-developed metallization along the interphase boundaries in the microstructure.

If the claim is reasonably valid that the strength as well as deformation behaviour of the composite are significantly governed by metallization at the particle boundaries, then one is prompted to think that it might well be feasible to hot-extrude the billet into wire directly after warm compaction, eliminating any extended high-temperature sintering step altogether. Preliminary experiments [10] show a promising response. The warm-compacted billet was put into the extrusion chamber and heated up to the desired temperature. The extrusion process, having a single-step extrusion ratio of 9:1, was essentially successful, although the quality of the wire coming out (Fig. 7) was not quite closely comparable with that of the wires produced by the original route. It is believed that the preheating period, coupled with the slow rate of extrusion at an elevated temperature, contributed toward *in situ* metallization to the required level of development, and thus was conducive to the preliminary success of the process.

Although nucleation of a new phase is generally more favourable at grain boundaries, the probable influence of the oxygen affinity of YBCO to favour silver oxide losing oxygen preferentially in its vicinity cannot altogether be overruled. A careful study of relevant micrographs, such as Fig. 2, reveals that the metallic phase clusters particularly around the YBCO–Ag_2O boundaries, much in favour of the Ag_2O grain boundaries. This observation indeed conforms to the phenomenological model of sintering of this composite aggregate [8]. At elevated temperatures, the YBCO may act as some kind of a "sink" for the oxygen liberated from Ag_2O decomposition by way of incorporating that oxygen into its lattice. Note that the phenomenon of oxygen liberation has the effect of raising the partial pressure of oxygen locally to a much higher level, and this is expected to promote oxygen incorporation into the YBCO lattice. When coupled with the volume shrinkage associated with silver oxide decomposition [8], formation of a "partial vacuum" is favoured preferentially around the interphase boundaries. The absence of any such "sink" away from the interphase interface enhances the build-up of a localized "pressure gradient" sloping downward to the YBCO particle. Thus, we may have

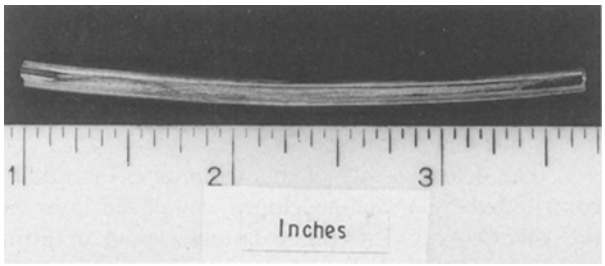

Figure 7 Photograph of YBCO–Ag_2O wire hot-extruded directly from warm-compacted billets, eliminating the sintering operation (1 in. = 25.4 mm).

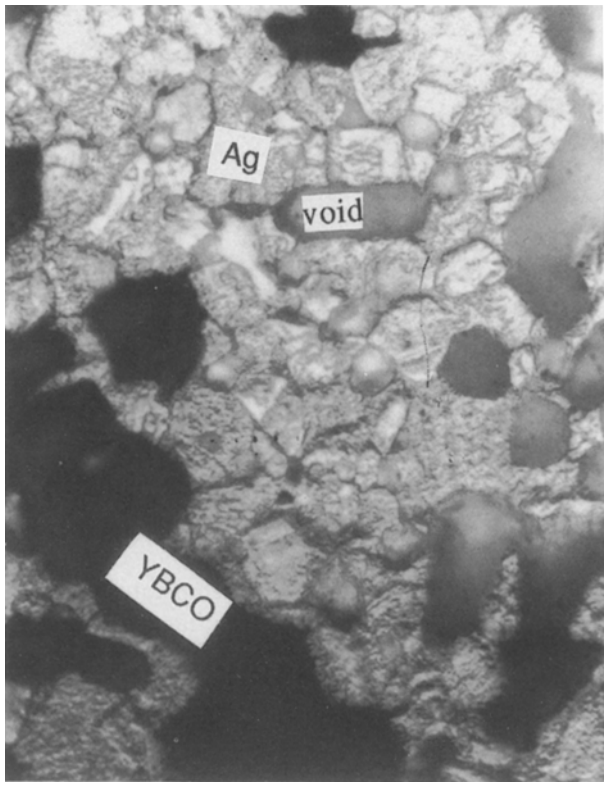

Figure 8 Optical micrograph (× 1000) of a sintered specimen illustrating superior densification in the vicinity of the YBCO–Ag boundary.

