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Zr diffusion coefficient and activation energy calculations based on EDXRF measurement and evaluation of mechanical characteristics of $YBa_2Cu_3O_{7-x}$ bulk superconducting ceramics diffused with Zr nanoparticles

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ABSTRACT

This study reports two main mechanisms on the $YBa_2Cu_3O_{7-x}$ bulk superconductor for the researchers: (I) determination of the diffusion coefficient and activation energy of Zr nanoparticles in the $YBa_2Cu_3O_{7-x}$ matrix over the annealing temperature range of 500–945 °C by means of the energy dispersive X-ray fluorescence (EDXRF) technique, and (II) change of the mechanical performances belonging to the $YBa_2Cu_3O_{7-x}$ bulk superconducting materials by Zr inclusions with the aid of Vickers microhardness (H_v) measurements performed at various indentation loads ($0.245\ N \leq F \leq 2.940\ N$) for the first time. The results obtained from the first part show that the zirconium diffusion coefficient increases dramatically with the enhancement of the diffusion annealing temperature, presenting that at higher temperatures more Zr nanoparticles begin to penetrate into the Y123 matrix. Thus, two different diffusion coefficients (in grains and over grain boundaries) are determined for the Zr individuals in the Y123 materials. The thickness dependences of the Zr diffusion coefficients are defined by the equations $D_1 = 1.47 \times 10^{-4} \exp(-1.05\ eV/k_BT)$ and $D_2 = 2.23 \times 10^{-3} \exp(-1.03\ eV/k_BT)$ in grains and over grain boundaries, respectively. The related activation energies (−1.05 eV and −1.03 eV) may be attributed to the relatively slow migration in the former region and rapid migration over the latter region, respectively. In other words, the physical and mechanical properties of the Y123 superconducting samples improve with the Zr additives owing to the elimination of the defects. The second part also indicates that the Zr nanoparticles lead to change in the microhardness characteristic of the Y123 bulk superconductors. Whereas the microhardness parameters such as Vickers microhardness (H_v), elastic modulus and yield strength of the undiffused sample tend to increase systematically, those of the diffused samples decrease with the enhancement of the applied load, meaning that the former sample shows the reverse indentation size effect (*RISE*) behavior while the latter superconductors exhibit Indentation Size Effect (*ISE*) feature. Additionally, in the second part, the load independent (true) microhardness values are analyzed by Meyer's law, elastic/plastic deformation (*EPD*), proportional sample resistance (*PSR*), indentation-induced cracking (*IIC*) and Hays–Kendall (*HK*) approach. It is found that the three models (Meyer's law, *EPD* and *PSR*) fail to explain the evaluation of the microhardness with the applied load. However, the *IIC* model is found to be superior to other models for the pure sample exhibiting the *RISE* behavior, whereas the *HK* approach is observed to be the most successful model for the description of the mechanical properties of the Zr diffused Y123 bulk superconductors obeying *ISE* feature. To sum up, it is not wrong to generalize that the *IIC* model is the best approach for the Y123 superconductor presenting the *RISE* feature, while the *HK* approach defines perfectly the mechanical properties of the Y123 materials obtaining the *ISE* behavior.

1. Introduction

$YBa_2Cu_3O_{7-x}$ (Y123) superconducting ceramic is the most prominent in the type-II superconductors because of the first material achieving the superconductivity above the liquid nitrogen temperature (77 K) [1,2]. Moreover, the simple chemical composition, low material cost, easy availability of the starting powders, simplicity of the synthesis procedure, high critical transition temperature and current density values, low (useful) resistivity and less toxic than Tl and Hg-based superconductors enable us to use the material in the practical applications [3,4]. Furthermore, easy adaptations into the applications in industries and technologies ranging from the electric power generation and transmission to the digital electronics of the Y123-based superconductors have attracted great attention of the researchers for several years. However, inherit brittleness (poor

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mechanical properties) of the Y123 superconducting samples limits the use of these materials in technological applications (especially in the form of wires) [4]. Thus, the researchers have aimed to improve the mechanical properties of the Y123 superconductors by using different methods such as the chemical addition/substitution, transition metal evaporation and change of the preparation conditions (operational procedure, sintering ambient, composition, heat-treatment, dopant type and quantity). It is necessary to underline that the mechanical characteristics of the Y123 samples are significantly improved by the presence of the cation inclusions in the material matrix as a result of the elimination of the pore surfaces and granularity [5]. The evaluation of the physical and mechanical properties of the studied materials can be examined by means of the microhardness measurements. As well known, these measurements (used to determine the resistance of a material against a load applied on the specimen surface) are nondestructive, easy and useful methods to investigate the material quality for the industrial applications [6–9]. The related mechanical characteristics of the material can also be studied by different available methods in the literature.

In the present work, we discuss the role of Zirconium (Zr) nanoparticles on the physical and mechanical properties of the Y123 bulk superconducting materials (exposed to Zr diffusion) in the temperature range 500–945 °C via the microhardness measurements. The results of the measurements are analyzed by different models such as Meyer's law, elastic/plastic deformation (*EPD*), proportional sample resistance (*PSR*), indentation-induced cracking (*IIC*) and Hays–Kendall (*HK*) approach. Additionally, the temperature dependences of Zr diffusion coefficients in grains and over grain boundaries are evaluated using EDXRF measurements, and related activation energies are described by the Arrhenius relation, which is one of the most striking features of the paper. To the best of our knowledge, no detailed work has been published on the diffusion coefficient and activation energy of Zr nanoparticles in Y123 bulk superconductor with the aid of EDXRF measurements except for our recent study, which includes the calculations of the diffusion coefficient and activation energy values determined from the XRD patterns [10].

