JOURNAL OF MATERIALS SCIENCE 30 (1995) 6047–6052

$YBa_2Cu_3O_{7-x}$ superconductive tapes and wires: a peritectic sintering procedure to improve the quality

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$YBa_2Cu_3O_{7-x}$ tapes were made by a powder-in-binder technique, using polysulphone (PSF) as the organic polymer and *N*-methyl-2-pyrrolidone (NMP) as the solvent. The suspension is cast onto a glass substrate plate to form the tape (Doctor Blade method) and is consequently immersed into a non-solvent to remove the solvent by phase inversion. In this paper we describe the different steps in an improved "peritectic" thermal treatment that are necessary to make the green product into a superconductive tape. Three steps are important in this heat treatment. First the polysulphone binder has to be removed as much as possible without reacting with the $YBa_2Cu_3O_{7-x}$ material. Next the sample has to be sintered into a dense ceramic material. In order to improve the intergranular connections, the sample is partially melted at relative low temperature in vacuum. The sample is subsequently heated up in oxygen to the normal sinter temperature. At this high temperature the $YBa_2Cu_3O_{7-x}$ phase will be restored by a peritectic reaction of the Y_2BaCuO_5 with a liquid phase. The final step is a two step anneal to ensure the full oxidation of the superconductor.

1. Introduction

One of the main problems in the synthesis of $YBa_2Cu_3O_{7-x}$ superconductors is without any doubt the thermal treatment. Due to the low diffusion rates in solid state reactions, the material has to be sintered at high temperature into a dense ceramic material with good intergranular connections in order to obtain high quality superconductors. It is relatively easy to make a $YBa_2Cu_3O_{7-x}$ superconductor with a critical temperature (T_c) of about 90 K. The critical current density (J_c) however is highly dependent on the morphology and microstructure of the material and thus on the sinter parameters. To reach high J_c values it is necessary to improve the intergranular connections which act as weak links for the supercurrent. Many different thermal treatments were developed to reach this goal. Melt growth (MG) [1–3], quench and melt growth (QMG) [4–6] and rapid thermal processing (RTP) [7–9] are just some of the names associated with these processes that can be found in the literature. The principle however is the same for all these variations on the thermal treatment. $YBa_2Cu_3O_{7-x}$ is heated up to a temperature above its melting point at which it decomposes into Y_2BaCuO_5 (the green phase) and a liquid phase. The liquid phase stimulates the grain growth and reduces the weak links by improving the intergranular connections and grain boundaries. When the sample is subsequently cooled down, the $YBa_2Cu_3O_{7-x}$ structure will be restored by a peritectic reaction at about 950 °C. The main drawback of these procedures is that the sample has to be (partially) melted at temperatures above 1000 °C which are very difficult to control. Moreover, when the mobility of the liquid phase is too large the shape of the sample is lost. For the synthesis of tapes and wires this has to be avoided at all cost. In a previous paper [10] we reported on the first results of using an improved *peritectic* thermal treatment for tapes and wires which involves the partial melting of the samples at low temperature in vacuum. Here we have investigated the different steps of this thermal treatment by X-ray diffraction (XRD) and infra-red spectroscopy (i.r.) and studied the influence of different parameters on the quality of the superconductor. During the heat treatment, the PSF binder has to be removed. This process was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in different atmospheres. The superconductive properties were determined by transport current and a.c.-susceptibility measurements.

2. Experimental procedure

The "green product" tapes were made by mixing a commercial (superconductive) $YBa_2Cu_3O_{7-x}$ powder with a solution of the polysulphone binder

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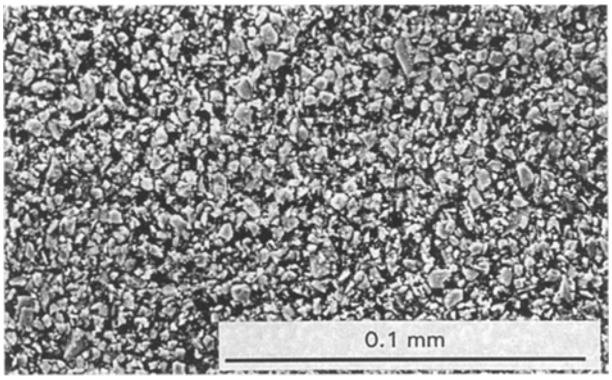

Figure 1 SEM micrograph (× 625) of green YBCO tape Y25–92/8.