particularly well-developed pressure gradients distributed selectively around the interphase boundaries in the microstructure. Accordingly, the effect of "localized pressure sintering" should be more pronounced around that region, leading to the development of relatively defect-free interphase boundaries. In that respect, Fig. 8 is claimed to be a metallographic evidence of the *in situ* pressure-sintering effect at high temperature. It illustrates that the metallic phase in the vicinity of the ceramic phase is comparatively denser, and the interphase boundary relatively defect-free, while there are some residual voids away from it, situated in the metallic phase. The importance of having nearly defect-free regions at the interparticle boundaries cannot be overemphasized, particularly in reference to the powder processing route of fabrication technology. The voids still remaining after sintering are located essentially in the metallic silver matrix, and are undoubtedly much less harmful than interparticle boundary defects. Further, it goes without saying for this particular material that minimizing boundary defects will also contribute towards improvement of its electrical properties.

In developing the model of densification during sintering, it had been postulated [8] that the metallic phase flowed into voids and discontinuities as if "fluid". Any explanation for liquefaction below the melting temperature of silver, however, was missing. In that context, a probable mechanism is now being strongly suggested. It is believed that a small amount of copper from the YBCO lattice diffuses into the silvery phase; and since copper forms a low-melting

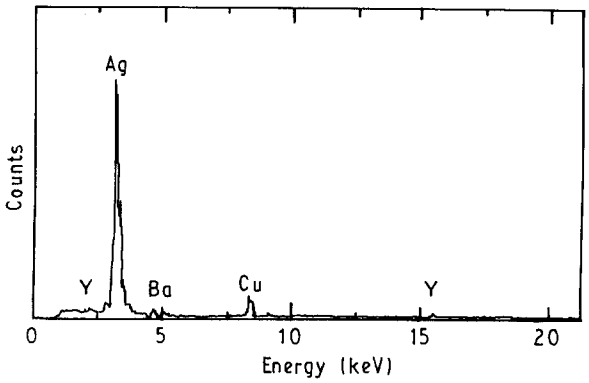

Figure 9 Result of a typical EDAX analysis conducted on the silvery phase of the duplex microstructure of the sintered composite. The presence of copper in the silver is clearly revealed.

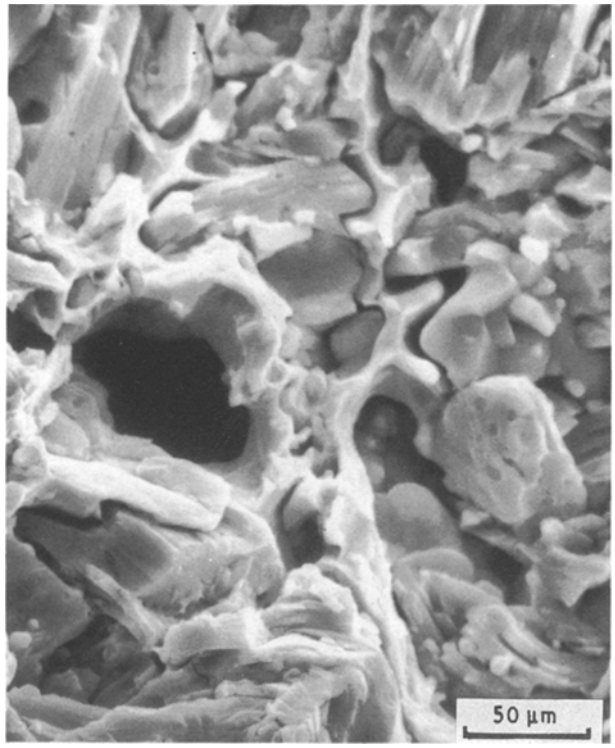

Figure 10 Scanning electron micrograph of a composite specimen that had been sintered. A distinctive flow pattern of silver (white stream) through and in between the YBCO particles (dark grey) is clearly visible.

eutectic with silver, the liquidus temperature is effectively brought down from the melting point of pure silver (962 °C) to below the sintering temperature (880 °C). In confirmation, energy-dispersive X-ray analysis (EDAX) conducted on the "silver" in the sintered microstructure shows the presence of copper in it (Fig. 9). In addition, the scanning electron micrograph of Fig. 10 records the distinctive flow pattern of silver (white streams) in the microstructure, illustrating how, in a fluid state, it was "sucked inwards" between the ceramic particles (dark grey).

