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Stability of $YBa_2Cu_3O_7$, $Y_2Ba_4Cu_7O_{15}$ and $YBa_2Cu_4O_8$ superconductors under varying oxygen partial pressure, total gas pressure and temperature

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The phase stability of a YBCO type superconductor has been studied for different total gas pressures, oxygen partial pressures and temperatures by using a oxygen-hot-isostatic-process. A total gas pressure versus temperature phase diagram at constant oxygen partial pressure (10 MPa), and an oxygen partial pressure versus temperature phase diagram at constant total gas pressure (200 MPa) were obtained. The dependence of the phase transformation temperature of the YBCO type superconductor on the oxygen partial pressure and the total gas pressure was examined. The phase stability analysis reveals for the first time that the transformation temperature of this YBCO type superconductor depends on both the total gas pressure and the oxygen partial pressure.

1. Introduction

The relationship between phase stability of YBCO type superconductors, sintering temperature, T, and vgen partial pressure, p_{O_2} was reported in the form a phase diagram by Karpinski et al. The phase diagram showed that $YBa_2Cu_4O_8$ (124 phase) was stable at high p_{O_2} and low T, $YBa_2Cu_3O_8$ (123 phase) at low p_{O_2} and high T, and $Y_2Ba_4Cu_7O_{15}$ (123.5 phase) at high p_{O_2} and high T. Their samples were canned in an encapsule containing oxygen gas as a pressure medium to sintering [1], therefore the total not be distinguished. Wada et al. also reported a p_{O_2}-T phase diagram for a p_{O_2} in the range from 10^{-4} to 1 MPa and T in the range 970–1270 K by using TG and DTA analysis [2], but they did not consider p_{tot} either. In the present work, the superconducting samples were synthesized using a oxygen hot isostatic process (O_2-HIP) under various p_{tot}, p_{O_2} and T to examine the stability condition for different phases of YBCO type superconductors.

2. Experimental

All samples were prepared by solid state reactions using O_2-HIP (Kobe Steel, O_2-Processor HIP). Raw materials Y_2O_3 (Shin-Etsu Chemical, Lot No. 0449-SU), $BaCO_3$ (Sakai Chemical, Lot No. 0021) and CuO (Soekawa Chemicals, Lot No. 03432A) had a purity higher than 99.9%. These powders were mixed in an atomic ratio of Y:Ba:Cu=1:2:4 by a glass mortar in ethanol for 15. h. This mixture was reacted twice at 1200 K for 48 h in air with intermediate grinding. The powder was uniaxially pressed into pellets under 20 MPa (10 mm diam. and 2 mm thickness). The pellets were then O_2-HIPped at various treatment temperatures in two different ways:
(1) Changing p_{O_2} at constant p_{tot} of 200 MPa.
(2) Changing p_{tot} at constant p_{O_2} of 10 MPa.

The heating rate was 400 K/h. The samples were cooled in two different ways:

(1) Quenching by adiabatic expansion of the pressure medium gas, in other words by releasing p_{tot} from the maximum treating pressure, e.g. 200 MPa, to 0.1 MPa in about 2 min. The cooling rate of the atmosphere was about 12000 K/h (3 K/s), from the treatment temperature to about 1073 K, then furnace cooled to room temperature at a rate of about 2000 K/h (0.6 K/s). Q-marks in the figures of the present work indicate this cooling condition. Samples close to phase transition lines were quenched.

(2) Cooling down naturally after turning off the heater. The cooling rate was about 2000 k/h (0.6 K/s).

A typical O_2-HIPping program is shown in fig. 1. Most of the samples were kept for 5 h at each treatment temperature.

X-ray diffractograms were taken to identify crystalline phases. There was not any appreciable difference in the X-ray diffractograms between samples treated for 5, 10 and 20 h at 1173 K under P_{tot} of 200 MPa with p_{O_2} of 40 MPa. All other samples were treated for 5 h.

3. Results

In fig. 2, the log p_{tot}–T phase diagram at a constant p_{O_2} (10 MPa) is shown for a p_{tot} range of 10–200 MPa and a T range 1200–1500 K. The open squares, the asterisks and the solid triangles show the condition at which the 124 phase, the 123.5 phase with CuO and the liquid phase were stable respectively. The A–A′ curve shows the phase boundary between the 123.5 phase with CuO and the 124 phase, and the B–B′ is the melting line. Data points in brackets are from the results of Karpinski et al. [1].