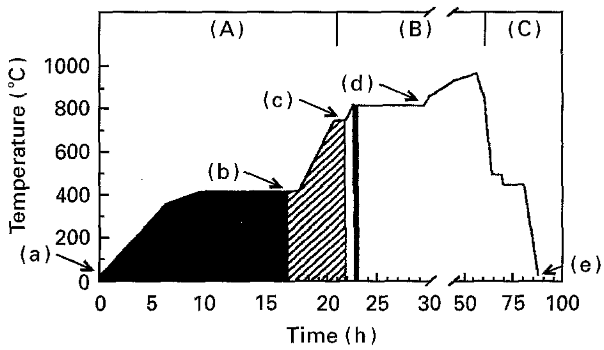

Figure 2 Thermal treatment for Y–Ba–Cu–O tape and wires including a peritectic melting step. (■) vacuum; (▨) O_2 ($p < 1.013 \times 10^5$ Pa); (□) $p = 1.013 \times 10^5$ Pa.

in *N*-methyl-2-pyrrolidone [11]. The suspension with composition Y25–92/8 (powder-to-binder ratio = 92 wt % / 8 wt % and binder-to-solvent ratio = 25 wt % / 75 wt %) was cast onto a glass substrate plate (Doctor Blade method) to form the tape and was consequently immersed into a non-solvent where the phase inversion takes place. Because of its good film-forming properties, water was used as the non-solvent. The immersion time in the non-solvent was kept very short (maximum 10 min) in order to avoid the formation of macropores by the very fast extraction of the solvent by water and to minimize the potential reaction of the $YBa_2Cu_3O_{7-x}$ material with H_2O [12]. The thickness of the green tape was about 0.27 mm and the average density (determined by gas picnometry) was found to be about 4.47×10^3 kg m^{-3}. This relatively high value indicates that the majority of the pores that can be observed in the scanning electron microscopy (SEM) micrograph (Fig. 1) are open. This porous microstructure is typical for the phase inversion technique and has to be sintered into a dense ceramic material in order to produce superconductors with a high critical current density.

It is therefore necessary to subject the green tape to a high temperature heat treatment (Fig. 2). In this thermal treatment three steps can be identified. First (A) the polymer binder (PSF) has to be removed as much as possible without reacting with the $YBa_2Cu_3O_{7-x}$ material. In the second step (B) the material is sintered which reduces the porosity and ensures that good intergranular connections are formed. In this step the vacuum melt procedure is included. In the final anneal step (C) the material is oxidized in order to produce the superconductive $YBa_2Cu_3O_7$ structure with a T_c of 90 K. During the thermal treatment the sample was oven-quenched to room temperature in oxygen at different times (Fig. 2(a–e)) and analysed by XRD, i.r. and SEM/EDX to determine the different phases in the sample and possible impurities.

