Improvement of corrosion resistance of high temperature superconducting Y-Ba-Cu-O films

I. von Lampe, F. Zygalsky, H. Nagibzadeh, G. Hinrichsen
Technical University of Berlin, Institute of Materials Science and Technology, Englische Str. 20, D-10587, Germany
lamp0634@mailbox.TU-Berlin.DE

Abstract. The corrosion resistance of high temperature superconducting (HTC) Y-Ba-Cu-O (YBCO) films and doped YBCO films (lanthanum La, calcium Ca, silver Ag) was studied and their lifetimes in saturated steam environment at 75°C were determined. The results indicate an enhancement of stability against environmental degradation for the films with increasing La content. We suppose, that this enhancement is attributed to poor water solubility of lanthanum hydroxide protective films, which were formed in the first step of corrosion.

1. Introduction
Most of the commonly utilized HTSC YBCO films tend to degrade rapidly when exposed to the atmosphere due to reaction with H₂O and CO₂ [1-4]. There are two major ways applied to prevent the environmental degradation of HTSC films. The first involves the formation of protective barriers which serve to slow the diffusion of corrosive reagents. The application of metals as silver [5] as well as insulating metal oxides such as MgO, LaAlO₃, and SrTiO₃ [6], amorphous carbon [7] and polymer layers such as poly(methylmethacrylate) (PMMA), and poly(tetrafluoroethylene) (PTFE) [8, 9] have been studied. The second way to improve the corrosion resistance of YBCO is the modification by cations [10-14].

In this study, the degradation behaviour of YBCO films and with Ca, La, Ag, Ca/La and Ag/La doped YBCO films in water vapor environment (75°C) is compared.

2. Experimental
The HTSC films were prepared following the polymer precursor method [15-17]. The metal salts in form of nitrates and polymethacrylic acid (PMAA) (ratio of salt :PMAA = 1:2) were dissolved in dimethyl formamide at room temperature. Single crystalline SrTiO₃ substrates were spincoated by the clear solutions, and the transparent films were dried at 170°C in an air circulating oven. The annealing process was performed in a tube furnace. The air in the quartz tube was exchanged by argon (60 min, 200°C). Then, the temperature was increased to 750 – 800°C using a heating rate of 25°C/min. After about 25 min storage at maximum temperature argon was exchanged by oxygen, and finally the specimens were cooled in oxygen with a rate of 15°C/min.

The precursor films and their thermal degradation in argon were characterized by FTIR of these films deposited on silicon substrates [18,19]. The spectra of Ag, Ca, and La PMAA salt films respectively of La/Ca and La/Ag doped precursor films were measured after drying at 160°C and, after annealing, at 200°C, 300°C, and 400°C, respectively, in argon atmosphere.
In addition, the HTSC films (thickness: 100-200nm) were characterized by X-ray diffractometry, electrical measurements and scanning electron microscopy (SEM) before and after corrosion. The X-ray investigations were carried out on a Siemens diffractometer D-5005 and the SEM was performed on a Philips XL 20. For the electrical measurements to prove the HTSC properties using the standard 4-point technique a minirefrigerator was applied.

The corrosion investigations were carried out in a steam chamber situated in a thermostat at constant temperature of 75°C and relative air humidity of 98%. The quasi dc 4-point resistivity measurements of the films contacted by gold wires, attached by silver paste, were described as a function of time. The lifetime was defined as the time interval the electrical resistance reached values ≥ 20kΩ.

3. Results and discussion

The polymer precursor method is especially suitable for the preparation of metal ion doped YBCO films. This method ensures the uniform distribution of the metal ions and the preparation of smooth, c-axis oriented HTSC films.

FTIR investigations were used to demonstrate that La$^{3+}$, Ca$^{2+}$ and Ag$^+$ form PMAA salts similar to Y$^{3+}$, Ba$^{2+}$, and Cu$^{2+}$ [18]. The spectra of Ag, La, and Ca salt films dryed at 160°C exhibit the absorption bands concerning salt formation (1650 - 1540 cm$^{-1}$) [17, 19]. After annealing of films in argon at 200°C the spectra of Ca and La salts of PMAA are similar, anhydride as well as salt groups are detected by strong absorption bands. In the Ag-PMAA spectrum the salt absorption bands nearly disappear and is conform with that of PMAA. It is assumed that the thermal degradation of Ag salt to Ag$_2$O took place at 200°C, while the Ag$_2$O is degraded at 300°C to Ag metal and oxygen [20]. Ag metal has another function than Ca or La ions, which will be incorporated in the YBCO lattice. In agreement with other authors [21] we suppose that the Ag metal produces very small „micro“ melting zones which improve the crystallization conditions for the formation of the YBCO structure. Using the FTIR investigations of La/Ca respectively La/Ag doped YBCO precursor films it was impossible to detect an influence of metal ion dopands on thermal degradation, which obviously is superimposed by Cu-PMAA decomposition.