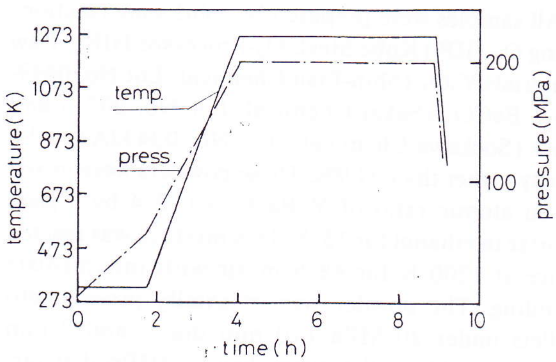

Fig. 1. Typical O_2-HIPping program. Heating rate is 400 K/h. Pressure medium was an argon–oxygen gas mixture (O_2%=0.1, 1, 3, 5, 10 and 20) and held at temperatures between 1173 K and 1473 K for 5 h or more.

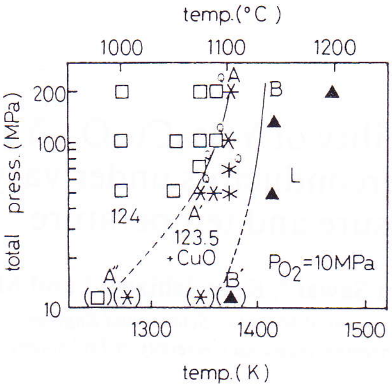

Fig. 2. Log p_{tot}–T phase diagram at p_{O_2} = 10 MPa. This phase diagram shows the p_{tot} effects on the phase stability of an YBCO type superconductor. The marks "Q" indicate quenched samples. The open squares, the asterisks and the solid triangles show the condition at which the 124 phase, the 123.5 phase with CuO and the liquid phase were stable, respectively. The marks in brackets in fig. 2 are the results of Karpinski et al. The A–A′ curve shows the phase boundary of the 123.5 phase with CuO and the 124 phase, and the A′–A″ curve shows the phase boundary of the 123.5 phase with CuO and the 124 phase including the results of Karpinski et al. The B–B′ curve is the melting line.

The figure should not be called a "phase diagram" in the precise sense, because the number of reaction components is variable and the length of the reaction period may not be large enough. The name was used following the usage of other authors [1]. The experimental conditions are very similar except for p_{tot} and p_{O_2}. The reaction period was more precisely specified (and quenching was adapted to preserve the high temperature phase) than in the reported work of ref. [1]. Considering these reasons, the results of the present work could more adequately be called a "phase diagram".

In fig. 3, the log p_{O_2}–T phase diagram at a constant p_{tot} (200 MPa) is shown for the p_{O_2} range 1–40 MPa and the T range 1100–1500 K. The solid circles show the condition at which the 123 phase with CuO was

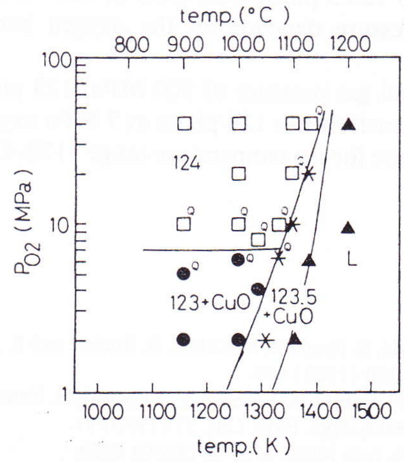

Fig. 3. Log p_{O_2}–T phase diagram at $p_{tot}=200$ MPa. All samples were kept for 5 h or more at the conditions indicated. After heat treatment, Q-marked samples were quenched by adiabatic expansion of the surrounding atmosphere (about 12000 K/h), the others were cooled down at a rate of about 2000 K/h. The solid circles show the condition at which the 123 phase with CuO was obtained. The other marks have the same significance as in fig. 2.

stable. All other marks have the same significance as in fig. 2.