2. Experimental details

Previously, we reported the effect of Zr diffusion on electrical, microstructural and superconducting properties of $YBa_2Cu_3O_{7-x}$ (Y123) bulk superconductors prepared by the conventional solid-state reaction technique via electrical resistivity ($\rho - T$), transport critical current density (J_c), X-ray diffraction (*XRD*), scanning electron microscopy (*SEM*) and electron dispersive X-ray (*EDX*) measurements [10]. Moreover, the diffusion coefficient and corresponding activation energy values of zirconium in Y123 system were calculated by the successive removal of thin layers on the specimen and measurement of the lattice parameter *c* at room temperature. In the current work, the EDXRF method is used to find the Zr concentration in the diffusion regions (in grains and over grain boundaries) of the Y123 bulk superconducting samples [11]. An annular Am-241 radioactive source (50 mCi) with the emission photon energy of 59.54 keV is used for the excitation of Zr inclusions. Similarly, an ultra LEGe detector is used at 15.6 keV for the intensity measurements belonging to the Zr L_α peaks. The concentration of Zr particles is determined by the sequential removal of thin layer (about 5–10 μm) from the specimen surface and then the measurement of the EDXRF intensity. Hence, the sensitivity ($N \geq 4 \times 10^{18}$ cm^{-3}) of the EDXRF technique allows us to find the Zr concentration in the matrix atoms. In this respect, the diffusion coefficient of Zr in the Y123 superconductor is estimated by the differentiation of the measured distribution curve [10]. Moreover, the role of Zr nanoparticles on mechanical properties is examined by Vickers microhardness (H_v) measurements performed at room temperature with Shimadzu HVM-2 model digital microhardness tester. The indentation load is varied from 0.245 to 2.940 N during a loading time of 10 s at the different locations on the specimen surfaces. The accuracy in the determination of the indentation diagonals is noted to be ±0.1 μm. Additionally, the microhardness results allow us to evaluate some important mechanical properties (Vickers microhardness, elastic modulus, yield strength, fracture toughness and brittleness index) for the industrial applications of the superconducting materials studied in this work. At the same time, the findings of the microhardness measurements are analyzed by different models such as Meyer's law, *PSR*, *EPD*, *IIC* and *HK* approach. Here, the undiffused sample is labeled as Zr0 whereas the Y123 bulk superconductors exposed to Zr diffusion at different annealing temperature such as 500, 600, 700, 800, 900 and 945 °C will be hereinafter denoted as Zr1, Zr 2, Zr 3, Zr 4, Zr 5 and Zr6, respectively.

3. Results and discussion

3.1. Determination of the diffusion coefficient and activation energy of Zr nanoparticles

As well known, the diffusion of an impurity is related to its diffusivity (diffusion coefficient). The effective diffusion coefficient can be explained by the diffusion through the pore space of porous media [12]. In other words, the greater diffusion coefficient a material (impurity) has, the faster the impurity diffuses into the target material. With the aid of the diffusion coefficient, the researchers can easily determine the location sites (diffusion mechanism) of the impurity in the target lattices. Although several methods are noted to calculate the diffusion parameter for the impurity material in the polycrystalline type-II superconductors [13,14], the most common four methods are arranged as the follows:

(1) The successive removal of thin layers on the specimen surface and the sample resistivity measurement,
(2) the variation of the lattice parameters inferred from the XRD curves,
(3) the radio tracer, and
(4) the EDXRF method.

Even if the last technique is more expensive than the others, it is the most reliable and useful. In the present study, the EDXRF technique is performed to describe the diffusion coefficient of the Zr inclusions in the Y123 system at different temperatures ranging from 500 °C to 945 °C. The concentration of the Zr (impurity) diffusion from a constant source into a semi-infinitive solid can be calculated by the following relations [15–17]:

$$N(x,t) = N_0\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{1}$$

where $erf\left[\frac{x}{2\sqrt{Dt}}\right]$ demonstrates the error function with the argument $y = \left[\frac{x}{2\sqrt{Dt}}\right]$

$$erf(y) = \left(\frac{2}{\sqrt{\pi}}\right)\int_0^y erf\left(-y^2\right) \tag{2}$$

here $N_0 = N(0,t)$ presents the constant concentration on the specimen surface, $N(x, t)$ denotes the impurity concentration level, *D* shows the diffusion coefficient and *t* refers the diffusion-annealing time. According to the equations, it is necessary to underline that the specimen thickness is related with the impurity concentration. Fig. 1 indicates the concentration profile of Zr over the thickness of the Y123 bulk superconducting (Zr6) sample prepared at 945 °C for 24 h. It is visible from the figure that there are two concentration regions. First of them is attributed to the near-surface region (x = 0–40 μm) while the second curve is associated with the inner region (x ≥ 41 μm) of the sample. The Zr diffusion coefficients belonging to the regions in the Zr6 sample are calculated to be about $D_1 = 7.38 \times 10^{-9}$ cm^{2}s^{-1} and