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Relaxation of defects introduced into $YBa_2Cu_3O_{7-x}$ by mechanical milling ☆

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Abstract

$YBa_2Cu_3O_{7-x}$ compound ($T_C = 90$ K) was milled in a rotary mill for up to 30 h. Study of the thermal behaviour by differential scanning calorimetry revealed one exothermic peak in the temperature interval up to 400°C with the highest rate of heat release at T_{max}. The thermal effect increased with the time of milling. The shift of T_{max} with different heating rates (β) was measured for the rates 5, 10, 20 and 40°C min^{-1}. The linear dependence $\ln(\beta/T^2_{max})$ versus $1/T_{max}$ is typical for an Arrhenius process. The determined activation energy of heat release $E = 1.32$–1.67 eV (127.36–161.13 kJ mol^{-1}) corresponds to the activation energy of atomic oxygen diffusion in the $YBa_2Cu_3O_{7-x}$ lattice. Therefore this effect is related to the defect relaxation through diffusive redistribution of oxygen atoms.

Keywords: Arrhenius; DSC; Milling; Relaxation

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☆ Dedicated to Hiroshi Suga on the Occasion of his 65th Birthday.

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1. Introduction

Mechanical milling is an effective method for the production of fine superconducting powder. The accumulation of crystal strain during milling changes the lattice parameters, sinterability, transport and magnetic properties [1–3]. To understand better these processes, the detailed influence of plastic deformation during milling on the nature of the microstructural defects introduced into the powder must be studied. Differential scanning calorimetry (DSC) can provide important information on the dynamics of the behaviour of the oxygen subsystem in high T_C superconductors. In this paper, the relaxation process in milled $YBa_2Cu_3O_{7-x}$ (123) and $YBa_2(Cu_{1-y}Fe_y)_3O_{7-x}$ (123-Fe) compounds was studied by DSC.

2. Experimental

The 123 and 123-Fe compounds were prepared via the sol-gel method using tartaric acid. The obtained precursor was calcined at 900°C for 12 h in air. The final sintering temperature of pressed pellets was 970°C for 12 h in air.

Then the pellets were crushed and oxygenated at 450°C for 24 h in oxygen. Carbon content analysis via CO_2 volume measurement after sample combustion gave values below 0.1 wt%.

Crushed oxygenated samples were milled in a rotary mill with zirconia cylinders.

The thermal features of the investigated samples were defined by the DSC curves obtained with a Perkin-Elmer DSC-7 instrument in air while heating in the temperature range 50–450°C at a rate of $\beta = 5$–40°C min^{-1}. Indium and zinc were used to gauge the heat capacity scale and the temperature scale.

3. Results

The DSC curve of the crushed, oxygenated 123 presented in Fig. 1a shows no thermal effect up to 400°C. The endothermic effect beginning above 400°C can be ascribed to oxygen release from the sample. After 25 h of milling, the heating is accompanied by a heat release with the highest rate at T_{max} (Fig. 1b). On second heating of the same sample, the exothermic effect disappeared. From these experiments it is clear that the observed irreversible relaxation effect is caused by milling. Surface or bulk reactions can be responsible for such behaviour. An additional experiment was carried out to solve this question. The crushed oxygenated 123 powder was uniaxially pressed into a pellet and then measured. The thermal effect was similar, with a smaller intensity (Fig. 2). We can now conclude that the observed exothermal relaxation peak can be related to the bulk processes of annihilation of the crystal defects introduced into the 123 particles by plastic deformation.

To determine in detail what kind of processes are active during crystal defect annihilation, we performed experiments to provide calculation of the activation energies of the heat release.

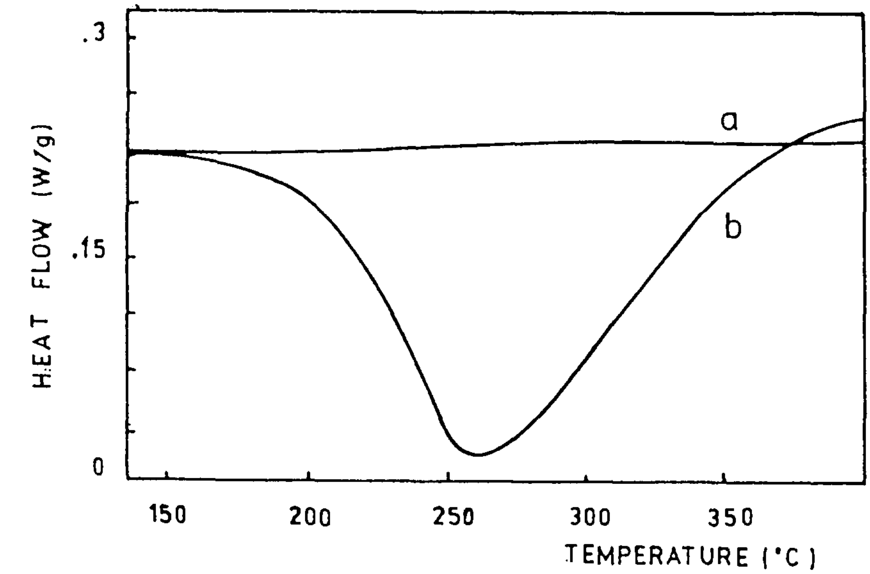

Fig. 1. DSC curves of crushed 123 sample (a) and after 25 h milling (b). Heating rate 10°C min^{-1}.