The HTSC films received from precursor films by annealing process [17] were characterized by X-ray, electrical measurements and SEM.

![Fig. 1 XRD of doped YBCO films](image)

![Fig. 2 Corrosion stability of YBCO films at 75°C](image)

The results of X-ray investigations show that the reflex intensities and the 2θ values are almost identical for doped and undoped films. An additional reflex appears in the diffractogram if the film was only doped with Ca (Fig. 1), which detects an impurity phase. The electrical measurements demonstrate that the transition temperature ($T_c$) of Ca and Ca/La doped samples is decreased, La, Ag, and Ag/La doped films have similar $T_c$ values as the undoped YBCO film (Tab. 1). The critical current density values ($j_c$) of Ca and Ca/La doped films are lower at 77K. The difference between the $j_c$ values of all doped films diminishes at 20K.
The results of corrosion investigations in saturated steam environment at 75°C prove (Tab.1, Fig. 2) that the corrosion stability increases with the content of La³⁺ in the YBCO films. The lifetime averages as defined above were determined from 5 – 10 experiments. A relative high spread of the measured lifetime values is attributed to the circumstance that the measurements were carried out without use of protective wax layer onto the contacts [12].

The corrosion stability of undoped and Ag doped films is similar, while that of the Ca doped films is something lower. The stability of La, La/Ca, and La/Ag doped films increases with concentration of La³⁺ ions. We suppose, that the poor solubility of formed La(OH)₃ films [22,23] is the reason for improved stability. The first step of corrosion is the formation of hydroxides. In contrast to La(OH)₃, both Ba(OH)₂ and Ca(OH)₂ are very well soluble in water. However, when in a second step of corrosion CO₂ is present poorly soluble Ba and Ca carbonate films are obtained.

**Table 1.** Transition temperatures and critical current densities of undoped and doped YBCO films before corrosion test and their corrosion lifetime averages

| Composition | T_c (K) | j_c at 77K (A/cm²) | j_c at 20K (A/cm²) | lifetime (min) |
|-------------|---------|-------------------|-------------------|----------------|
| YBa₂Cu₃O₇  | 89      | 4·10⁻⁵            | 5·10⁻⁶            | 25             |
| Y₀.⁸Ca₀.²Ba₂Cu₃O₇ | 80      | 2·10⁻⁴            | 10⁻⁵             | 13             |
| Y₀.⁷Ca₀.³Ba₂Cu₃O₇ | 78      | 3·10⁻⁴            | 5·10⁻⁵            | 10             |
| Y₀.⁶Ca₀.⁴Ba₂Cu₃O₇ | 78      | 10⁻³              | 2·10⁻⁵            | 5              |
| YBa₀.⁸La₀.²Cu₃O₇ | 86      | 2·10⁻⁵            | 3·10⁻⁵            | 100            |
| YBa₀.⁷La₀.³Cu₃O₇ | 87      | 4·10⁻⁴            | 2·10⁻⁶            | 220            |
| YBa₀.⁶La₀.⁴Cu₃O₇ | 87      | 2·10⁻⁵            | 10⁻⁵             | 310            |
| YBa₁.⁸Cu₃O₇+Ag (5wt%) | 89      | 5·10⁻⁸            | 2·10⁻⁷            | 35             |
| Y₀.⁸Ca₀.²Ba₀.₄La₀.₄Cu₃O₇ | 78      | 10⁻⁴              | 4·10⁻⁶            | 170            |
| Y₀.⁷Ca₀.³Ba₀.₄La₀.₃Cu₃O₇ | 79      | 2·10⁻⁴            | 5·10⁻⁶            | 320            |
| Y₀.⁶Ca₀.⁴Ba₀.₄La₀.₄Cu₃O₇ | 78      | 10⁻⁴              | 2·10⁻⁶            | 400            |
| Y₀.⁷La₀.³Ba₁.₇Cu₃O₇+Ag (3.₄wt%) | 88      | 3·10⁻⁴            | 2·10⁻⁶            | 210            |
| Y₀.⁶La₀.⁴Ba₁.₆La₀.₄Cu₃O₇+Ag (5wt%) | 88      | 5·10⁻⁵            | 2·10⁻⁶            | 360            |

SEM photographs show, that after corrosion at 75°C the surface of the Ca/La doped film looks relatively uniform, while the surface of Ca doped YBCO film is very craggy (Fig. 3, 4). EDX measurements after corrosion indicate that the carbon values of La doped films related to carbonate are lower than that of films without La. This result corresponds with XPS investigation of
Zhou [12] and supports the conception that poorly soluble La(OH)$_3$ is the reason for corrosion resistance increase.