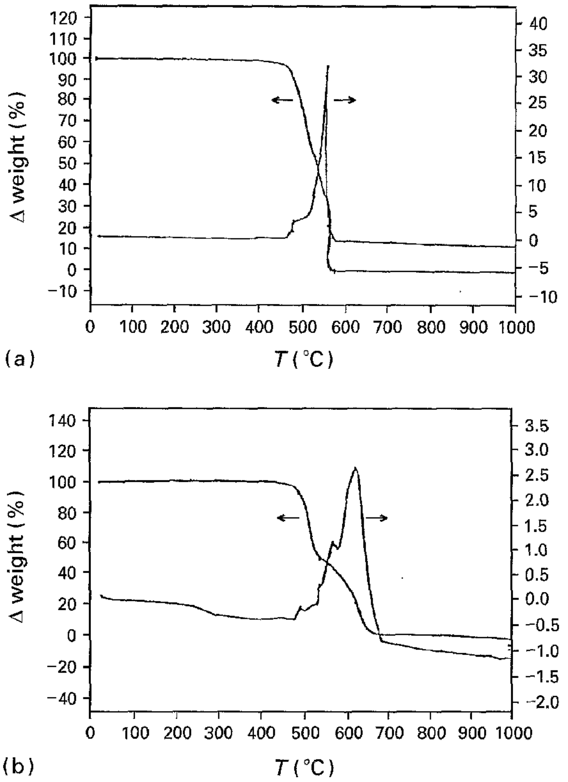

Figure 3 Thermal analyses (TGA/DTA) of PSF in (a) O_2 and (b) N_2 (heating rate 5 °C min^{-1}).

2.1. Removal of the PSF binder

When pure PSF is heated up slowly (~ 1 °C min^{-1}) to 650 °C in oxygen, the remaining ash content after two hours is less than 0.08 wt % which is comparable or better than that measured for more conventional polymers (like polyvinylalcohol, polyvinylacetate and hydroxypropylcellulose) that are used as temporal binders. From TGA/DTA measurements (Fig. 3), it is clear that the decomposition of PSF starts at ~ 400 °C, both in an oxygen and in an inert (nitrogen) atmosphere. In O_2 (Fig. 3(a)) the decomposition is complete at ~ 565 °C (ash content < 1 wt %). In N_2, however the temperature has to be ~ 680 °C before no more weight loss could be detected. The ash content is then still ~ 2 wt %. The reason is obvious: the main body of the PSF molecule consists of carbon. In an oxidizing atmosphere the carbon can be burned out as CO_2 which can be seen as a sharp DTA exotherm in Fig. 3(a). Due to the lack of oxygen when using a nitrogen atmosphere PSF will be thermally "cracked" and the products (mainly phenol, *p*-cresol and *p*-ethyl phenol) will be eliminated by evaporation. This can be observed as a broadening of the second step in the

TGA and the complexity of the DTA peak associated with this step in Fig. 3(b).

The first step of the decomposition occurs at approximately the same temperature in both cases and can be associated with the elimination of the sulphur group of PSF as SO_2. During this first step also some carbon is removed, otherwise the weight loss would be 14.48 wt % while the experimental values are obviously higher. These results about the decomposition of PSF are in very good agreement with the results that are found in the handbook of polymers [13]. When PSF is heated for 90 minutes at 450 °C, 16 wt % of gas is liberated. This gas consists mainly of SO_2 (76%), CO_2 (15%), CO (4.5%) and CH_4 (4.5%).

The obvious choice therefore would be to remove the PSF binder in an oxidizing atmosphere. However when a mixture of $YBa_2Cu_3O_7$ powder and PSF is heated in an oxidizing atmosphere, a reaction takes place. Using XRD the reaction product could be identified as $BaSO_4$. Because the amount of sulphur in the tape or wire is very small (powder-to-binder ratio $= 92$ wt % / 8 wt % and only 7.25 wt % of PSF is sulphur) it is sometimes very difficult to identify the XRD peaks of the $BaSO_4$. With the aid of i.r.-spectroscopy, the sulphate peaks are more easily detected and provided the confirmation that $BaSO_4$ was formed. Because $BaSO_4$ decomposes at a temperature above 1200 °C (higher than the melting point of $YBa_2Cu_3O_{7-x}$) it is not possible to remove it during the thermal treatment once this compound is formed. It is therefore imperative that the first step in removing the PSF binder is done in an inert atmosphere or in vacuum to eliminate the sulphur as SO_2. After this step an increase in the $BaCO_3$ content of the sample (sample b in Fig. 2) could be detected, which indicates that even without oxygen, $YBa_2Cu_3O_{7-x}$ was able to react with the remains of the PSF. The $BaCO_3$ was probably formed when the sample quenched and removed from the furnace. In the i.r. analysis of sample b the remains of PSF could still be detected, indicating that the binder was not yet completely removed. From its XRD spectrum it was clear that most of the oxygen was removed from the $YBa_2Cu_3O_{7-x}$ material and that the tetragonal $YBa_2Cu_3O_6$ phase was the principal component in sample b. No evidence of $BaSO_4$ could however be detected in sample b, neither in the XRD nor in the i.r. spectra. After this step the tapes are very fragile, suggesting little or no sintering. SEM analyses confirmed that the intergranular connections at this stage are very poor, but sufficient to allow careful manipulation.

