

## CORROSION BEHAVIOR OF HIGH-TEMPERATURE SUPERCONDUCTOR $YBa_2Cu_{3-y}Ag_yO_{7-x}$ IN THE PRESENCE OF WATER

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**Abstract** — Because of the presence of water vapor,  $YBa_2Cu_3O_{7-x}$  degrades easily in the atmosphere and thus very difficult to put it to practical use. When Cu is partially substituted with Ag, however, there is not much a decrease in the critical temperature ( $T_c$ ) :  $T_c$  is 89 K compared with 91 K without substitution. Moreover, partial substitution of Ag increases density, hardness, and superconducting particle size and above all improves considerably its stability in water. In this study  $YBa_2Cu_3O_{7-x}$  and  $YBa_2Cu_{3-y}Ag_yO_{7-x}$  as a result of a partial substitution of Ag for Cu were synthesized by pyrophoric method. We investigated their stabilities in water by XRD, SEM, and EPMA after immersing samples in distilled water for 3 hours. We can see that  $YBa_2Cu_{2.94}Ag_{0.06}O_{7-x}$  was the largest particle size and anti-corrosion behavior.

**Key words:** Superconductor,  $YBaCuO$ ,  $YBaCuAgO$ , Pyrophorisis, Water, Corrosion

### INTRODUCTION

Since the discovery of the oxide superconductor of high critical temperature in 1986 [Bednorz and Müller, 1986; Chu et al., 1987], a variety of researches have been carried out vigorously. At present the work has been concentrated on utilizing superconductor in practical application by enhancing its mechanical natures [Peterson and Ekin, 1988; Cook et al., 1987].

Because the  $T_c$  of Y system superconductor is above 90 K, which is high enough to use practical liquid nitrogen (b.p.=77 K), among many other high  $T_c$  superconductors developed, this Y-Ba-Cu-O system is preferentially being studied for practical application due to its superior chemical durability. We believe the discovery of Y system superconductor be a epoch-making event sooner or later.

Although  $YBa_2Cu_3O_{7-x}$  has been generally known to be the most stable high  $T_c$  superconducting compound, it still has many problems to overcome [Yan et al., 1987; Barns and Laudise, 1987]. To avoid that difficulty, substitution or addition of Ag, Al, Co, Fe, Zn, or Au etc. has been studied [Kumar et al., 1993; Siegrist et al., 1987; Muromachi et al., 1987; Noguchi et al., 1988; Eibschütz et al., 1993]. Specially, in case of substitution or addition of Ag, many researches have been performed because it vigorously improves current density more than any other metals. But unfortunately, their stability study with humidity in the air has been very scarce.

In this work, we synthesized  $YBa_2Cu_{3-y}Ag_yO_{7-x}$  by partial substitution of Cu with Ag and the degree of degradation was investigated by XRD, SEM, and EPMA after putting samples in distilled water of 25°C to compare their corrosion behaviors.

### EXPERIMENTAL

The starting materials are  $Y_2O_3$ ,  $CuO$ ,  $BaCO_3$  and  $AgNO_3$  in case of substitution. The powders of  $YBa_2Cu_3O_{7-x}$  and  $YBa_2Cu_{3-y}Ag_yO_{7-x}$

$Ag_2O_{7-x}$  phase were prepared by pyrophoric synthesis method, and  $y$  value varied as 0.00, 0.03, 0.06, 0.09, and 1.50.

A more detailed procedure of pyrophoric synthesis method to obtain ultrafine and homogeneous dark brown powder can be found elsewhere [Bhattacharya et al., 1990; Yang et al., 1989; Kim et al., 1993]. This powder was then pressed into circular disks under 400 MPa.

The diameter and thickness of the pellet were 15.35 mm and 1 mm respectively. After the pellet was calcined at 910°C for 24 hours, it was cooled gradually and sintered at 500°C for 24 hours. Then, it was cooled to room temperature in the air.

The samples were immersed in distilled water for 3 hours and then XRD, SEM, and EPMA analyses were carried out to examine the extents of degradation. The XRD patterns were recorded using a Rigaku III/A type automated diffractometer equipped with a crystal monochromator employing Cu-K $\alpha$  radiation in the 2 $\theta$  range of 10°-60°. The surfaces of samples were observed by SEM (Scanning Electron Microscope) and EPMA (Electron Probe Microanalyzer) using a Hitachi X-650 and JEOL JXA-8600 type respectively.