All the earlier discussion here, as well as related previous publications [7, 8], appears to have an underlying tone expressing non-participation of the ceramic phase as such in any deformation process of the composite. It may tacitly imply that the ceramic particles are completely unable to accommodate any deformation whatsoever. As an experimental investigation, a 9 h annealing treatment in air at 880 °C was given to both the sintered billet and the extruded wire of starting composition 50 vol % Ag_2O. Although the microstructure of the sintered billet did not change significantly, that of the extruded wire was altogether altered. The resulting microstructure of the latter (Fig. 11b) records a complete change of morphology of the YBCO phase. From a particulate dispersoid, the ceramic YBCO phase is transformed into a continuous interwoven network upon annealing. However, the sintered microstructure did not undergo any significant change upon annealing (see Fig. 11a). Our comparative study leads us to believe that this morphological transformation is induced by some energy stored in the ceramic phase of the extruded specimen. The only possible source for this stored energy is the work of deformation during extrusion. The inference is now clearly visible: in addition to the metallic phase, the ceramic phase is also accommodating some deformation during extrusion of the composite. This inference is indeed rather striking. In further support of it, a transmission electron micrograph (Fig. 12) of the extruded specimen reveals grain-boundary dislocations in the YBCO phase. The good welding achieved between the two YBCO particles can be deduced from the formation of a clear boundary with the observed interfacial dislocation array. The dislocation attached to the grain boundary and extending into one of the grains is most likely to be a dislocation generated during deformation. It is important to note that this dislocation, perhaps because of being in a ceramic phase, has survived a rather prolonged high-temperature annealing treatment. Accordingly, it may be expected in our fabrication route of YBCO–Ag composite superconducting wires that the deformation process would generate dislocations in the ceramic phase; at least some of them would remain after a post-extrusion oxygen anneal. Fig. 13 shows the resistive transition of a typical extruded wire after an oxygen annealing treatment. The specimen displays a sharp resistive transition at 91 K and the zero-resistance state is achieved at 82 K. This clearly demonstrates that the presence of silver in the microstructure has not degraded the T_c of the superconducting ceramic phase (YBCO).

4. Conclusions

1. The strength of the composite comes essentially from interparticle welding, and that is significantly enhanced by metallization at the surface of the Ag_2O particles. Warm compaction of the powder mix promotes this metallization.

2. The deformability of this material is essentially contributed by a well-developed metallized layer at the YBCO–Ag_2O interphase boundaries. A uniform and finely distributed duplex microstructure significantly improves the deformability.

