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Interfacial Reaction between Ag and $NdBa_2Cu_3O_{7-\delta}$ Superconductor Prepared by Low-temperature Process

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Abstract

The interfacial reaction between Ag and $NdBa_2Cu_3O_{7-\delta}$ (Nd123) was examined from the viewpoint of low-temperature processing of superconducting materials. The incongruent melting temperature of an Nd123 sample was measured to be as low as 960°C in N_2. Addition of 10 mass% of Ag to Nd123 decreased further the incongruent melting temperature of Nd123 to 920°C. By a model experiment using an Ag pellet embedded in Nd123, it was revealed that an Ag-dissolved (Ba,Cu)-rich phase was formed near the interface with Ag. Based upon these results, Ag-added Nd123 ceramic samples were prepared by the partial melting process at temperatures below the melting point of Ag, 960°C. Superconducting properties of the ceramic samples were improved by the addition of Ag. © 1999 Elsevier Science Limited. All rights reserved

Keywords: composites, interfaces, superconductivity, oxide superconductors.

1 Introduction

The $NdBa_2Cu_3O_{7-\delta}$ (Nd123) superconductor is attractive for the application because of its higher J_c values than those of $YBa_2Cu_3O_{7-\delta}$ (Y123) under higher magnetic fields.[1–3] Fabrication of Nd123 superconducting thick films on flexible metallic substrates is of technological importance for the practical use as wires. The only usable metallic substrate is silver since it does not degrade superconducting properties such as T_c even if a reaction with superconducting oxides occurs. Two major problems arise for the thick film fabrication of Nd123 on the Ag substrate; one is the processing temperature and the other is the mechanical strength. The high-quality Nd123 thick films can be prepared only on oxide substrates by the melting process at temperatures above 1000°C,[4,5] which exceeds the melting point of silver as low as 960°C.

Addition of Ag to Y123 is known to be effective to reduce the incongruent melting temperature of Y123.[6] Moreover, mechanical properties of Y123 can be improved by the Ag addition. Since the similar effects were expected for Nd123, we prepared Ag-added Nd123 ceramics by the sol–gel process.[8] It was found that the incongruent melting temperature of our sample in N_2 was below the melting temperature of Ag. Therefore, it is important to know how Ag affects the processing of Nd123 because the Ag addition is promising in fabricating the thick films on the Ag substrate.

In this work, we investigated the low-temperature processing of the Ag-added Nd123. Firstly, thermal behavior of sol–gel-derived Ag/Nd123 powders was examined. Secondly, the interfacial reaction between Ag and Nd123 was analyzed by a model sample. Finally, the Ag-added Nd123 ceramic samples were prepared by the partial melting process at low temperatures and the superconducting properties were examined.

2 Experimental Procedure

The preparation of the Ag/Nd123 powders by the sol-gel process is based upon our previous work.[8] Oxide gels were prepared from $Nd(O\text{-}iC_3H_7)_3$, $Ba(O\text{-}iC_3H_7)_2$, $Cu(OH)_2$ and CH_3COOAg dissolved

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in a mixture of isopropanol and dimethylamino ethanol. The ratio of metal ions was Nd:Ba:Cu = 1:2:3, and the amount of Ag was 0, 5, and 10 mass% to final weight of the $NdBa_2Cu_3O_7$ composition. The gels were calcined at 500°C for 5 h in a dry 20% O_2/80% N_2 gas and then heated at 700°C for 10 h in vacuum. The crystalline phases evolved in the samples were identified by X-ray diffraction (XRD) method with a JEOL JDX-8P diffractometer using CuK_α radiation. Thermal analysis of the resultant powders was performed with a MAC Science TG/DTA-200 in N_2 gas with a heating rate of 10°C min^{-1}.

A model sample was prepared to analyze the interfacial reaction between Ag and Nd123. An Ag pellet was prepared by heating a consolidated Ag powder at 900°C for 1 h in air. Then the Ag pellet was embedded in the sol–gel-derived Ag-free Nd123 powder heat-treated in vacuum as described above. After the pelletization, the sample was heated at 920°C for 3 h in N_2. The microstructure of the sample was observed by scanning electron microscopy (SEM) with a JEOL JSM-5200 microscope.