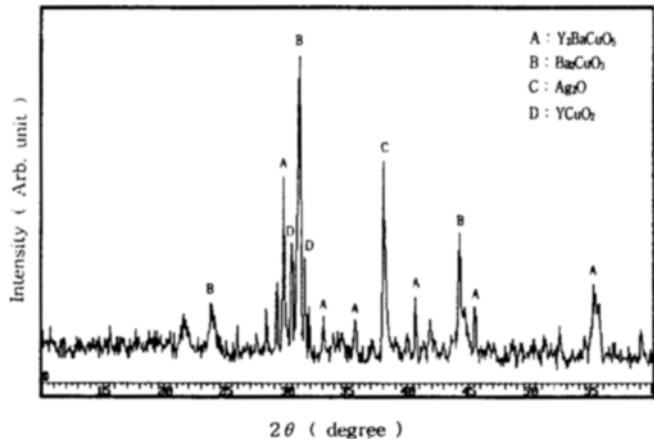
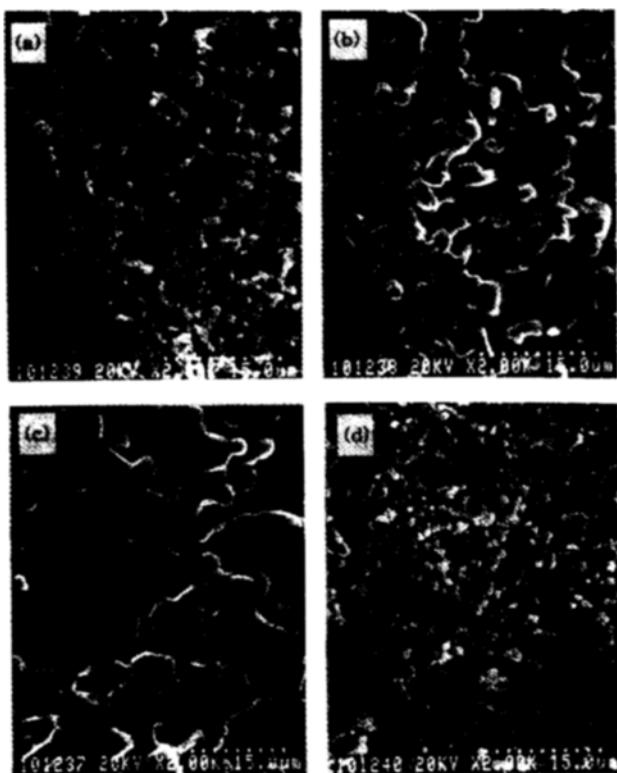
### RESULTS AND DISCUSSION

The  $YBa_2Cu_{3-y}Ag_yO_{7-x}$  ( $y=0-0.09$ ) sample revealed the  $T_c$  of 91 K and 89 K when  $y$  was 0 and 0.09, respectively with identical XRD pattern, which indicates that the partial substitution of Cu with Ag in the range has little effect on superconductivity.

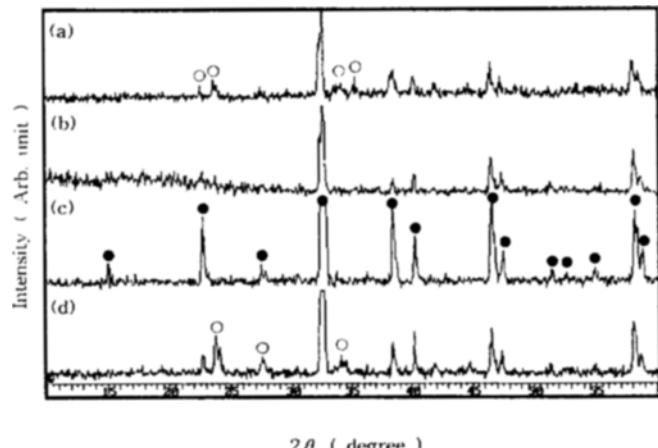
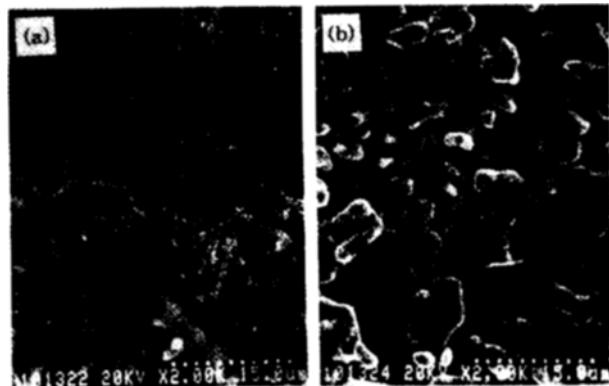
The x-ray diffraction pattern of the  $YBa_2Cu_{1.5}Ag_{1.5}O_{7-x}$  is shown in Fig. 1. We can see that  $Y_2BaCuO_5$ ,  $Ba_2CuO_3$ ,  $YCuO_2$ , and  $Ag_2O$  coexist without further reaction of Ag with Y or Ba compounds. Therefore it seems that the Ag substitution of this range does not deteriorate the superconductivity of the sample, being a flux pinning center to improve the critical current density [Sengupta et al., 1992].

