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Chemical Stability of High-Temperature Superconductors

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ABSTRACT

A review of the available studies on the chemical stability of the high-temperature superconductors (HTS) in various environments has been made. The $La_{1.8}Ba_{0.2}CuO_4$ HTS is unstable in the presence of H_2O, CO_2, and CO. The $YBa_2Cu_3O_{7-x}$ superconductor is highly susceptible to degradation in different environments, especially water. The $La_{2-x}Ba_xCuO_4$ and Bi-Sr-Ca-Cu-O HTS are relatively less reactive than the $YBa_2Cu_3O_{7-x}$. Processing of $YBa_2Cu_3O_{7-x}$ HTS in purified oxygen, rather than in air, using high purity non-carbon containing starting materials is recommended. Exposure of this HTS to the ambient atmosphere should also be avoided at all stages during processing and storage. Devices and components made out of these oxide superconductors would have to be protected with an impermeable coating of a polymer, glass, or metal to avoid deterioration during use.

1. INTRODUCTION

Since the breakthrough discoveries of superconductivity at ~35K in $La_{2-x}Ba_xCuO_4$, at ~92K in Y-Ba-Cu-O, at ~110K in Bi-Sr-Ca-Cu-O, and at ~125K in Tl-Ba-Ca-Cu-O system, research interest in these ceramic materials has been extraordinarily high as seen from the very large number of research reports generated during the short period of about the last five years. These high temperature superconducting (HTS) materials should find applications in various exotic technologies such as superfast levitated trains, electric cars, lossless power transmission lines, ultrafast computers and other microelectronic devices, high sensitivity electronics, medical diagnostics such as magnetic resonance imaging, ore purification through improved magnetic separators, nuclear fusion, smaller and cheaper particle accelerators, magnetic runways, etc. Knowledge about the chemical stability of these HTS is

essential from both a scientific as well as a technological viewpoint. The nature of the corrosion products from reaction of the HTS with various solvents and environments provides useful insight about the chemical bonding and oxidation states of these materials. Also, information on the resistance to environmental degradation is a prerequisite for any practical applications of the HTS. A large number of investigations have been reported on the effects of different environments on stability of the various oxide superconductors. The objective of this chapter is to review these studies and to make recommendations with regard to protecting the HTS from deterioration during use.

2. La-Sr-Cu-O SYSTEM

Only a few studies are available on the stability of this HTS in different environments. The initial stages of surface degradation of high-T_c superconductor $La_{1.8}Sr_{0.2}CuO_4$ by interaction with four different gaseous environments has been investigated [1] using UV photoelectron spectroscopy. Exposure to O_2 had little effect whereas water adsorbed dissociatively, resulting in the formation of surface hydroxides. Carbonatelike surface species were formed in the presence of CO_2 as well as CO. However, CO was much less reactive than CO_2.

The effects of annealing $La_{2-x}Sr_xCuO_4$ (x = 0, 0.1, and 0.15) in dry and wet O_2 (saturated with water at room temperature), at different temperatures between 200 and 930 ^oC, on its superconducting properties have been investigated [2]. There was no effect of annealing in dry O_2. However in moist O_2, the resistive properties degraded greatly. The degradation was greatest at 200 ^oC and decreased with increase in annealing temperature. The treatments had no effect on the Meissner signal. This probably indicates that the resistive degradation was due to the formation of some hydroxide species at the grain boundaries which decomposed as the treatment temperature was raised to 930 ^oC.

Degradation of powdered and sintered specimens of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and the partially chlorinated $La_{1.8}Sr_{0.2}CuO_{4-\delta-y/2}Cl_y$ (y = 0.1, 0.2, 0.3, 0.5, and 1) in ambient air and in contact with liquid water has been investigated [3]. Powder or sintered $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ showed no degradation after several months in the ambient atmosphere or even after contact with liquid water for several days. The powder or cold pressed (not sintered) partially chlorinated specimens were stable for several months under ambient conditions, but degraded within a few hours in liquid water. On the other hand, the sintered chlorinated samples degraded even in the ambient atmosphere resulting in the formation of $La(OH)_3$ and $SrCl_2.6H_2O$. The degradation rate increased with the chlorine concentration. A sintered pellet of y = 1 composition disintegrated into gray powder after just two days. A mechanism has been proposed [3] to explain the behaviors of different samples.