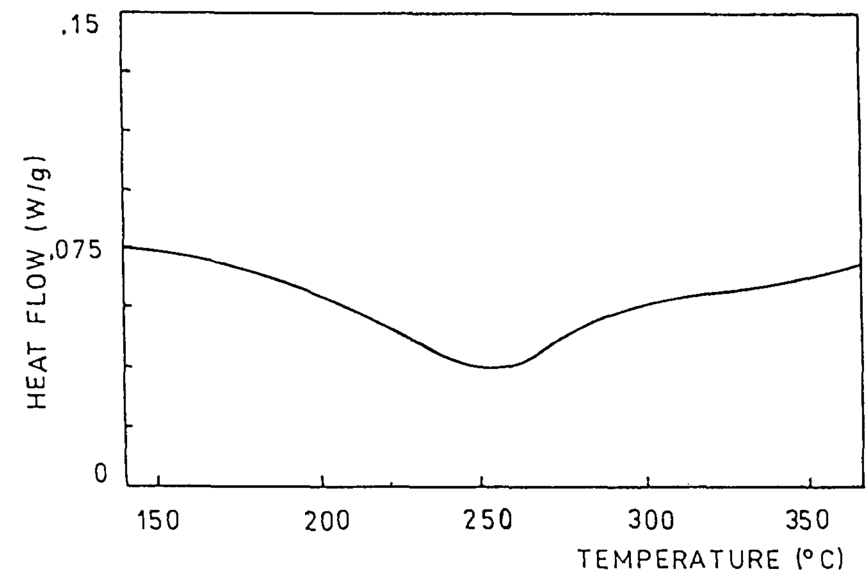

Fig. 2. DSC curve of crushed and uniaxially pressed 123 sample. Heating rate 20°C min^{-1}.

DSC is a simple technique for measuring the activation energy of heat release. For this purpose, we heated the 123 and 123-Fe samples, milled for 20, 25 and 30 h, at different heating rates in the range $\beta = 5, 10, 20$ and 40°C min^{-1}. The shift of T_{max} thus obtained allowed us to plot the measured dependence $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$. As

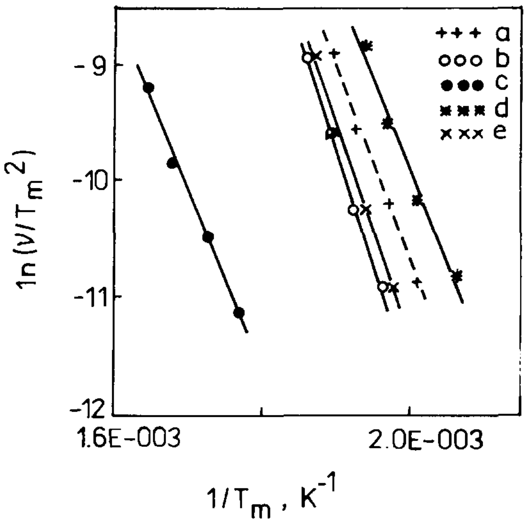

Fig. 3. Exothermal peak maximum as a function of heating rate for: a, crushed and uniaxially pressed 123; b,c,d, 123 milled 20, 25, 30 h, respectively; e, 123-Fe milled 25 h, $y = 0.02$.

Fig. 3 shows, this plot is linear, which is typical for an Arrhenius process. A simple expression relates the activation energy of the exothermal process to the slope of the Kissinger equation [4]

$$E = -R\frac{\mathrm{d}\ln(\beta/T_{max}^2)}{\mathrm{d}(1/T_{max})}$$

The activation energy E ranges from 1.32 eV (127.36 kJ mol^{-1}) to 1.67 eV (161.13 kJ mol^{-1}), values which are very close to the activation energy of atomic oxygen diffusion in orthorhombic 123, which lies, according to different estimates, in the range 1.3–1.7 eV [5, 6]. Therefore, the discovered defect annihilation effect is attributed to the diffusive redistribution of oxygen atoms.

Šesták and Koga [7] mention the same values of E for the process of oxygen absorption and diffusion through 123. We eliminated absorption in this case because no thermal effect was observed on measuring crushed powder, unlike uniaxially pressed and milled samples under identical experimental conditions.

4. Conclusions

We have discovered a relaxation effect in milled and uniaxially pressed 123 in the temperature range 150–400°C. We relate the observed exothermal relaxation peak to the bulk processes of annihilation of the crystal defects introduced into the 123 particles by plastic deformation.

The determined activation energies for 123 and 123-Fe samples in our experiments are close to the activation energy of atomic oxygen diffusion in orthorhombic 123. Therefore, the discovered effect of defect annihilation is associated with the diffusive redistribution of oxygen atoms.

Acknowledgements

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