RESEARCH NOTE

EFFECT OF SINTERING CONDITIONS ON MICROSTRUCTURE AND THE SUPERCONDUCTING PROPERTIES OF $YBa_2Cu_3O_{7-X}$

J. Javadpour and A. Yusefi

Department of Materials Science and Engineering
Iran University of Science and Technology
Tehran, Iran, javadpourj@iust.ac.ir - yusefia@iust.ac.ir

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Abstract $YBa_2Cu_3O_{7-X}$ tapes fabricated from precursor powder, were used to investigate the effect of sintering conditions on the microstructure. The sintering experiments were carried out in oxygen over the temperature range of 915 - 950°C. Scanning electron microscopy was used to examine the sintered products. The results indicated a significant increase in densification and grain growth when the tapes were heat treated above 915°C. The critical current density in the sintered tapes showed deteriotation when the sintering was done at temperatures above 915°C.

Key Words Superconductor, $YBa_2Cu_3O_{7-X}$, D.C. Susceptibility, Critical Current Density, Microstructure

چکیده در کار حاضر تأثیر شرایط سینترینگ بر ریز ساختار قطعات نازک $YBa_2Cu_3O_{7-X}$ مورد بررسی قرار گرفته است. آزمایشهای سینترینگ در اتمسفر اکسیژن و در محدوده دمایی ۹۱۵ - ۹۵۰ درجه سانتیگراد انجام شده است. نتایج بررسی ریزساختاری توسط SEM نشانگر افزایش دانسیته و رشد دانه‌ها در دمای بالاتر از ۹۱۵ درجه سانتیگراد می‌باشد. همینطور در قطعاتی که در دمایی بالاتر از ۹۱۵ درجه سانتیگراد سینتر شده‌اند افت چگالی جریان الکتریکی مشاهده شده است.

1. INTRODUCTION

One of the major goals in the processing of the polycrystalline ceramic superconductors is to produce solid parts which are mechanically strong and at the same time are able to carry a large amount of current [1-5]. It is well known that the physical properties of the engineering materials are strongly affected by their microstructure. Based on this, it was decided to analyze the influence of sintering temperature on the microstructural evolution and critical current density in the $YBa_2Cu_3O_{7-X}$ tapes. Most sintering studies on $YBa_2Cu_3O_{7-X}$, have been done by using calcined orthorhombic powders. Densification through this process generally produced microstructures with large grains (10-20μm in diameter) which at least from strength point of view are not desirable. In this work, we decided to examine densification behavior by reaction sintering route; a simpler one step process where phase transformation and sintering take place simultaneously. The main reason for choosing precursors as our starting material was their fine size. This translates into high surface energy and therefore maximum driving force for densification. Because of this advantage, it was thought this technique might result in producing dense, small grained microstructure at low temperatures. The paper reports on the preparation, microstructure and

superconducting properties of the tapes prepared by this route.

2. EXPERIMENTAL PROCEDURE

The precursor powder used in fabricating tapes was prepared by spray drying a mixture of aqueous metal nitrate solution consisting of $Y(NO_3)_3$, $Ba(NO_3)_2$ and $Cu(NO_3)_2$ in the desired stoichiometric ratio to form an intimatelly mixed starting powder. X-ray analysis of the as spray dried (decomposed powder) indicated the presence of $BaCO_3$, CuO and Y_2O_3 phases. $BaCO_3$ seems to be the stable phase rather than BaO after spray drying the precursor powder.

Preparation of the tape started by suspending 30 vol%. precursor powder in a (60:40 vol.%) solvent composed of methyl ethyl ketone and ethyl alcohol. The particles were dispersed by the addition of an appropriate amount of polymeric dispersing agent (fish oil) determined from sedimentation studies (0.75 wt.% of solid in this case).

Flexibility and strength to the unfired tapes were provided by the addition of 0.3 wt.% of polyvinyl butyral to the suspension. The resulting stable suspension was cast on to a glass surface using a doctor blade.

The organic binder vehicle was burned off by heating the as cast tape slowly (12°/hr) to 500°C in air. This was followed by a 1°C/min to temperatures between 915-950°C in oxygen. The soaking time at highest temperatures was 6hrs. The sintered tapes were approximately 100 μm thick. Microstructutes of the sintered tapes were characterized using scanning electron microscopy.