The Ag/Nd123 ceramic samples were prepared by the partial melting process. The sol–gel-derived-Ag/Nd123 powders were pelletized, heated in N_2 with patterns as shown in Fig. 1, and then annealed in O_2 at 400°C for 200 h. The temperature dependence of magnetization was measured with a Quantum Design MPMS SQUID magnetometer at 100 Oe. The electrical resistance was measured by a standard four probe method at 1 mA. The DC critical current density was measured at 77 K under various magnetic fields.

3 Results and Discussion

3.1 Interfacial reaction between Ag and Nd123

All the dried gels containing Nd, Ba, Cu and Ag were amorphous with a trace of the Ag metal which was confirmed by the XRD. After the calcination at 500°C for 5 h, the resultant powders consisted of Nd_2O_3, $BaCO_3$ and CuO. The Ag metal was also precipitated in the Ag-added samples. By heating the calcined powders at 700°C for 10 h in vacuum, the Nd123 phase was formed without any other oxide phases. According to the SEM observation and the EDS analysis, the average size of the Nd123 particle was 230 nm and the average composition was consistent with the Nd:Ba:Cu = 1:2:3 ratio.

The DTA curves of the resultant Ag/Nd123 powders measured in N_2 are shown in Fig. 2. The endothermic peak observed at 960°C for the Ag-free sample is due to the incongruent melting of Nd123. The peak position shifts to a lower temperature of 940 and 920°C for 5 and 10 mass% Ag-added samples, respectively. For the Ag-added samples, the endothermic peak is also observed at 960°C, which corresponds to the melting point of Ag.

The above result indicates that the incongruent melting of Nd123 is induced and accelerated by the presence of Ag at lower temperatures. In order to understand how Ag affects the melting of Nd123, the model sample was prepared and the microstructure was observed. The heating temperature of the model sample was 920°C corresponding to the incongruent melting temperature of the 10 mass% Ag-added sample. Figure 3 shows the SEM photograghs of the Nd123 region of the model sample. As shown in Fig. 3(a), one kind of grain is observed in the region far from Ag. According to the EDS analysis, the composition of this grain exactly corresponded to Nd:Ba:Cu = 1:2:3. On the other hand, three kinds of grains are seen in the region near the interface with Ag as shown in Fig. 3(b); needle-like grains, cubic-like grains, and grains without a distinct shape. The EDS analysis revealed that these grains were $Nd_4Ba_2Cu_2O_{10}$ (Nd422), Nd123 and a (Ba,Cu)-rich phase, respectively. The determination of the composition of the

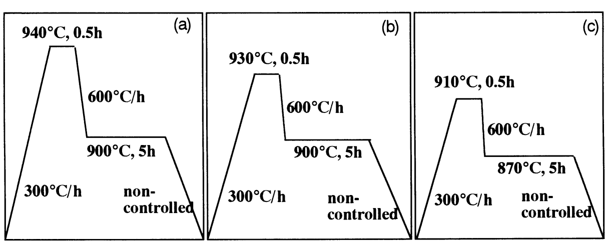

Fig. 1. Heating patterns for the partial melting process conducted for (a) 0, (b) 5 and (c) 10 mass% Ag-added Nd123 ceramic samples.

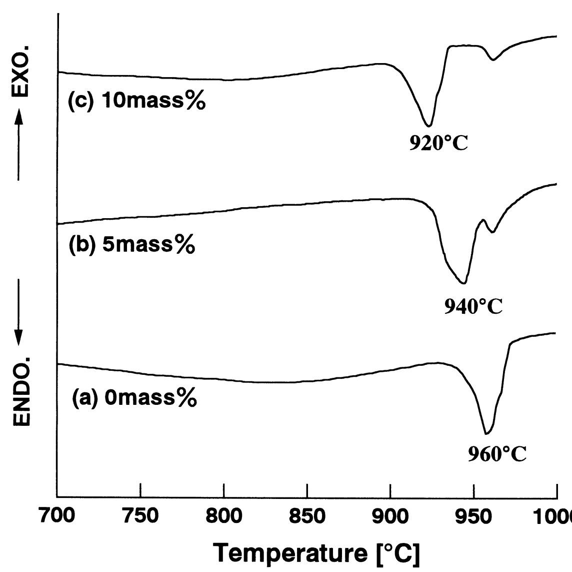

Fig. 2. DTA curves of the Ag/Nd123 powder samples measured in N_2 ambient.