The open circuit dissolution of $La_{1.8}Sr_{0.2}CuO_4$, as disks of rotating ring-disk electrodes, in 1M NaCl solutions containing 1-10 mM HCl has been examined [4]. This HTS was found to be unstable in dilute HCl media and dissolved at roughly half the rate of $YBa_2Cu_3O_{7-x}$ with mixed mass transfer and surface rate control. The rate of dissolution of CuO in these HCl solutions

was found to be at least an order of magnitude slower than that of the oxide superconductors. The average oxidation state of copper in $La_{1.8}Sr_{0.2}CuO_4$ was 2.2.

## 3. Y-Ba-Cu-O SYSTEM

The chemical stability of $YBa_2Cu_3O_{7-x}$ has been most widely studied in contact with various gases, solvents, and solutions, particularly with water, as described below.

3.1. REACTION WITH WATER

Reactivity of $YBa_2Cu_3O_{7-x}$ HTS with water is anticipated because of the presence of barium and Cu^{3+} in this compound. Several reports have appeared on the study of the effects of humidity [5-30] and water [5,6,9,10,13,28,31-43] on chemical stability, superconductivity, and other properties such as strength degradation [25] and crack propagation [11] in $YBa_2Cu_3O_{7-x}$.

The following mechanism has been proposed [5,6] for the reaction of $YBa_2Cu_3O_{7-x}$ with water:

$$2YBa_2Cu_3O_{7-x} + 3H_2O \longrightarrow Y_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + (0.5-x)O_2 \quad (1)$$
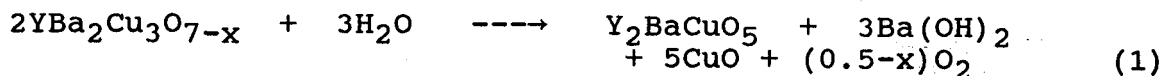
During this reaction the formal valence of Cu changes from +2.3 to +2. $Ba(OH)_2$ has reasonable solubility in water as given in Table I. On exposure to the ambient atmosphere, $Ba(OH)_2$ further reacts with CO_2 to form barium carbonate:

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O \quad (2)$$

Crystals of $BaCO_3$ slowly grow and precipitate out of the solution since it is only sparingly soluble in water (Table I). Formation of $BaCO_3$ continues and white needle shaped crystals settle on the bottom of the container.

TABLE I. Solubilities of Various Salts in Water [87]

Salt	Solubility (g/100 ml H_2O)	Salt	Solubility (g/100 ml H_2O)
$Ba(OH)_2$	3.04	$BaCO_3$	0.002 (20 °C) 0.006 (100 °C)
$Sr(OH)_2$	0.41 (0 °C) 21.83 (100 °C)	$SrCO_3$	0.0011 (18 °C) 0.065 (100 °C)
$Ca(OH)_2$	0.185 (0 °C) 0.077 (100 °C)	$CaCO_3$	0.0014 (25 °C) 0.0018 (75 °C)
$Y(OH)_3$	Insoluble	CuO	Insoluble
$Cu(OH)_2$	Insoluble	$2CuCO_3 \cdot Cu(OH)_2$	Insoluble

Variations in solution pH as a function of time by the reaction of $YBa_2Cu_3O_{7-x}$ HTS powder or monolithic sample with

