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Densification of high $T_c$ superconductor $\mathrm{YBa_2Cu_3O_{7-x}}$ by hot isostatic pressing: A novel approach

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In this letter a relation is derived between hot isostatic pressing (HIP) temperature, the initial oxygen concentration of sintered $\mathrm{Y-Ba-Cu-O}$ powder, the relative density, the oxygen pressure, and the oxygen concentration during HIP densification. The maximum attainable relative density is calculated as a function of HIP pressure. It turns out that degassing oxygen during HIP densification processing has considerable effects on densification maps. Using corrected and modified densification maps a recipe for manufacturing highly dense $\mathrm{YBa_2Cu_3O_{7-x}}$ is presented.

The progress towards major applications of the bulk high $T_c$ superconductors has been hampered by the low transport critical current densities of the sintered compounds and their degradation in high magnetic fields. One of the explanations for the source of the weak coupling between the superconducting regions has been suggested to be the poor connectivity due to the insufficient densification and the presence of microcracks. One of the methods to tackle this problem is to apply a high pressure at high temperature, called hot isostatic pressing (HIP), to attain material with optimum superconducting properties, i.e., a maximum critical temperature, $T_c$ and a maximum current density $J(T_c, T)$.

Consequently, polycrystalline $\mathrm{YBa_2Cu_3O_{7-x}}$ should bear as many resemblances to a perfect fully dense $\mathrm{YBa_2Cu_3O_7}$ single crystal as possible, namely: a maximum oxygen content, favorable for a high $T_c$ and a high $J(T_c, T)$, a maximum relative density ($6370 \, \text{kg/m}^3$), and large grains which are both favorable for a high $J(T_c, T)$ as well. Therefore, the initial $\mathrm{YBa_2Cu_3O_{7-x}}$ powder must have a maximum oxygen content in order to approximate $\mathrm{YBa_2Cu_3O_7}$. However, because of the high HIP temperature during HIP densification, the sintered $\mathrm{YBa_2Cu_3O_{7-x}}$ powder will strongly degas oxygen during a short time, thereby lowering its superconducting qualities. Effects of this degassing oxygen have been frequently overlooked in the literature.

In this letter, a relation is derived between HIP temperature ($T_{\text{hip}}$), the initial $x$ value (called $y$) of the sintered $\mathrm{YBa_2Cu_3O_{7-y}}$ powder, the relative density ($D$), the oxygen pressure ($P_o$) and the $x$ value of the $\mathrm{YBa_2Cu_3O_{7-y}}$ during HIP densification which is called $z$. With this relation and with ($P_o, T, x$) equilibrium values from Ref. 1, the maximum attainable relative density ($D_{\text{max}}$) is calculated as a function of HIP pressure ($P_{\text{hip}}$).

Ashby's densification maps\(^2\) (density versus HIP pressure), corrected for $P_o$, are calculated for $\mathrm{YBa_2Cu_3O_7}$ at $T_{\text{hip}} = 700, 800, \text{and} \, 900 \, ^\circ \text{C}$. These novel maps differ considerably from original maps found in literature\(^3\) and make the calculation of the required time span for HIP densification more accurate. With the help of these corrected diagrams, a recipe for making highly dense $\mathrm{YBa_2Cu_3O_7}$ is presented.

Theoretically the HIP-densification process may be described in terms of pressure-dependent mechanisms (depending on pressure and temperature) and pressure-independent mechanisms (depending on temperature only, called sintering). At high densities ($>0.85$), the densification during sintering of $\mathrm{YBa_2Cu_3O_{7-x}}$ is negligibly small. Because of oxygen degassing, an increasing oxygen pressure will occur, depending on the HIP temperature that opposes the HIP pressure applied. Densification then is caused by an effective HIP pressure ($\text{HIP pressure applied minus oxygen pressure}$) exerted by the capsule wall on the $\mathrm{YBa_2Cu_3O_{7-x}}$. Therefore pressure densification will stop as soon as the oxygen pressure becomes equal to the HIP pressure applied and high HIP pressures ($>200 \, \text{MPa}$) are required for preparation of highly dense ($>0.95$) $\mathrm{YBa_2Cu_3O_{7-x}}$.

In total four assumptions are made in this work for calculating the oxygen pressure inside the HIP capsule, the $x$ value of the $\mathrm{YBa_2Cu_3O_{7-x}}$ during HIP densification and the maximum attainable relative density. First, it is assumed that there is no loss of HIP pressure because of the stiffness of the capsule wall. Second, the oxygen gas inside the HIP capsule obeys the gas law, $PV = NkT$.\(^4\) Third, the capsule wall is gas tight and chemically inert for $\mathrm{YBa_2Cu_3O_{7-x}}$ and $\mathrm{O_2}$. Fourth, although (de)gassification takes time, as soon as the $x$ value of a $\mathrm{YBa_2Cu_3O_{7-x}}$ sample is adapted to the oxygen pressure ($P_o$) and temperature ($T$), there exists a fixed relation between $x$, $P_o$, and $T$, called ($P_o, T, x$)-equilibrium as displayed in Fig. 1, which can be derived from data presented in Ref. 1. During HIP densification, the material is assumed to stay continuously with the $P_o, T, x$ equilibrium, since oxygen is only weakly bound to $\mathrm{YBa_2Cu_3O_{7-x}}$ and consequently the time lapse needed to establish a new ($P_o, T, x$)-equilibrium after disturbance of either $P_o$, $T$, or $x$, is only short.