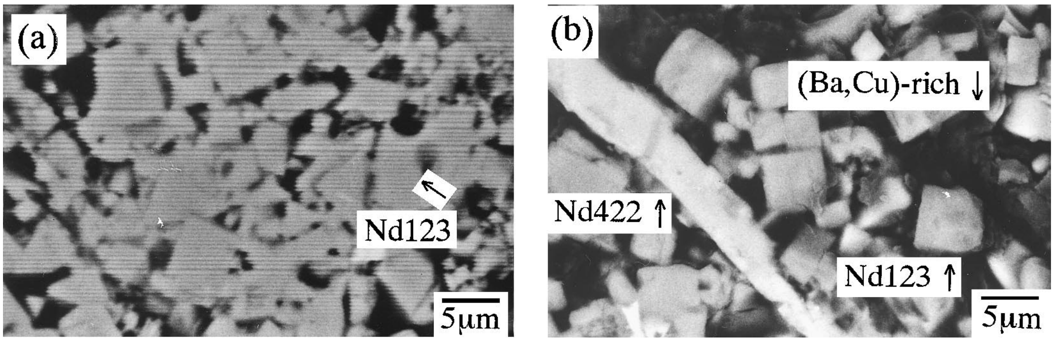

Fig. 3. SEM photographs of the Nd123 region in the model sample: (a) far from the Ag pellet and (b) near the interface with the Ag pellet.

(Ba,Cu)-rich phase was difficult, but probably it is $BaCu_2O_2$ since the heat-treatment was conducted in reducing N_2 atmosphere. A small amount of Ag was also detected in the (Ba,Cu)-rich phase. Therefore, the decomposition reaction of Nd123,

$$\text{Nd123} \rightarrow \text{Nd422} + \text{Liquid}(\text{Ba-Cu-O}),^{9,10}$$

is considered to be induced by the reaction between Ag and a Ba–Cu–O system.

3.2 Preparation and superconducting properties of Ag/Nd123 ceramic samples

In the above section, it was revealed that the incongruent melting temperature of Nd123 was decreased by the addition of Ag. Since the melting proceeds near the interface with Ag, it is necessary that Ag distributes uniformly in the Nd123 matrix when the partial melting process is carried out. Therefore, the sol–gel-derived AgNd123 powders can be useful precursors because of the homogeneous distribution of components with the relatively small particle size.

Figure 4 shows the XRD patterns of the Ag/Nd123 samples obtained by the partial melting process. Nd123 remains the main phase for all the samples added with 0, 5 and 10 mass% Ag. The small amount of the Nd422 phase results from the incongruent melting. Since the sample was rapidly cooled from the incongruent melting temperature, 940, 930 or 910°C to the sintering temperature, 900 or 870°C as shown in Fig. 1, the formation reaction of Nd123 from Nd422 and the (Ba,Cu)–O liquid phase probably did not proceed.

The T_c values of the samples determined by the measurement of the resistivity and the magnetic susceptibility are summarized in Table 1. The $T_{c(\text{onset})}$ and the $T_{c(\chi)}$ values are almost the same among three samples. On the contrary, the $T_{c(\text{end})}$ values increases from 76 to 82 to 86 K with the increasing amount of Ag from 0 to 10 mass%. This is attributed to the decrease in weak links between