The apparent density of the sintered tapes was measured using the Archimedes principle. Formation of the orthorhombic phase was verified using X-ray diffraction. The onset of superconducting temperature was measured by performing d. c. susceptibility experiment. In addition, the critical current density, Jc in the sintered tapes was measured using 4-probe technique. Jc values were measured at 77K in zero applied field with the criteria of 1μV/cm.

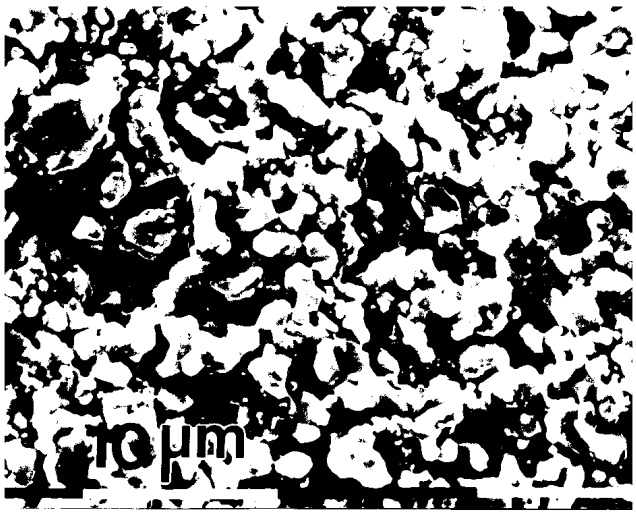

Figure 1. SEM image of as cast tape.

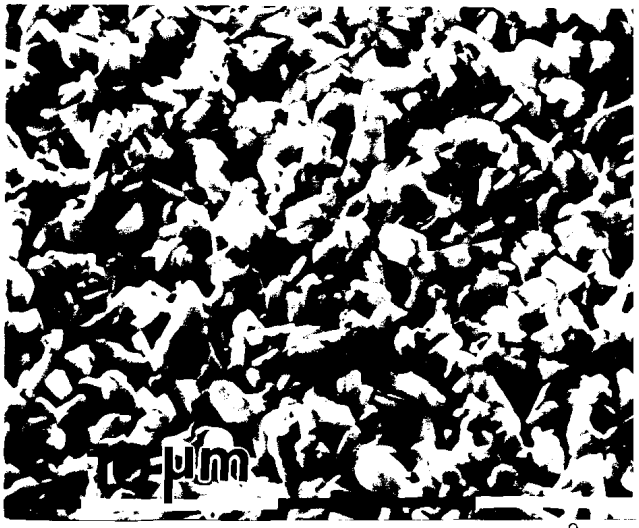

Figure 2. SEM image of sample sintered at 915°C for 6hrs.

3. RESULTS AND DISCUSSION

As mentioned before, due to the formation of orthorhombic superconducting phase at