water are shown in Fig. 1. The solution pH suddenly jumps from
~6 to ~9.5-10 within a few minutes due to nearly instantaneous
release of Ba^{2+} ions into solution by ion-exchange resulting in
the formation of $Ba(OH)_2$ (cf. reaction 1) which is a strong
base. The pH further increases slowly and remains stable at ~12
for about a day and then slowly drops to ~9.5 during the next
few days. The drop in pH is due to the removal of $Ba(OH)_2$ from
the solution, by its reaction with the atmospheric CO_2 according
to reaction (2), as a white precipitate of $BaCO_3$. The solution
pH of samples B and C which were isolated from the atmosphere
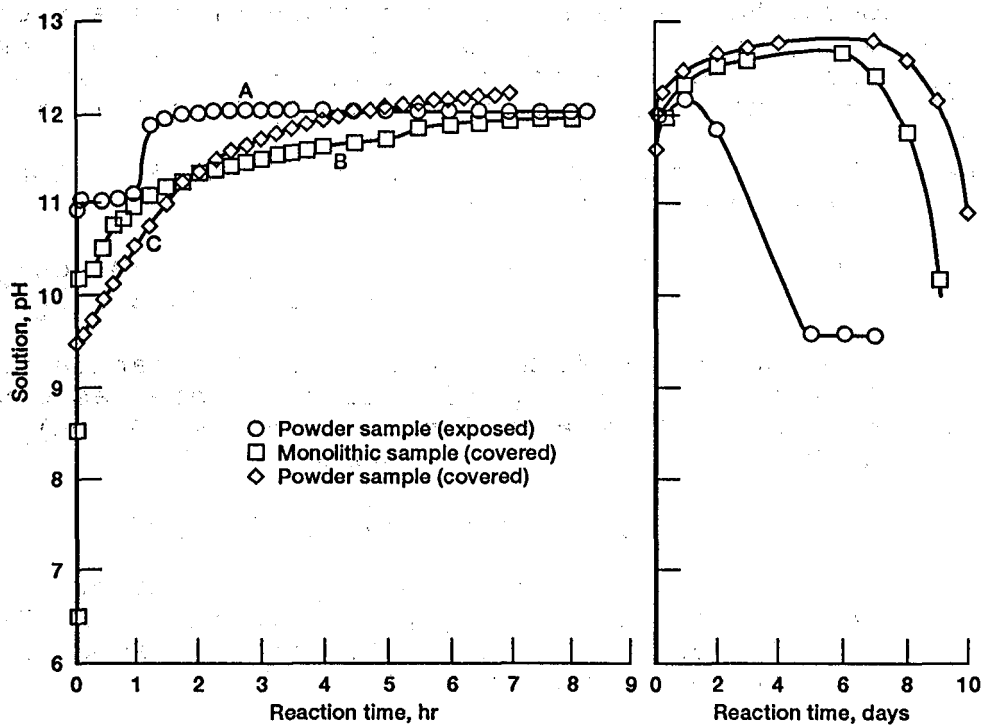kept on increasing slowly even after six to seven days.

Fig. 1. Variations in solution pH with time during the reaction
of $YBa_2Cu_3O_{7-x}$ HTS with water at room temperature.
A-1.442 g powder in 50 ml water exposed to atmosphere;
B-1.452 g monolithic sample, 0.454x1.026x0.704 cm^3;