4. Conclusion

The results of this study indicate that in particular the substitution of Ba$^{2+}$ by La$^{3+}$ is the key factor for the generation of chemically resistant YBCO phase. The lifetime increases with La$^{3+}$ concentration. The Ca/La doped films show the highest lifetime average values. Obviously, the compensation of valences assists the crystallization conditions and favours the crystal transition into the tetragonal structure which has higher chemical stability [12].

The Ag/La doped samples exhibit also an increase of corrosion stability with La concentration, and their $T_c$ values are not decreased as it is observed for Ca and La/Ca doped films.

The authors would like to thank D. Wepler for the FTIR measurements.

References

[1] J. Zhou, D. Riley, A. Manthiram, M. Arendt, M. Schmerling and, J. McDevitt, Appl.Phys.Lett. 63(1993)548
[2] R. Zhao, and S. Myhra, Physica C 230(1994)75
[3] R. Börner, W. Paulus, and R. Schöllhorn, Adv.Mater. 1(1995)55
[4] W. Günther and R. Schöllhorn, Physica C 271(1996)241
[5] J. Singh, H. Leu, R. Poeppel, E. Voorhees, G. Goudey, and K. Winsley, J.Appl.Phys.66(1989)3154
[6] B. David, D. Grundler, R. Eckart, K. Fanghänel, J. Krumme, V. Doermann, and O. Dössel, Supercond.Sci.Tech. 7(1994)287
[7] J. Tatum, J. Tsai, M. Chopra, and S. Chan, J.Appl.Phys. 77(1995)6370
[8] R. Aga, S. Yan, Y. Xie, and J. Wu, Physica C 366(2002)216
[9] S. Morohashi, Mater.Sci.Engn. A 109(1989)321
[10] J. Zhou, S. Savoy, J. Zhao, R. Riley, Y. Zhu, A. Manthiram, and J. McDevitt, J.Amer.Chem.Soc.116(1994)9389
[11] J. Zhou, S. Savoy, R. Lo, J. Zhao, M. Arendt, Y. Zhu, A. Manthiram, and J. McDevitt, Appl.Phys.Lett.66(1995)2900
[12] J. Zhou, R. Lo, S. Savoy, M. Arendt, J. Armstrong, D. Yang, J. Talvachio, and J. McDevitt, Physica C 273(1997)223
[13] P. Slater and C. Graves, Supercond.Sci.Tech. 5(1992)205
[14] R. Kita, A. Sakuragi, and K. Yokoyama, Physica C 392-6(2003)484
[15] J. Chien, B. Gong, Y. Yang, I. Cabrera, J. Effing, and H. Ringsdorf, Adv.Mater.Sci.Lett.3(1990)305
[16] I.v.Lampe, A. Schmalstieg, S. Götze, J.-P. Müller, F. Zygalsky, H.-J. Lorkowski, and M. Matalla, J.Mater.Sci.Lett.16(1997)16
[17] I.v.Lampe, F. Zygalsky, G. Hinrichsen, H. Springer and H. Schubert, J.Mater.Sci.Lett.21(2002)133
[18] I.v.Lampe, D. Schultze, F. Zygalsky, Polym.Degrad.Stab. 73(2001)87
[19] R. Hussain, S. Sulfiqar, D. Mohammad, I. Mc Neill, Polym.Degrad.Stab. 45(1994)115
[20] H. Nojima, H. Shintaku, M. Nagata, M. Koba, Japan.J.Appl.Phys. 30(1991)L1166
[21] B. Holzapfel, D. Verebelyi, C. Cantoni, M. Paranthaman, B. Saales, R. Feenstra, D. Christen, and D. Norton, Physica C 341-8(2000)1431
[22] P. Rudolf, Diss. TU Berlin (1995)
[23] H. Remy, Lehrbuch Anorganische Chemie (Geest & Portig K-G,Leipzig, 1952) Bd. II 520