4. Discussion

In fig. 3, 123 phase with CuO transforms into 124 phase under about 7 MPa p_{O_2} for T in the range 1173–1373 K. This result is quite different from that Karpinski et al., who showed that the phase transformation temperature from 124 phase to 123 phase with CuO is about 1100 K in the p_{O_2} range 0.1–0.6 MPa [1]. Figure 3 also shows that the phase transformation temperature from 124 phase to 123.5 phase with CuO and from 123 phase with CuO to 123.5 phase with CuO depends on the p_{O_2}. The 123.5 phase with CuO stable temperature range becomes smaller as p_{O_2} rises and finally disappears. This result is similar to that of Karpinski et al., but the phase transformation temperature and the melting points in our results are higher than the results of Karpinski et al. The work of Karpinski et al. and Wada et al. suggested that the 124 phase was stable in the low p_{O_2} region, but fig. 3 shows that the 124 phase is not stable at low p_{O_2} if p_{tot} is high.

Figure 2 shows the effects of the total gas pressure on phase stability. The phase transformation temperature from the 124 to the 123.5 phase with CuO, shown by the A–A′ solid curve increases as p_{tot} rises. Ishizaki suggested that the standard Gibbs energy of the reactions may be affected by high gas pressure [3,4]. The marks in brackets in fig. 2 are based on the results of Karpinski et al. Including his results, the phase transformation temperature is shown by the A′–A″ dashed curve.

Our results show that the phase transformation temperature from 124 phase to 123.5 phase with CuO is 1350 K at $p_{tot}=200$ MPa and $p_{O_2}=10$ MPa, and the results of Karpinski et al. show that the phase transformation temperature is 1250 K at $p_{tot}=p_{O_2}=10$ MPa. Both results suggest that the phase transformation temperature increases as p_{tot} rises.

Using figs. 2 and 3, the three-dimensional log p_{tot}–log p_{O_2}–T phase diagram may be obtained as shown in fig. 4. Figure 3 is included in fig. 4 as the ABCD plane ($p_{tot}=200$ MPa) and fig. 2 is included as the EFGH plane ($p_{O_2}=10$ MPa). Figure 4 also includes the results of Karpinski et al. in the OICD $p_{O_2}=p_{tot}$ plane. Considering the three-dimensional phase dia-

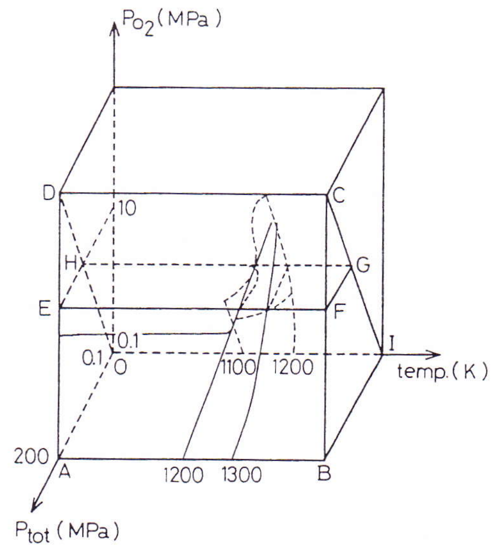

Fig. 4. The three dimensional log P_{tot}–log P_{O_2}–T phase diagram of the YBCO type superconductor. Fig. 3. Corresponds to the ABCD plane, and fig. 2 to the EFGH plane. Fig. 4 also includes the results of Karpinski et al. as the OICD plane.

gram, the results obtained by Karpinski et al. are indeed recovered at the condition $p_{tot} = p_{O_2}$, and agree reasonably well with the present results.

5. Conclusions

The three-dimensional $\log p_{O_2}$–$\log p_{tot}$–T phase diagram of an YBCO type superconductor has been determined. This phase diagram shows that
(1) The phase transformation temperature from 124 phase to 123.5 phase with CuO at 10 MPa of oxygen partial pressure increases as the total gas pressure rises.
(2) The phase transformation temperature from 124 phase to 123.5 phase with CuO and from 123 phase with CuO to 123.5 phase with CuO at 200 MPa of total gas pressure depends on the oxygen partial pressure.
(3) At a total gas pressure of 200 MPa, 123 phase with CuO transforms to 124 phase at 7 MPa oxygen partial pressure for the temperature range 1170–1370 K.

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