To complete the binder removal, oxygen is allowed into the furnace and the sample is consequently heated up to ~750 °C to burn out the remains of PSF as CO_2. The best results were obtained when a reduced oxygen pressure (~500 Pa) or air was used during this process. From the XRD and the i.r. spectra of sample c it became clear that $BaSO_4$ is formed during this step of the thermal treatment if the sulphur was not completely eliminated during the first vacuum step at ~500 °C. When attempting to remove the binder (step A in Fig. 2) in an oxygen atmosphere (1.013×10^5 Pa), $BaSO_4$ could be detected in all analysed samples (c to e). It is therefore imperative that the first vacuum step is done at sufficiently high temperature (~500 °C) and for at least 5 h to minimize the formation of $BaSO_4$. In both the XRD as in the i.r. spectra of sample c, a small increase in the amount of $BaCO_3$ could also be detected.

2.2. Sintering and annealing

To sinter the sample into a dense ceramic material and ensure that good intergranular connections are formed we have developed a peritectic heat treatment. First the sample is heated up to ~825 °C (the melting plateau) in a flow of oxygen at a pressure of 1.013×10^5 Pa. At this (oxygen) pressure, this temperature is too low to melt $YBa_2Cu_3O_{7-x}$. After stabilization of the temperature, the oxygen flow is stopped and the furnace is pumped down to a pressure below 1 Pa. By reducing the pressure in the furnace, $YBa_2Cu_3O_{7-x}$ will melt at lower temperature. During this vacuum step the Cu^{2+} will be reduced to Cu^{+} and $YBa_2Cu_3O_{7-x}$ will be decomposed into Y_2BaCuO_5 and a liquid phase. The liquid phase reduces the weak links by improving the grain boundaries and thus the intergranular connections. When oxygen is allowed back into the furnace, the liquid phase will crystallize and Cu will be oxidized again. In the XRD spectrum of sample d (Fig. 4(a)) the diffraction peaks of Y_2BaCuO_5 (+) can clearly be observed. Together with the presence of the $BaCuO_2$ (□) and CuO (◇) phases, which are the result from the solidification of the liquid phase, they indicate that the sample had indeed partially melted. The presence of $BaCuO_2$ also indicates that the crystallization of the liquid phase is quite fast and that the temperature is too low for the peritectic recombination reaction. In the XRD spectrum some small peaks of the $BaCO_3$ and $BaSO_4$ can also be observed. The advantage of this vacuum melt procedure is that the entire process is done at temperatures below 1000 °C and that there are no short temperature peaks necessary which are very difficult to control and to reproduce. The temperature can be stabilized between 800 and 900 °C without any risk of melting the sample. The melting of the sample is activated by pumping the furnace down to a pressure below 1 Pa and is deactivated by allowing oxygen again in the oven, raising the pressure to 1.013×10^5 Pa. Because the pressure in the furnace is relatively easy to control, a flexible way is found to control the partial melting of the $YBa_2Cu_3O_{7-x}$ material. The combination of the temperature, the pressure and the time of the vacuum step determines how effective the melting of the sample will be and also influences the mobility of the liquid phase. When too much of the material is melted, it will be very difficult to remove the green Y_2BaCuO_5 phase again and when the mobility of the liquid phase is too large it will be able to flow and the shape of the sample is lost.