The latter has been verified by the following oxygen degassing experiment: some $\mathrm{YBa_2Cu_3O_{7-x}}$ powder has been put in a quartz glass test tube and positioned at the closed end of the tube. The open end is connected to a manometer. Then the tube and the manometer are evacuated. At that moment nonequilibrium ($P_o, T, x$) values are $0 \, \text{MPa}, 20 \, ^\circ \text{C}$, and $0.1$. Now the closed end of the tube is
FIG. 1. \((P_{O_2}, T, x)\) equilibrium combinations for YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\). Using Eq. (3) equal density curves are filled in for YBa\(_2\)Cu\(_3\)O\(_7\), \(y = 0\). Path (1), path (2), and path (3) show a HIP densification at \(P_{\text{hip}} = 200\) MPa. Along paths 1 and 2, \(T_{\text{hip}} = 900^\circ\)C, whereas along path 3, \(T_{\text{hip}}\) is slowly cooled from 900 \(^\circ\)C to room temperature.

placed in an oven at 800 \(^\circ\)C. After about only 90 s there is no noticeable change of \(P_{O_2}\). \((P_{O_2}, T, x)\) equilibrium values are now 0.03 MPa, 800 \(^\circ\)C, and 0.4. At 600 and 700 \(^\circ\)C equilibrium is found in about 160 and 120 s, respectively. Based on this experiment, it may be concluded that indeed during HIP densification of YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\), a process that takes several hours, the YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) obeys the \((P_{O_2}, T, x)\) equilibrium values of Fig. 1 at every instant. It has to be emphasized that this experiment has been performed with loose powder to determine the time to achieve \((P_{O_2}, T, x)\) equilibrium. It is assumed that the equilibrium time does not differ much in dense or partially dense specimens during the HIP process since oxygen is only weakly bound to YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\).

In order to predict the HIP map correctly, the oxygen pressure inside the HIP capsule and the \(z\) value of YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) during HIP densification have to be calculated. The relative density \((D)\) is given by:

\[
D = \frac{V_1}{V_1 + V_2},
\]

where \(V_1\) represents the total volume of the grains and \(V_2\) represents the volume of the pores. The number of oxygen molecules in volume \(V_2\), degassed from the YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) is assumed to obey the gas law:

\[
P_{O_2} V_2 / kT = V_1 (z - y) / 2v_y,
\]

where \(v_y\) represents the volume of a YBa\(_2\)Cu\(_3\)O\(_7\) unit cell \((173.86 \times 10^{-30} \text{ m}^3)\) and \(k\) is Boltzmann’s constant. Combining Eq. (1) with Eq. (2) yields:

\[
D = \left(1 + \frac{(z - y)kT}{2v_y P_{O_2}}\right)^{-1}.
\]

Together with the \((P_{O_2}, T, x)\) equilibrium combinations depicted in Fig. 1, Eq. (3) relates the four variables \(y, z, T,\) and \(P_{O_2}\) to \(D\) during HIP densification of sintered YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) powder. In this way, equal density curves are depicted in Fig. 1 for \(y = 0\). At high densities \((D > 0.85)\) HIP densification stops completely when \(P_{O_2}\) becomes as high as \(P_{\text{hip}}\). Now the maximum attainable relative density \((D_{\text{max}})\) can be calculated by assuming \(P_{O_2} = P_{\text{hip}}[\text{Eq. (3)}].\)

To illustrate Fig. 1 in more detail, suppose one wants to HIP densify a sintered YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) powder at \(T = T_{\text{hip}} = 900^\circ\)C and \(P_{\text{hip}} = 200\) MPa. The optimum HIP capsule, as described above, is completely filled with the powder and sealed airtight. Under these circumstances the relative density is \(D_0 = 0.65\). When this capsule is heated to 900 \(^\circ\)C, Fig. 1 indicates that \(z\) and \(P_{O_2}\) both increase strongly to \(z = 0.286\) and \(P_{O_2} = 24.8\) MPa, respectively (path 1). In order to prevent the HIP capsule from tearing or blowing up during heating, \(P_{\text{hip}}\) must be continuously at least as high as \(P_{O_2}\). When \(P_{\text{hip}}\) is raised to 200 MPa, the YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) starts to densify along path 2, while \(z\) decreases and \(P_{O_2}\) increases. The densification process continues until \(P_{O_2}\) becomes as high as \(P_{\text{hip}}\). At that moment \(D_{\text{max}} = 0.945, z = 0.252,\) and \(P_{O_2} = 200\) MPa. For the sake of comparison: at 700 and 800 \(^\circ\)C these values are \(D_{\text{max}} = 0.975, z = 0.131\) and \(D_{\text{max}} = 0.961, z = 0.190\), respectively. By slowly lowering \(T_{\text{hip}}\) to room temperature according to path 3, \(D\) increases to \(D = 1.0\) and \(z\) decreases to \(z = 0.0\). In experiments reported in the literature\(^5\) this effect upon cooling is usually omitted.