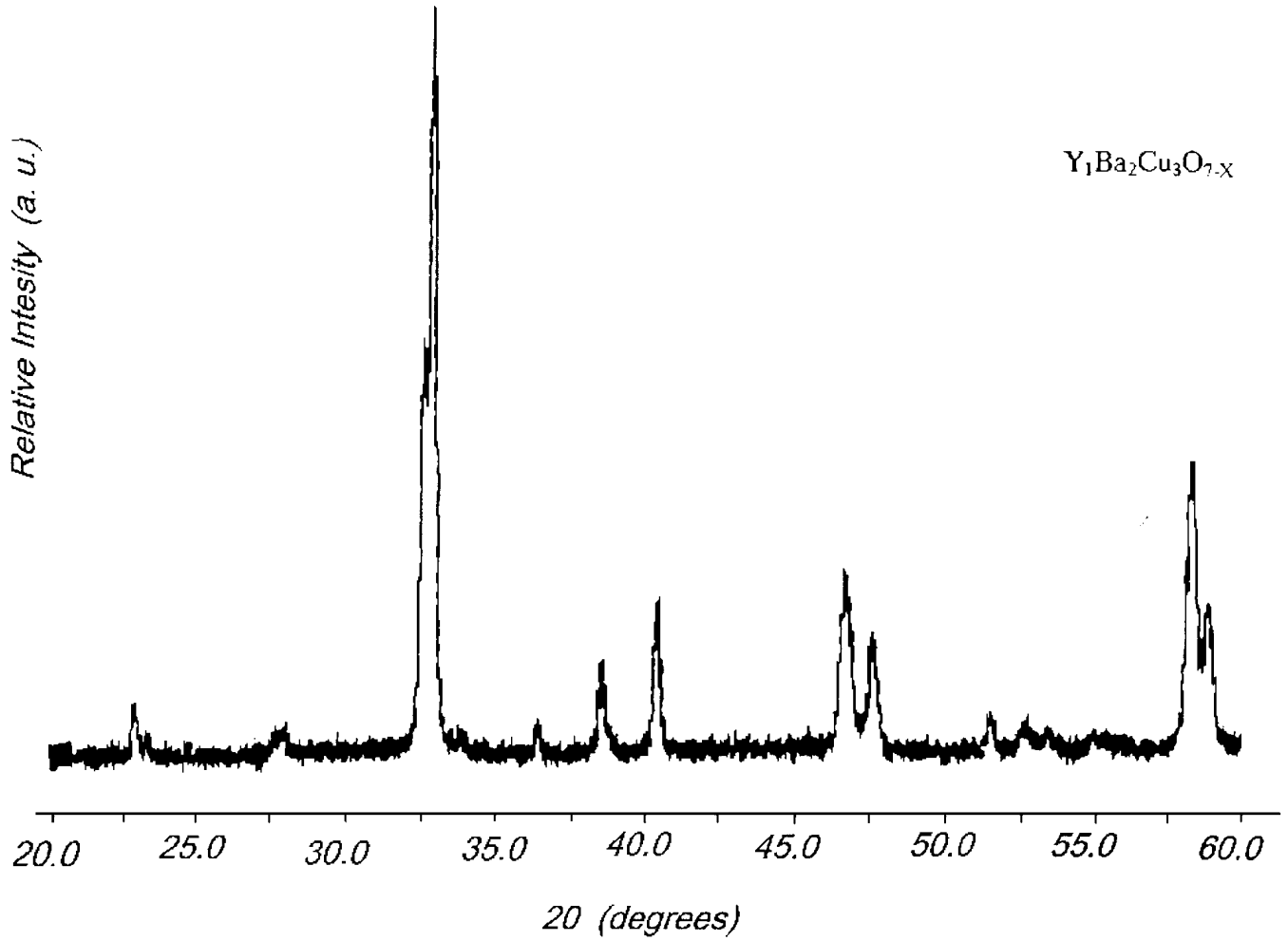

Figure 3. X-ray diffraction pattern of sample sintered at 915°C for 6hrs.

temperatures above 900°C, the sintering of the as cast tapes were done in oxygen over the temperature range of 915-950°C. The Microstructure of a piece of the as cast tape is shown in Figure 1. The most noticeable feature in this microstrcuture is the relative uniformity in the microstructure, which is highly important in obtaining defect free sintered products.

Figure 2. presents the microstructure after sintering at 915°C for 6hrs. As seen from the micrograph the densification has started with the measured density of around 88% of the theoretical value. The microstructure consists of grains in the range of 2-3 μm in size. The X-ray diffraction pattern from this sample is displayed in Figure 3. As seen, all the peaks in the pattern belong to the orthorhombic superconduting structure.

The onset of superconducting temperature for this sample is 92K as determined by d. c. susceptibility experiment (Figure 4). The microstructure of the sample sintered at 930°C for 6hr, is shown in Figure 5. The significant change in densification and grain size at this temperature is accompanied by what appears to be melting. This observation is consistent with the earlier reports regarding the formation of a liquid phase as phase development reaction proceeds in the $YBa_2Cu_3O_{7-X}$ system [6-8].