It is well known [14–16] that the $YBa_2Cu_3O_{7-x}$ phase will be restored by the peritectic reaction of the green Y_2BaCuO_5 phase and a liquid phase. This reaction however is very slow and often incomplete. A high sinter temperature and a long sinter time

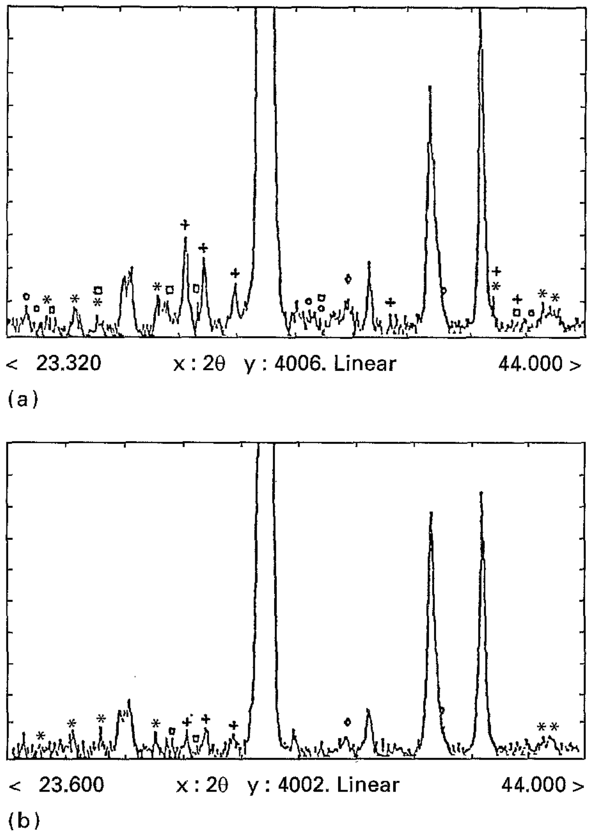

Figure 4 XRD spectrum of (a) sample d (after the vacuum melt step) and (b) of sample e (after peritectic reaction and annealing): Y_2BaCuO_5 (+), $BaCuO_2$ (□), CuO (◇), $BaCO_3$ (○) and $BaSO_4$ (*).

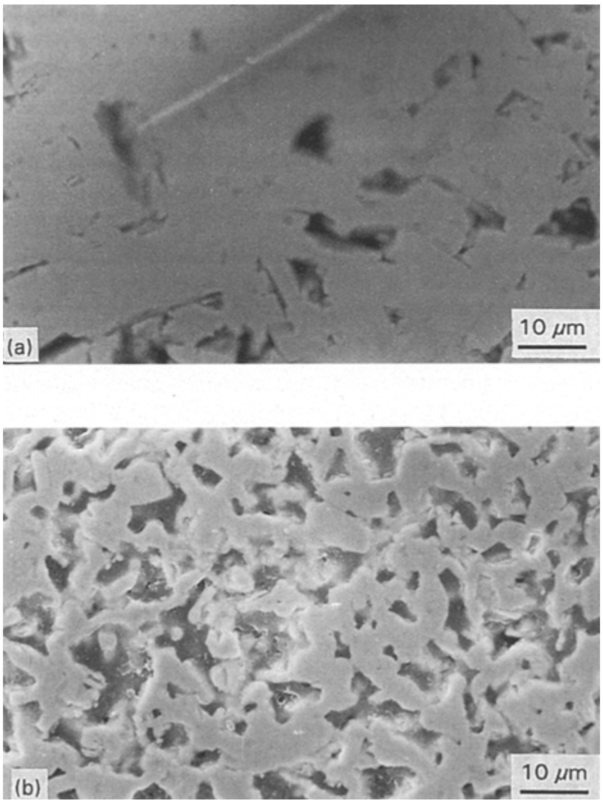

Figure 5 SEM micrographs of a $YBa_2Cu_3O_{7-x}$ subjected to (a) a peritectic and (b) a conventional treatment (6 h at 960 °C).