C-1.387 g powder in 50 ml water; B and C were exposed to
the ambient atmosphere after six and seven days,
respectively. (From Bansal and Sandkuhl [5])

The leaching of $YBa_2Cu_3O_{7-x}$ in water is reported [31] to be
a highly incongruent process; BaO rapidly leaches away whereas
yttrium and copper oxides hardly dissolve in water. This is in
agreement with the results of Bansal and Sandkuhl [5]. The XRD
pattern of $YBa_2Cu_3O_{7-x}$ powder which had been immersed in water
for ten days still showed [5] the presence of the perovskite
phase indicating the corrosion reaction was not yet complete.
Surprisingly, Nakada et al [32] have reported $YBa_2Cu_3O_{7-x}$ to be
inert to water at 22-24 °C.
SEM micrographs [5] of the surface of a specimen which had
been immersed under water for ~nine days at room temperature are
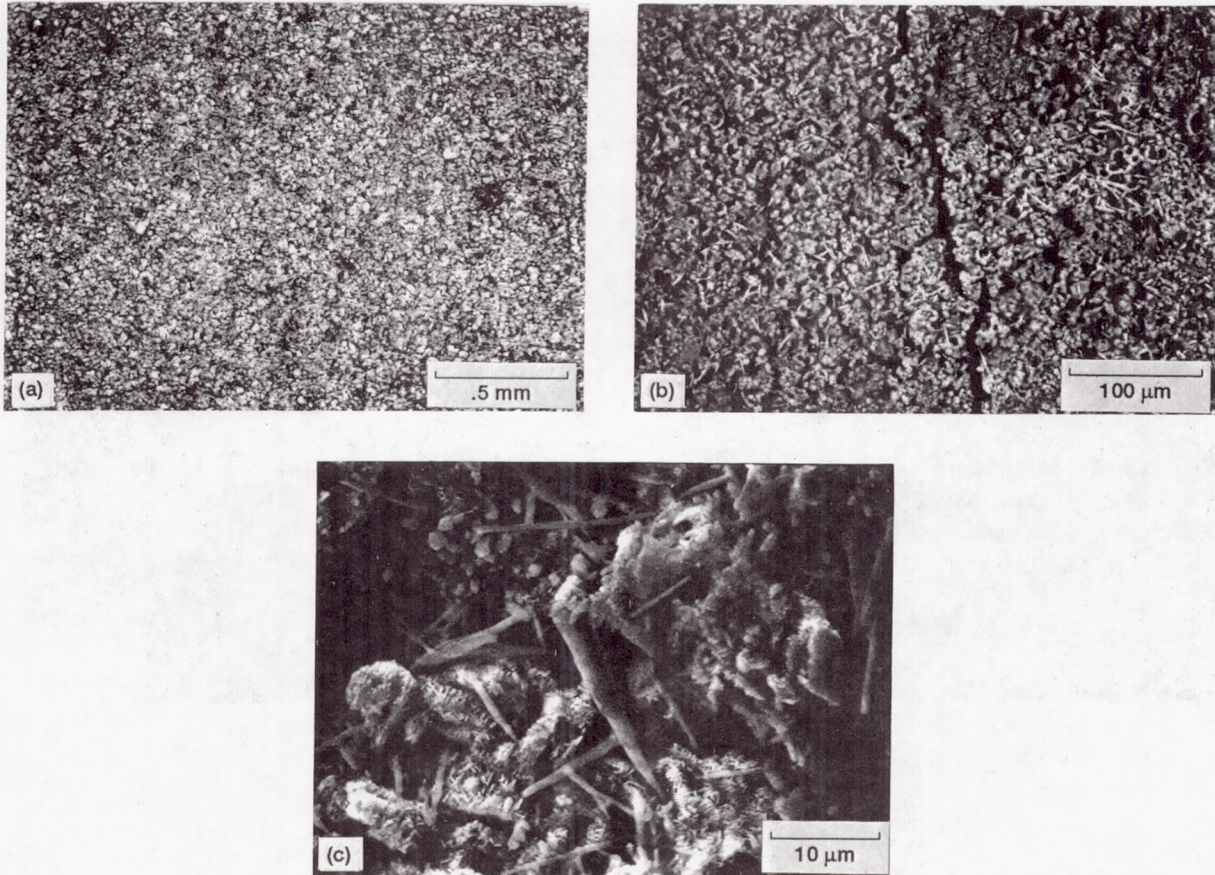given in Fig. 2. Also shown, for comparison, is a micrograph of