3. Preliminary verification has been obtained in favour of the feasibility of bulk hot deformation of the

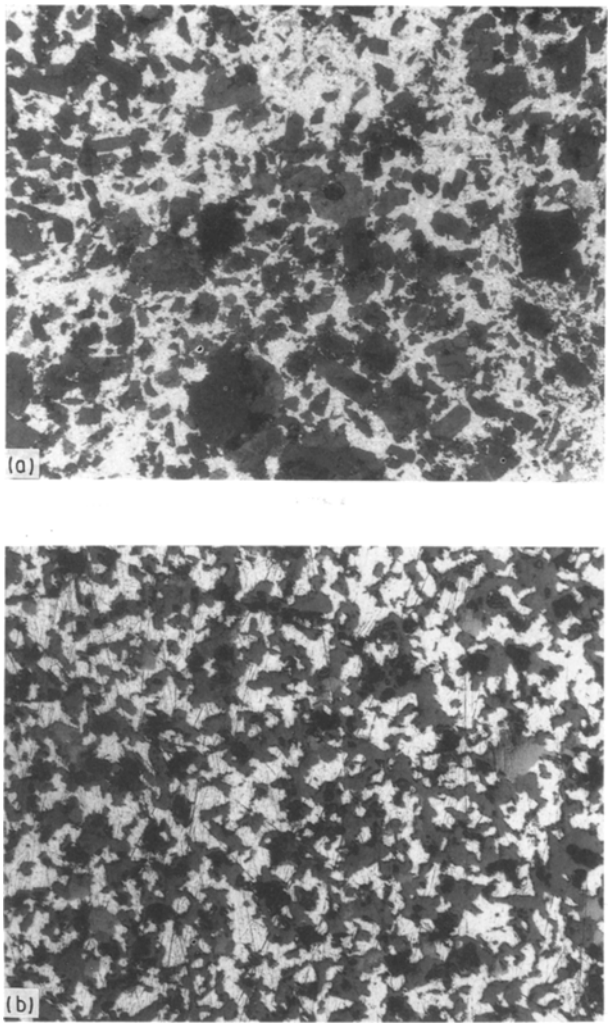

Figure 11 Optical micrograph (× 500) of specimens subjected to annealing in air at 880 °C, (a) after sintering and (b) after extrusion. Note the morphology of the YBCO phase (dark).

powder compact without any need for prior high-temperature sintering.

4. Densification during sintering of this material is predominantly governed by localized *in situ* pressure-sintering effects brought about by decomposition of the silver oxide and the associated liquefaction of the metallic silver formed. This mechanism ensures superior densification around the interparticle boundary regions.

5. Part of the large plastic deformation undergone by the sintered billet is accommodated by the so-called brittle ceramic phase. As a result, dislocations capable of acting as effective flux-pinning centres are generated inside the superconductive ceramic grains. Further, suitable post-deformation thermal treatment is seen to achieve a continuous interwoven network of the superconductive ceramic phase in the composite microstructure. The above observations point to a direction of probable improvement of superconducting properties of the composite concerned.

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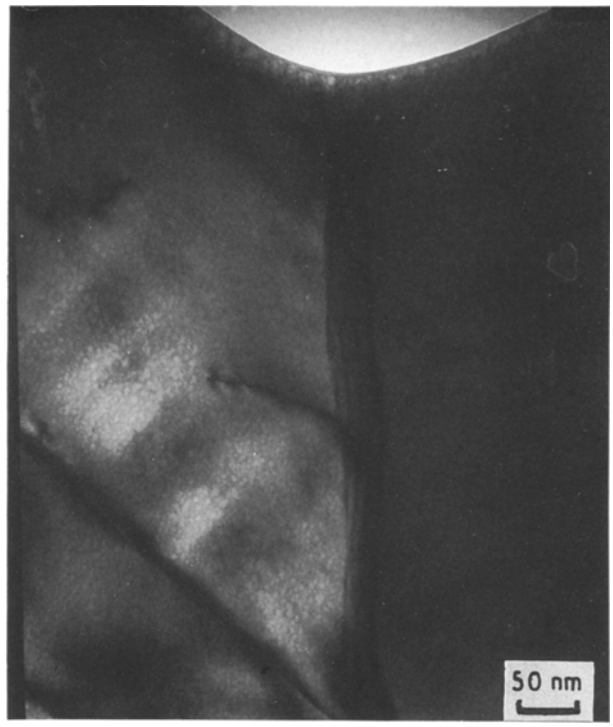

Figure 12 Transmission electron micrograph of wire specimen subjected to a post-extrusion anneal. Dislocations at the grain boundary between two YBCO grains are to be noted.

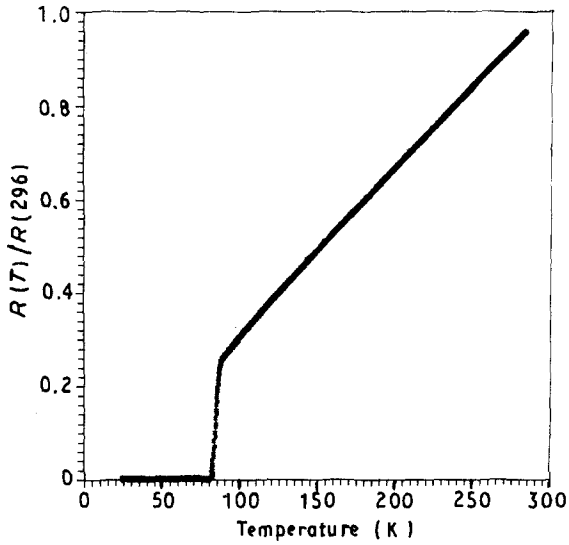

Figure 13 Resistive transition of 50 vol % Ag_2O–YBCO extruded wire after a post-extrusion oxygen anneal.

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