Fig. 2 shows the SEM results. We can notice that the average particle size of the sample without substitution (Fig. 2-a) is smaller than that of the case of substitution (Fig. 2-b and c). It seems

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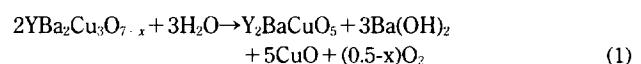
Fig. 1. X-ray diffraction pattern of  $\text{YBa}_2\text{Cu}_{1.5}\text{Ag}_{1.5}\text{O}_{7-x}$ .Fig. 2. Secondary electron images of  $\text{YBa}_2\text{Cu}_{3-y}\text{Ag}_y\text{O}_{7-x}$  superconductors at (a)  $y=0$ , (b)  $y=0.03$ , (c)  $y=0.06$ , and (d)  $y=0.09$ .

that the particle size grows by Ag substitution, which indicates that Ag acts as a catalyst for superconducting crystallite growth. We confirmed that the density increased due to decrease of the grain boundaries in case of Ag substitution. Moreover, the sample with  $y=0.06$  (Fig. 2-c) turned out to have the highest density and largest particle size. Over  $y=0.06$ , however, the  $\text{Ag}_2\text{O}$  particles seem to become physical resistances for an atom to cross the interphase boundary or for interdiffusion of the species for superconducting crystallite growth. The particles of Fig. 2-d that has the molar ratio of 0.09, show such an effect. Also judging from the reports that the current density of YBCO almost doubles when 4-5 wt% of Ag was added to YBCO [Dwir et al., 1989;

Fig. 3. X-ray diffraction patterns of  $\text{YBa}_2\text{Cu}_{3-y}\text{Ag}_y\text{O}_{7-x}$  superconductors after treated in water at  $25^\circ\text{C}$  for 3 hrs, (a)  $y=0$ , (b)  $y=0.03$ , (c)  $y=0.06$ , and (d)  $y=0.09$ .Fig. 4. Secondary electron images of  $\text{YBa}_2\text{Cu}_{3-y}\text{Ag}_y\text{O}_{7-x}$  superconductors after treated in water at  $25^\circ\text{C}$  for 3 hrs at (a)  $y=0$ , (b)  $y=0.06$ .

Nobuhito et al., 1989; Park et al., 1994], the Ag substitution in the range examined in this study would enhance the current density considerably.

The samples of Fig. 2 were dipped in distilled water for 3 hours. Their XRD patterns after the corrosion tests can be seen in Fig. 3 showing that the superconducting peaks of the sample with  $y=0.06$  (Fig. 3-c) survived most. It has the largest particles, thus resulting in comparatively least corrosive attack by water. Superconducting peaks of (a) and (d) with  $y=0.00$  and 0.09 respectively disappeared and  $\text{BaCO}_3$  peaks appeared instead.  $\text{BaCO}_3$  is known to be formed by decomposition of superconducting phases according to Yan et al. [1987]. They have proposed the following mechanism for the reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with water:



In exposure to the air,  $\text{BaCO}_3$  is formed by the following reaction:



The solubilities of  $\text{Ba}(\text{OH})_2$  and  $\text{BaCO}_3$  are 3.04 g/100 ml and 0.0022 g/100 ml [Weast, 1982-1983] at  $15^\circ\text{C}$  in water respectively.