These authors reported formation of an eutectic between $BaCuO_2$ and CuO around 900°C near 60% CuO. Differential thermal

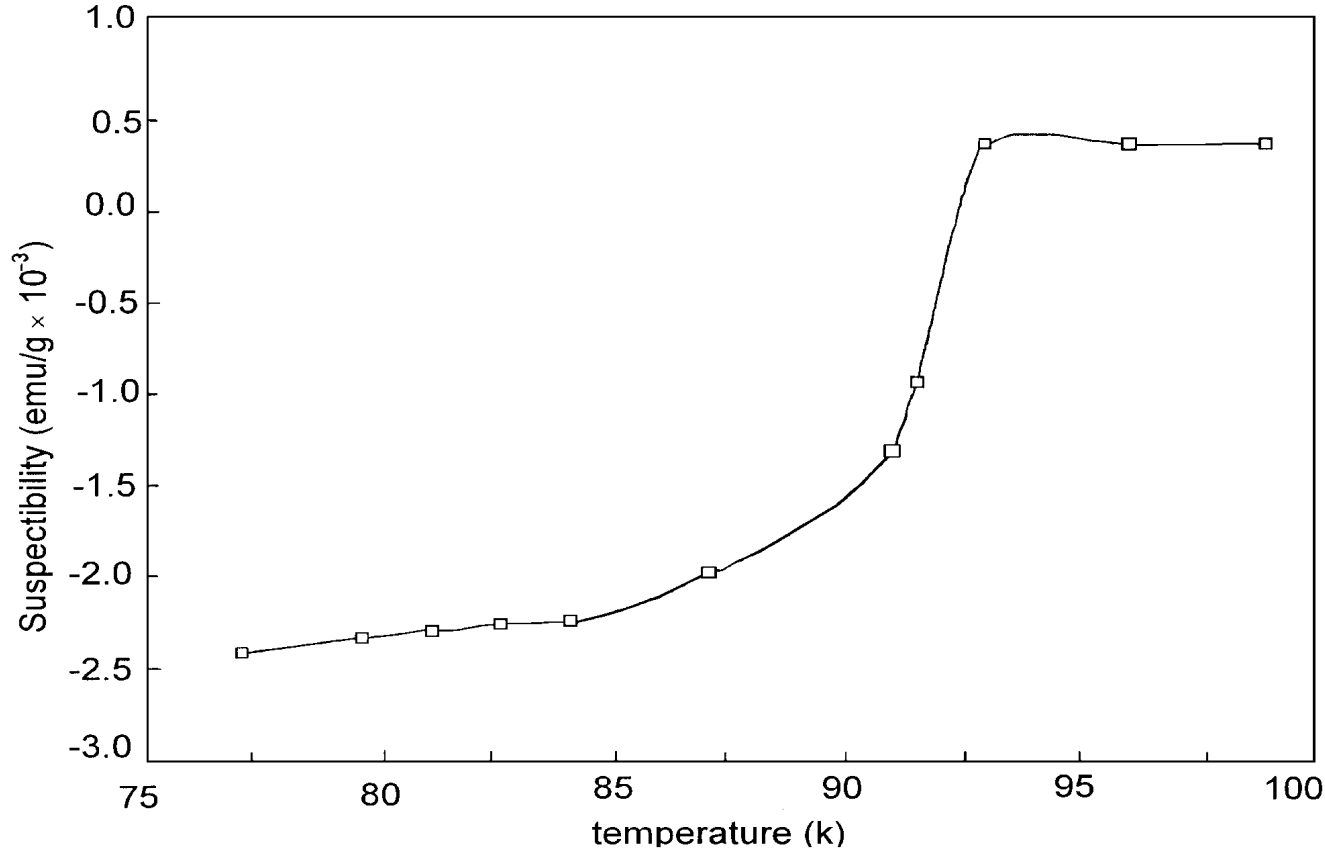

Figure 4. D. C. susceptibility datum for sample sintered at 915°C for 6hrs.