are therefore recommended. Slowly heating up (0.1 °C min^{-1}) the sample to the sinter temperature in oxygen proved to be the most effective way. At $\sim$890 °C the [$YBa_2Cu_3O_{7-x}$, $BaCuO_3$, CuO] mixture will melt congruently. This liquid phase will undergo a peritectic reaction at about 950 °C with the Y_2BaCuO_5 phase, and the $YBa_2Cu_3O_{7-x}$ material is restored.

The final step in the thermal treatment is a two-step anneal (5 h at 500 °C and 10 h at 450 °C) to make sure that the material is fully oxidized and the orthorhombic phase is formed with a T_c of about 90 K. From the XRD spectrum of sample e (Fig. 4(b)) it is clear that the main component of the material is very close to the pure $YBa_2Cu_3O_7$ phase. The amounts of Y_2BaCuO_5, $BaCuO_3$ and CuO phases are clearly less than what was observed in sample d (Fig. 4(a)) which indicates that the peritectic reaction has taken place. The fact that they can still be detected indicates that the sinter temperature of 950 °C is in fact rather low for the peritectic reaction. The sinter temperature is however high enough to remove the $BaCO_3$ that was formed in the previous steps of the thermal treatment and no evidence of this structure could be detected by XRD or i.r. As already mentioned, once $BaSO_4$ is formed it is impossible to decompose it during the rest of the heat treatment and it will be detected in the resulting sample. The amount of $BaSO_4$ in sample e (Fig. 4(b)) is relatively high because the sample was oven-quenched at different stages of the heat treatment. When the heat treatment was done without any interruptions the $BaSO_4$ could hardly be detected by XRD or i.r. spectroscopy.

3. Results and discussion

The superconductive properties were determined by transport current and a.c.-susceptibility measurements. After the thermal treatment the samples show a very sharp normal-superconductor transition ($\Delta T_c < 0.75$ K) with a critical temperature (T_c^{zero}) of about 90 K. The difference in microstructure of samples subjected to a peritectic and a classical thermal treatment is shown in Fig. 5. The SEM micrograph of the sample that was subjected to the peritectic treatment (Fig. 5(a)) clearly shows the effect of the melt treatment; the individual grains can no longer be distinguished from each other and the grain boundaries are no longer visible. While the density of the green product is mainly dependent on the binder-to-powder ratio, the apparent density after the peritectic thermal treatment is for all samples approximately the same: $\sim$97% of the theoretical value (determined by gas picnometry) [12]. From the SEM micrographs it is clear that this value cannot be the geometric density of the bulk material and that therefore the pores that can be observed must be open pores.

The critical current density was determined by transport current measurements and a.c.-susceptibility measurements using the Bean model. In Fig. 6 the J_c dependence on the sinter temperature is shown for different melting plateaus. In this figure two regions of J_c values can be identified. When the sinter temperature is 930 °C < T (sinter) < 955 °C the critical current density of the samples is 150–250 A cm^{-2}: about twice the value that could be achieved using a conventional thermal treatment [10]. For 955 °C < T (sinter) < 970 °C J_c values between 350 and 450 A cm^{-2}

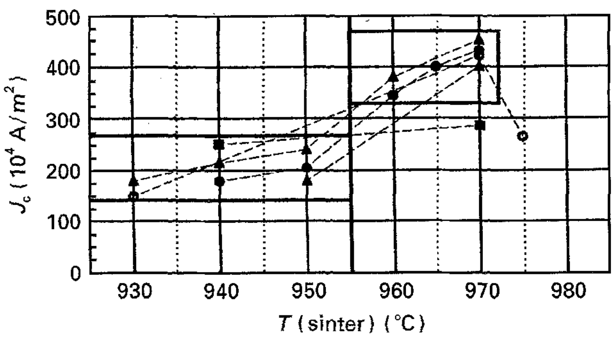

Figure 6 Critical current density (J_c) versus sinter temperature for different melting plateaus (828 °C (△), 850 °C (○) and 880 °C (■): $p < 1$ Pa; 900 °C (▲) and 930 °C (●): $p = 300$ Pa).