In order to get an idea about the time required to follow path 2 and path 3 Ashby’s computational scheme\(^2\) is used to calculate final relative density maps \((D \text{ vs } P_{\text{hip}})\) for YBa\(_2\)Cu\(_3\)O\(_7\) powder (initial powder particle radius 5 \(\mu\)m, initial relative density \(D_0 = 0.65\)). The values for the input variables were taken from Ref. 3. In the ordinary maps \(P_{O_2}\) is neglected, although it has a substantial effect since the effective HIP pressure \((P_{\text{eff}} = P_{\text{hip}} - P_{O_2})\) is responsible for densification. Taking \(P_{O_2}\) into account three novel HIP maps are calculated for \(T_{\text{hip}} = 700, 800,\) and 900 \(^\circ\)C and depicted in Figs. 2(a), 2(b), and 2(c), respectively.

Each map exhibits four curves, representing HIP times of 1, 4, 16, and 64 h. In every HIP map, the curve \((P_{\text{eff}} = 0, y = 0)\) for YBa\(_2\)Cu\(_3\)O\(_7\) is drawn. These curves represent densities for which \(P_{O_2}\) has become as high as \(P_{\text{hip}}\) i.e., when \(P_{\text{eff}} = P_{\text{hip}} - P_{O_2} = 0\). For the sake of comparison, the dashed curve \((P_{\text{eff}} = 0, y = 0.1)\) for YBa\(_2\)Cu\(_3\)O\(_7\) is drawn as well. The horizontal lines in area \(A\) and the vertical lines in areas \(B\) and \(C\) represent constant \(z\) values of YBa\(_2\)Cu\(_3\)O\(_7\) \(\_ x\) calculated with Eq. (3) and \((P_{O_2}, T, x)\) equilibrium values of Fig. 1. These \(z\) values de-
By comparing Figs. 2(a), 2(b), and 2(c) with each other at a constant $P_{\text{hip}}$ the following important conclusions can be drawn: the smallest HIP time required to reach the $(P_{\text{eff}} = 0, y = 0)$ curve is attained at the highest $T_{\text{hip}}$, Fig. 2(c). Further, the highest possible value of $D$ is attained at the lowest $T_{\text{hip}}$ and the highest possible $z$ value is attained at the lowest $T_{\text{hip}}$, Fig. 2(a) (area A). Sinter densification goes faster at the highest $T_{\text{hip}}$ and does not depend on $P_{\text{hip}}$ (area C).

With Fig. 2 the time span required for HIP densification, according to path 2 and path 3 in Fig. 1 at $P_{\text{hip}} = 200$ MPa, can be estimated. Figure 2(c) indicates that the time span required for path 2 to reach $D_{\text{max}} = 0.945$ at $900 \, ^\circ\text{C}$ is about 2 h. While keeping $P_{\text{hip}} = 200$ MPa, the reasons of slowly lowering $T_{\text{hip}}$ (path 3) are threefold: the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ restores all the degassed oxygen, the material approximates full relative density, and the material experiences maximum grain growth. Suppose that all this is achieved within the shortest time span by cooling from a particular temperature $T_0$ and that the cooling curve can be described by:

$$T_{\text{hip}} = T_0 \exp\left(-\frac{t}{\tau}\right),$$

where $\tau$ stands for characteristic times of the various processes involved. From Fig. 2 an upper value of $\tau$ of 100 h can be estimated by considering the time necessary to reach maximum density at the various temperatures as starting from $D_{\text{max}} = 0.945$ at $900 \, ^\circ\text{C}$. As a consequence, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with $z = 0.06$ and a density of 0.99 (Fig. 1) can be produced by slowly cooling during 35 h from $900 \, ^\circ\text{C}$ at 200 MPa down to about $600 \, ^\circ\text{C}$. In order to experience some extra grain growth during cooling, the temperature decrease can be stopped for a while.

In this letter a relation is derived between HIP temperature, the initial oxygen concentration of sintered Y-Ba-Cu-O powder, the relative density, the oxygen pressure, and the oxygen concentration during HIP densification. It is concluded that degassing oxygen during HIP densification process has considerable effects on densification maps. Thanks are due to professor M. Ashby, Cambridge, U.K. for discussions on hip-map calculations.

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