Ag Doping Effects of GdBa$_2$Cu$_3$O$_{7-\delta}$ Films by Low Fluorine MOD Method

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Abstract: A series of Ag-doped GdBaCuO superconducting films were prepared by low fluorine MOD process on buffered Hastelloy substrates. The effects of Ag doping on the microstructures and superconducting properties of GdBCO thin films were investigated. It was found that an optimum addition of about 5 mol % Ag lead to better c-axis orientation and surface microstructure of the resultant films. Meanwhile, the pyrolysis process shortened and the superconducting performance is improved with a wide available window.

1. Introduction
REBa$_2$Cu$_3$O$_{7-\delta}$ (REBCO) (RE = Y, Gd, etc.) coated conductors have been intensively focused due to their great potential in practical applications [1-3]. Compared with YBCO, GdBCO superconductors have a higher critical temperature (~90 K) and can keep relatively good current density value ($J_c$) in high magnetic field[4,5]. The metal–organic deposition (MOD) route is considered as a cost-effective and non-vacuum technique which can produce REBCO coated conductors with high performance [6,7].

In recent years, several groups studied[8-10] the effects of Ag doping in YBCO bulks or films. It is reported that in melt-textured polycrystalline, Ag particles segregate in the grain boundaries of YBCO which results in a thinner effective grain boundary and a higher $J_c$[8]. Enhancement of $J_c$ was also found in Ag-doped PLD-YBCO films under low magnetic field [9].

But for MOD process, Ag doping was rarely reported[12]. In this study, a series of Ag doped GdBa$_2$Cu$_3$O$_{7-\delta}$ (GdBCO) films are prepared on buffered Hastelloy substrates by low fluorine MOD. A few positive results are achieved, showing that optimum addition about 5 mol % of Ag in GdBCO solutions lead to rapid pyrolysis process, better c-axis orientation as well as surface microstructure and then a higher $J_c$ value.
2. Experimental

The precursor solution was prepared by dissolving TFA salts for Gd, Ba and a fluorine free organic
salt for Cu with the 1:2:3 cation ratio into propionic acid with the total metal concentration of 1.5
M/L. Silver trifluoroacetate was added with the molar proportions ranging from 2.5 mol % to 20
mol %. A few drops of diethanol amine were added to the solution to increase its stability. The
precursor solution was dip coated on LaMnO$_3$/MgO/Y$_2$O$_3$/Al$_2$O$_3$/ Hastelloy substrates. Gel films
formed after dip coating followed by a fast pyrolysis process at 300º C (20K/min) in a humidified
oxygen atmosphere. Growth was performed at 770º C for 1.5h in humid N2/O2 atmosphere and then
annealed at 450º C for 1h in dry oxygen atmosphere. For reference, a pure GdBCO sample was
prepared by traditional low fluorine route as well.

Metallographic optical microscope (MM) was used to observe the surface quality of the
pyrolyzed films. The phase purity and the texture of GdBCO films were investigated by X-ray
diffraction (XRD) using Cu Kα radiations (Rigaku D/MAX2000PC). The film thickness was measured
by a step profiler system. A typical thickness for all present films are around 400nm. The surface
morphology of the YBCO film was observed by field emission scanning electron microscopy (SEM).
The critical current density was inductively measured by a CryoScan system at 77 K.

3. Results and discussion

Fig. 1 shows the typical metallographic optical microscope(MM) images of GdBCO precursor films
quenched at 500º C during temperature ramping with two kinds of solutions(normal low fluorine
solution and 5 mol % Ag doped low fluorine solution) pyrolyzed under the same condition (20 K/min).
Typical wrinkles are observed on the pyrolyzed sample using normal low fluorine solution, as shown
in Fig. 1(a). The precursor film with 5 mol % Ag doped low fluorine solution shows a smooth and
crack-free microstructure in Fig. 1(b). It is demonstrated that the Ag doped low fluorine solution has
beneficial effect on the stress relief and minimization of the surface degradation of pyrolyzed films.

Figure 1. MM images of the samples quenched at 500º C with and without
Ag doping (a) normal low fluorine solution without Ag (b) 5mol% Ag
doped solution

The XRD θ–2θ patterns of GdBCO-Ag fired at 770º C are shown in Fig. 2. It is seen that all
GdBCO-Ag films are pure (00l) orientation without undesirable phases while Ag phase hardly
detected. However GdBCO(200) peak is frequently found in pure GdBCO films, which is further
confirmed by SEM morphologies. It is believed that although Ag may not occupy the space in lattice
of GdBCO, it plays role on the suppression of a-axis of GdBCO films.
It is found that GdBCO(004) peak intensity improve significantly by proper addition of Ag close or equal to 5 mol %. GdBCO films keep good orientation as the percent of Ag doping varing from 2.5% to 10%. However high doping content as 20 mol % may degrade the texture of GdBCO. Obradors et al.[12] believed that the decrease of the peritectic temperature of the Ag–RE–Ba–Cu–O system was the reason for the enhancement of c-axis orientation. Further work is needed to explain the reason why c-axis nucleation becomes easier, since the growth mechanism of thin film and bulk is different.

Figure 2. XRDθ–2θ patterns of GBCO-Ag thin films

Fig. 3 shows the SEM morphologies of all derived films. The a-axis oriented grains with needle-shape and more pores are observed in pure GdBCO film. GdBCO films obtained by proper addition of Ag close or equal to 5mol% level show less pores and higher rate of c-axis orientation were. In addition, no distinct Ag was detected on GdBCO matrix except only negligible Ag nanoparticles was detected by EDX, which is consistent with the XRD patterns . As the content of Ag doping increases up to 20% mol, large Ag precipitates with grain size of 100–200 nm emerge as confirmed by EDX, indicating that a large quantity of Ag prefers to gather at film surface rather than segregate in matrix, as shown in Fig. 3.

Figure 3. SEM images of GdBCO films (a) pure GdBCO (b)2.5% Ag doping (c)5% Ag doping (d)10% Ag doping(e)20% Ag doping
The highest inductive critical current density(1.5MA/cm^{2}) at 77 K was obtained by 5 mol Ag doping. It is essential to note that $J_c$ values are improved by Ag doping. Although the $J_c$ value(0.65MA/cm^{2}) appear degrading with a high doping content up to 20 mol %, it is still slightly higher than the undoped ones’ (0.6MA/cm^{2}). A possible explanation for the positive result of $J_c$ is the enhancement of c-axis nucleation of GdBSCO and the improvement of surface quality caused by moderate Ag doping. In case of 20 mol % Ag addition, the degradation of $J_c$ may be caused by the large amount of impurities, inhomogeneity and decline of texture.

4. Conclusions

In summary, a series of Ag doped GdBCO films were prepared by low fluorine MOD method. The effects of Ag doping on the microstructures and superconducting properties of GdBCO films were investigated. The results showed that optimum addition of Ag close or equal to 5 mol % in the GdBCO solutions lead to better c-axis orientation and surface microstructure and then a higher $J_c$.

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