could be obtained using the thermal treatment shown in Fig. 2. The reason for this is obvious; in an oxygen atmosphere at ambient pressure the peritectic reaction temperature is about 955 °C [14–16]. From XRD measurements it was clear that in samples that were sintered below this temperature a relative high amount of the green Y_2BaCuO_5 phase was still present. When this phase is located at the grain boundaries it forms an effective barrier for the current and limits the J_c value. We were however unable to locate any Y_2BaCuO_5 particles in the samples by EDX or electron probe X-ray microanalysis (EPMA) mapping experiments. This means that the green phase is probably distributed homogeneously throughout the entire sample. When the sinter temperature is higher than the peritectic temperature, the $YBa_2Cu_3O_{7-x}$ phase will be restored by the reaction of Y_2BaCuO_5 with a liquid phase. The amount of green phase in these samples is indeed much lower and with a sinter temperature of 970 °C it can hardly be detected by XRD. This is consistent with the sudden increase that can be observed in the J_c curve as a function of sinter temperature (Fig. 6). When the sinter temperature exceeds 970 °C the sample is melted again. The result is a higher concentration of Y_2BaCuO_5 and a reduction in the critical current density. These high temperatures should be avoided because the mobility of the liquid phase is too high and the shape of the sample is often destroyed.

When the melting plateau is below 880 °C, the treatment can be done in vacuum ($p < 1$ Pa). For a higher melting temperature too much liquid phase is formed and its mobility is too high in vacuum. The high mobility can cause the liquid phase to be separated from the solid Y_2BaCuO_5 phase and this can lead to problems for the peritectic recombination reaction. The results are: superconductive samples with a large amount of the Y_2BaCuO_5 phase and a lower J_c. Higher melting temperatures can however be used if the time of the vacuum treatment is kept very short, the (oxygen) pressure in the oven is higher or a combination of these two. For the samples in Fig. 6 that were treated at 900 and 930 °C the (oxygen) pressure in the furnace was 300 Pa. When vacuum was used the shape of the samples was completely destroyed due to the melting. When the pressure in the furnace is raised to 300 Pa, the critical current densities of the samples are again within the expectations as can be seen in Fig. 6. The same results are obtained when the pressure was less than 1 Pa but the time was kept very short (about 5 to 10 min instead of 30 min) but it is much more difficult to control the process and the results were difficult to reproduce. The actual temperature of the melting plateau does not seem to have a very large effect but more experiments are needed to confirm this. These results are comparable to measurements on pressed bulk material, made with the same powder and subjected to the same heat treatment. Despite the relatively porous structure of the tape or wire, the J_c values are comparable to those obtained for bulk material. This means that the phase inversion procedure to make the tape or wire and the possible contamination due to the PSF binder, do not have a noticeable negative effect on the superconductive properties of the $YBa_2Cu_3O_{7-x}$ material. The presence of some remaining $BaSO_4$ in the tape or wire does not seem to affect the superconductive properties very much. The amount of $BaSO_4$ in the samples is very small and it was not possible to get an exact quantitative analysis of the amount of sulphur in the samples. There is no evident correlation of the amount of sulphur in the sample and the J_c values. We believe that the contamination is so small that it has no significant effect on the superconductive properties of our samples because the porosity of the sample, the weak link behaviour of the grain boundaries and the presence of the Y_2BaCuO_5 phase are the limiting factors for the critical current density.