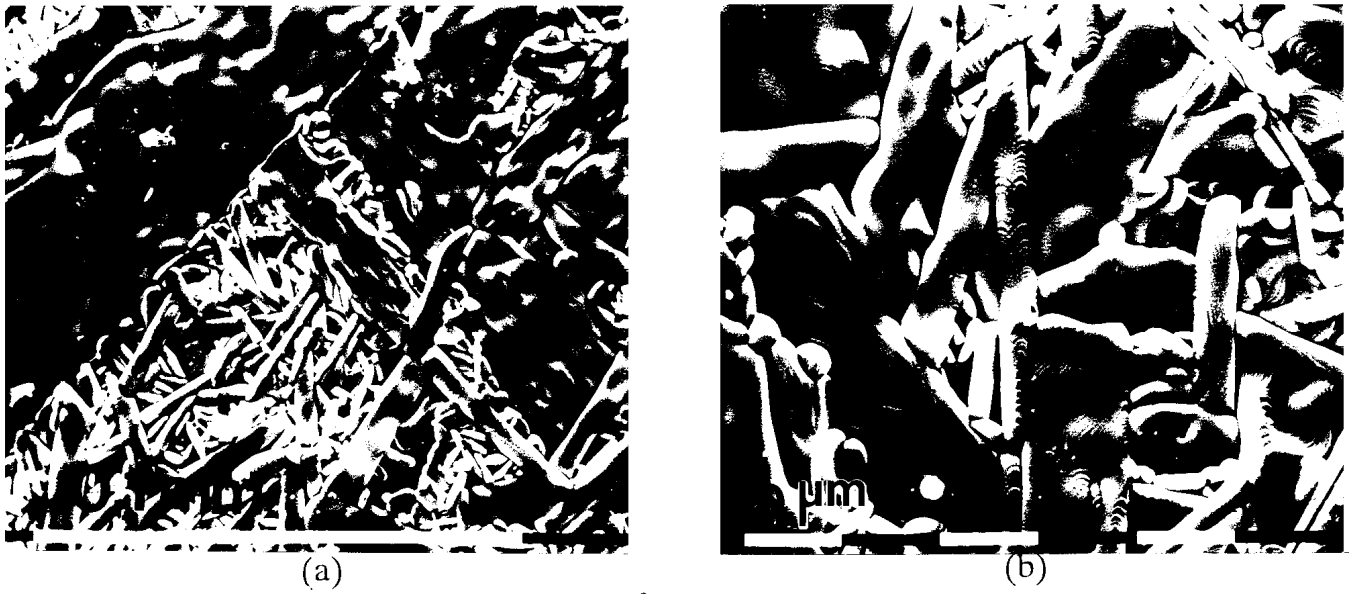

Figure 5. (a) SEM image of sample sintered at 930°C for 6hrs. and (b) same sample at higher magnification.

analysis was performed on the precursor powder in order to verify the presence of liquid phase in our sample. The results indicated an endothermic peak around 900°C in agreement with temperature range reported previously for the eutectic melting of a barium cuprate phase [6]. The presence of liquid facilitates sintering by providing a capillary pressure between the

Figure 6. SEM image of sample sintered at 950°C for 6 hrs.

particles. The liquid also aids in faster rearrangement of particles. While liquid phase is advantageous in promoting higher densities, it can also lead to discontinuous grain growth and coarse grained microstructures. This is illustrated in Figures 5a and 5b where grains as large as 0.05mm in diameter are distributed in a matrix of smaller grains.

Figure 6 shows the microstructure of the tape sintered at 950°C for 6hrs, As shown in this micrograph the number and size of the enlargedgrains increases at higher sintering temperatures. Both firing schedules (930 and 950°C) produced similar microstructures with grain size being the primary difference.

Close examination of the tape sintered at 930 and 950°C for 6hrs (Figures 5b and 6) show cracks running across some of the large grains. The fracture of these grains is most likely due to the anisotropic growth of grains in this system [9].

As shown in Table I, with the increase in the sintering temperature above 915°C, the density of the samples rises, while the transport critical current density, Jc shows a declining trend. It is proposed that one of the major factor contributing to the decrease in the values of Jc, is the formation of cracks in the microstructure as discussed previously.

4. CONCLUSIONS

It has been demonstrated that superconducting tapes can be prepared by reaction sintering of the precursor powder. This procedure yielded a dense microstructure at the relatively low temperature of 915°C. Densification was greatly enhanced by the presence of a liquid phase at higher temperatures. The presence of the liquid was also responsible for excessive grain growth in the sintered microstructure. Excessive anisotropic grain growth and the formation of stress relieving cracks in the microstructure were found to be detrimental to transport critical current density in the samples.

5. REFERENCES

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TABLE 1. Density and Jc Values for Various Heat Treatments.

Sample	Sintering Condition	Density %Theoretical	Jc (A/cm2)
A	915/6 h O2	88	520
B	930/6 h O2	93	210
C	950/6 h O2	97	170

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