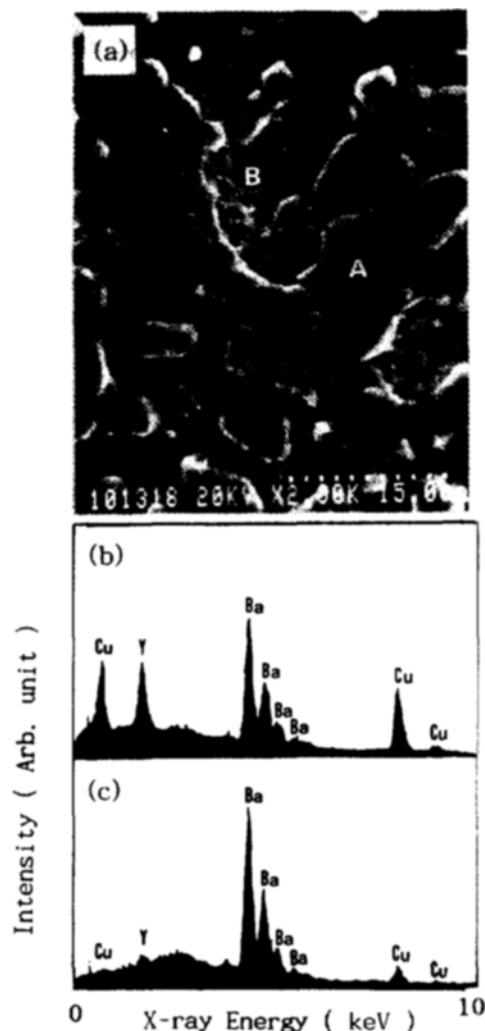


Fig. 5. (a) Secondary electron images of  $\text{YBa}_2\text{Cu}_{2.97}\text{Ag}_{0.03}\text{O}_{7-x}$  after treated in water at  $25^\circ\text{C}$  for 3hrs, (b) and (c) EPMA spectra of grain A and grain B, respectively.

$\text{Ba}(\text{OH})_2$  formed in contact with water transforms into  $\text{BaCO}_3$  reacting with  $\text{CO}_2$  in the air. This corrosion mechanism can be applied successfully in Fig. 3-b of  $y=0.03$  which has medium-sized particles: many of the superconducting peaks disappeared, but  $\text{BaCO}_3$  peaks did not show up yet implying the mass transport of water molecules to superconducting phase will be the rate-determining step in corrosive reaction. Thus the larger the superconducting particles grow, the more stable in corrosive environment.

The SEM results of the samples (a) and (c) of Fig. 3 after the water dipping for 3 hours can be found in Fig. 4. The sample without substitution clearly shows the formation of  $\text{BaCO}_3$  having white needle-shaped crystallites while the sample with substitution of  $y=0.06$  remained almost unchanged. This coincides with the results of Bansal et al. [1988] and Nakada et al. [1987]. They explained the formation of  $\text{BaCO}_3$  is from the faster reaction of Ba than Y or Cu in the Y system superconductor.

The EPMA study was carried out for the sample of  $y=0.03$  substitution after the corrosion experiment for 3 hrs. The result along with SEM picture is shown in Fig. 5. According to EPMA results, Ag preferentially resides in the superconducting phase

grain (region A in Fig. 5-a) which has a mole ratio  $1:2:3$  for Y : Ba : Cu. Meanwhile, the grain boundary region (region B in Fig. 5-a) is Ba-rich where Ag exists considerably less than region A. It seems that Ag migrates to superconducting phase and acts as a catalyst for superconducting crystallite growth.

## SUMMARY

In case of a partial substitution of Ag for Cu, Ag selectively catalyzes superconducting crystallite growth and thereby enhances stability in water with a little degradation of its superconductivity.

The water corrodes the superconducting phase to form  $\text{Ba}(\text{OH})_2$  and then transforms to  $\text{BaCO}_3$  in the air as a final corrosion product. The mass transport of  $\text{H}_2\text{O}$  molecules to superconducting phase seems to be the rate-determining step in this corrosive reaction.

Substitution of  $y=0.06$  yielded the best result in terms of anti-corrosion behavior due to the largest particle size in the range of substitution investigated in this study. This reasons that the larger the superconducting particles grow, the more stable they become in corrosive environment.

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