4. Summary and conclusions

Suspension spinning in combination with a phase inversion technique is an easy, low cost way to produce $YBa_2Cu_3O_{7-x}$ tape and wire. With polysulphone as the polymer binder it is possible to use very high powder-to-binder ratios. The remaining ash content of PSF after a heat treatment in an oxidising atmosphere is very low (< 0.08 wt %). With the aid of TGA/DTA measurements we were able to determine that in the first step of the decomposition of the binder, sulphur is removed as SO_2. In combination with the $YBa_2Cu_3O_{7-x}$ superconductor special care has to be taken for this step because the sulphur that is not eliminated from the sample will react (during the heating to the sinter temperature) with $YBa_2Cu_3O_{7-x}$ and $BaSO_4$ is formed. Because of its high decomposition temperature it will be impossible to remove this compound again once it is formed. The best way to remove the sulphur is using vacuum or an inert gas atmosphere during this step in the thermal treatment. The remains of the binder are subsequently removed in an oxygen atmosphere mainly as CO_2, CO and CH_4. During this process some $BaCO_3$ can be formed but this will be eliminated again during the sintering of the sample.

For a classical heat treatment J_c values of about 100 A cm^{-2} were obtained. The main reason for this relative low value can be found in the powder that was used as the starting material. The powder does not sinter very well and the same values for the critical current were found for pressed bulk samples. To improve the critical current density of the samples by trying to improve the inter granular connections, we have developed a "peritectic" thermal treatment. XRD and i.r. spectroscopy were used to study the different steps in the heat treatment. In this treatment the sample is partially melted at relative low temperature (800–870 °C). The melting of the sample is activated by pumping the furnace vacuum ($p < 1$ Pa). The $YBa_2Cu_3O_{7-x}$ will decompose into Y_2BaCuO_5 and a liquid phase. By allowing oxygen back into the furnace and raising the pressure to 1.013×10^5 Pa, the liquid phase will solidify (into $BaCuO_2$ and CuO) and the decomposition of the $YBa_2Cu_3O_{7-x}$ phase is stopped. The easy control of the pressure in the furnace and the low temperature at which this process takes place, allow a flexible and fast control of activating or deactivating the melting procedure. The maximum temperature of the melting plateau that could be used in vacuum is about 870 °C. At higher temperature too much liquid phase is formed and its mobility is too large. It is however possible to use higher temperatures for the melting plateau but the pressure in the furnace has to be increased (and controlled) or the melting time has to be kept very short. We believe that it should be possible to find a corresponding pressure for every temperature of the melting plateau. Controlling the process is however much easier when vacuum is used and the temperature is limited to about 870 °C.

After the melting step the material has to be sintered at high temperature. The green Y_2BaCuO_5 phase that was formed during the melting step has to be removed again by a peritectic reaction at a temperature of about 955 °C. Samples that were sintered at a lower temperature still contain a relatively high amount of Y_2BaCuO_5 phase and the critical current density of these samples is between 150 and 250 A cm^{-2}. At temperatures higher than 955 °C the $YBa_2Cu_3O_{7-x}$ phase is restored by the peritectic reaction of the Y_2BaCuO_5 with a liquid phase. In these samples the amount of green phase is very small and is sometimes very difficult to detect by XRD. The critical current density of these samples is between 350 and 450 A cm^{-2}. Further optimization of this thermal treatment is still necessary. Preliminary results using bulk samples that were made starting from a Y_2O_3, $BaCO_3$, CuO precursor resulted in samples with J_c values of about 600 A cm^{-2}.

Acknowledgements

The authors wish to thank V. Bukenbergs W. Adriansens and R. Leysen from the membrane group at VITO for the synthesis of the wires and tapes, R. Kemps, H. Chen and P. Diels for the SEM/EDX, EPMA and XRD analyses. Further special thanks to R. Mouton and H. Vlaeminck (University of Gent) for the TGA/DTA and density measurements and to M. Hereygers, J. Janssens and H. Desseyn (RUCA: University of Antwerp) for the i.r. measurements.

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Received 22 December 1994
and accepted 2 May 1995