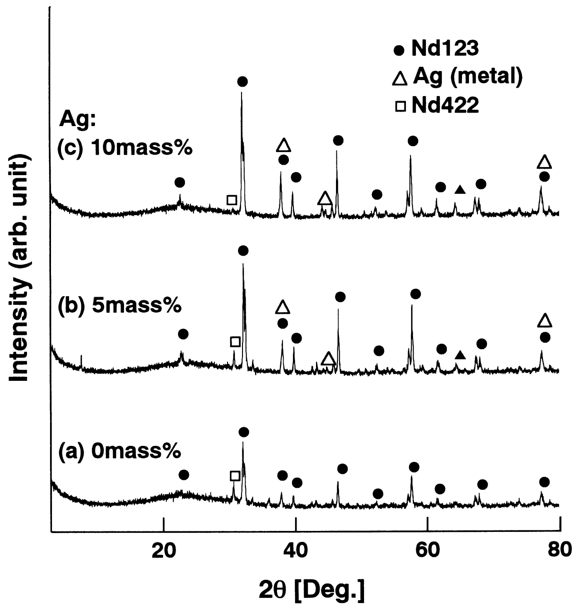

Fig. 4. XRD patterns of (a) 0, (b) 5 and (c) 10 mass% Ag-added samples after the partial melting process.

grains promoted by the Ag addition.[7] The effect of the Ag addition was more remarkably observed in the J_c properties. Figure 5 shows the J_c values as a function of the magnetic fields for the Ag/Nd123 samples at 77 K. The J_c values of the Ag-free Nd123 sample are relatively low. This is partly because the $T_{c(\text{end})}$ value of this sample is as low as 76 K. On the contrary, the Ag-added samples exhibit about three times larger J_c values than the Ag-free sample. In consequence, the magnetic field where the J_c becomes 0 is also higher for the Ag-added samples.

The transport properties of the superconducting ceramics are greatly dependent on their microstructure. As we reported previously,[8] the Ag-added Nd123 sample had more dense microstructure as compared with the Ag-free sample. Moreover, Ag filled voids in the Nd123 matrix. The improvement of the J_c characteristics of the Ag-added samples, therefore, is attributed to the changes of the microstructure and morphology

Table 1. Superconducting transition temperatures of the Ag/Nd123 ceramics prepared by the partial melting process

Ag content (mass%)	$T_{c(onset)}$(K)	$T_{c(end)}$(K)	$T_{c(\chi)}$(K)
0	92	76	93
5	92	82	93
10	93	86	93

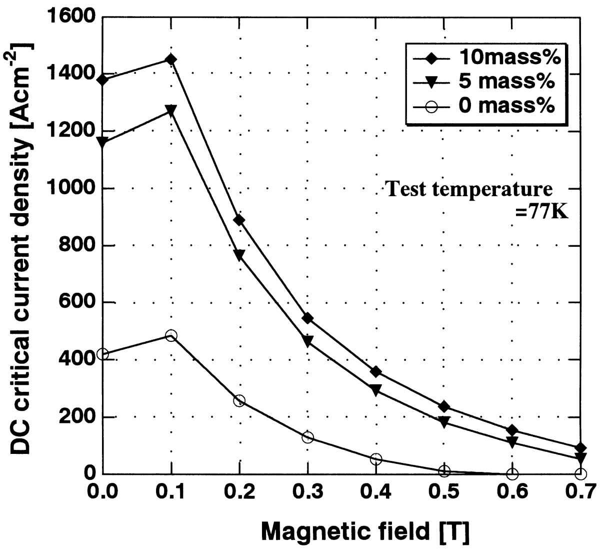

Fig. 5. The DC critical current density, J_c, of the samples as a function of the applied magnetic field at 77 K.

such as its densification and the decrease in pore, void or crack density.

4 Conclusion

The effects of the Ag addition on the processing temperature, microstructure and superconducting properties of $NdBa_2Cu_3O_{7-\delta}$ were investigated. The incongruent melting temperature of Nd123 decreased with the Ag addition, which could be explained by the occurrence of the reaction between Ag and Nd123 forming the Ag-dissolved (Ba,Cu)-rich phase. The Ag/Nd123 ceramic samples prepared by the partial melting process exhibited better superconducting properties such as $T_{c(\mathrm{end})}$ and J_c.

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