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Fig. 2. SEM micrographs of $YBa_2Cu_3O_{7-x}$ HTS surfaces: before (a) and after (b), (c) reaction with water at room temperature for nine days. (From Bansal and Sandkuhl [5])

the surface of an unreacted HTS sample. The sample surface has cracked after reaction with water and needle shaped crystals of $BaCO_3$ are present on the surface of the degraded sample.

The reaction of $YBa_2Cu_3O_{7-x}$ HTS with water or moisture leads to a rapid formation of surface layers of $Ba(OH)_2$ and $BaCO_3$ as found [13] from X-ray photoemission spectroscopy (XPS). Formation of $Ba_2Cu(OH)_6$, $BaCO_3$, CuO, and $Y(OH)_3$ as the corrosion products from the reaction of $YBa_2Cu_3O_{7-x}$ with moisture has also been reported [7]. However, Bansal and Sandkuhl [5] did not find the presence of any yttrium compound or $Ba_2Cu(OH)_6$ in the XRD patterns of the corrosion products. Probably $Ba_2Cu(OH)_6$

decomposes into copper hydroxide and barium hydroxide which
further reacts with CO_2 to form $BaCO_3$. The degree of degradation
of the HTS increases with increase in sample porosity [41,42]
and the reaction temperature.

SEM micrographs [5] of the surfaces of the HTS specimens
which had been exposed for ~30h to 100% relative humidity at
three different temperatures are presented in Fig. 3. The sample
surface reacted at 55 ^{O}C has been badly cracked and the one
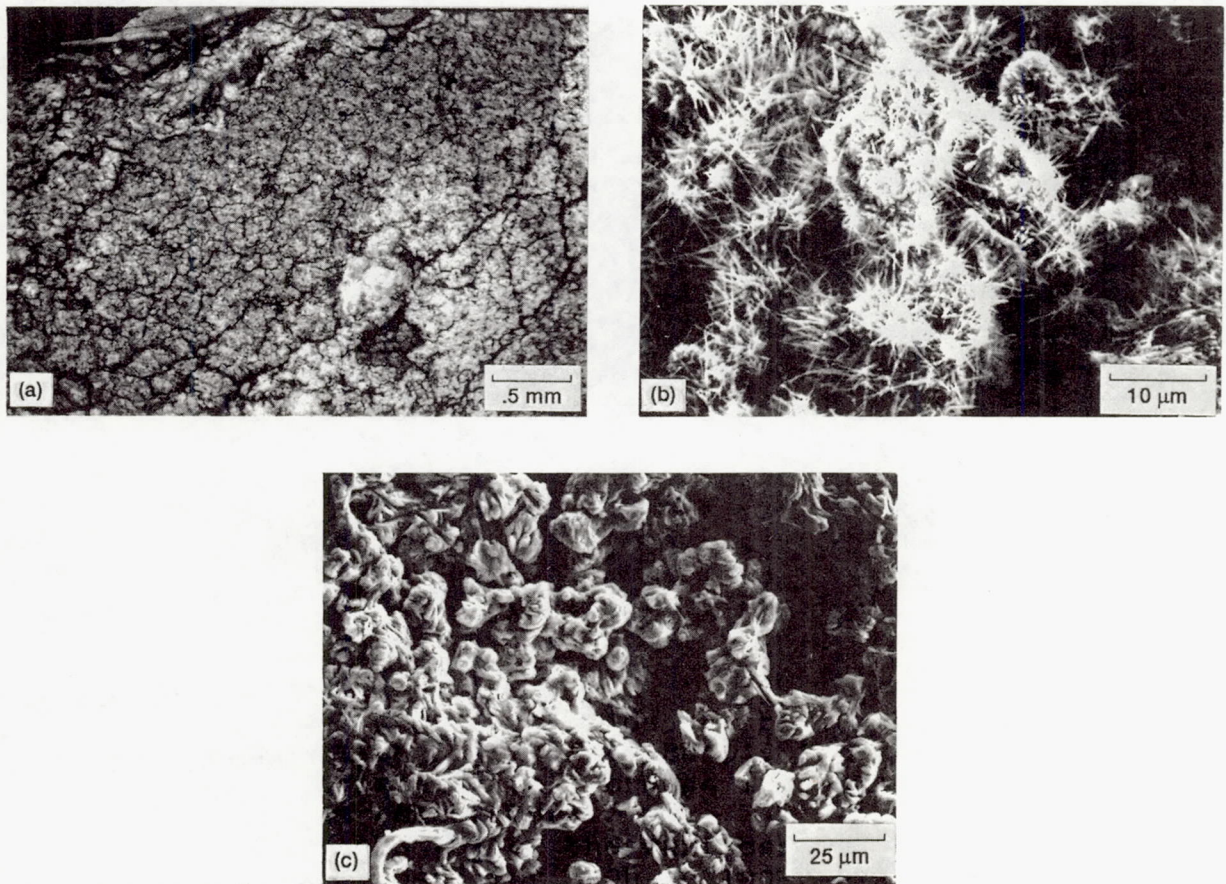

Fig. 3. SEM micrographs of $YBa_2Cu_3O_{7-x}$ HTS surfaces after
exposure to 100% humidity for 30 h at (a) 55 ^{O}C, (b) 40
^{O}C, and (c) 23 ^{O}C. (From Bansal and Sandkuhl [5])

reacted at 40 ^{O}C is covered with fine needle-shaped
microcrystals of $BaCO_3$. An HTS specimen which was exposed to
100% relative humidity at room temperature for about eight weeks

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was covered with a white layer and was slowly disintegrating into pieces. It appears that reaction with water initiates on the sample surface and progresses into the bulk of the material by diffusion of the atmospheric moisture. Water reacts with the HTS to form barium hydroxide and further converts into barium carbonate by reacting with the atmospheric carbon dioxide. Unfortunately, no protective reaction layer is formed and the corrosion process continues. The HTS surface gets irreversibly modified by adsorption of water even at cryogenic temperatures as found fron an XPS study [44].

Freshly prepared, phase pure HTS material showed no signal in the electron spin resonance (ESR) at room temperature. However, when the HTS was exposed to air or water, an ESR signal was observed [21-23] probably due to the formation of Y_2BaCuO_5. Thus, the ESR technique may be employed to follow the deterioration of this HTS. Surface degradation of HTS pellets and thin films in ambient atmosphere and 85% relative humidity at 50 ^{o}C have also been investigated [30] using XPS and scanning Auger electron microprobe. $BaCO_3$ and $Ba(OH)_2$ were formed on the pellet surface, but copper was completely absent in the surface layers after 48 h of exposure. The degradation of the thin films was much slower. The rate controlling process during the reaction is probably the diffusion of Ba to the surface and Cu depletion from the surface through the grain boundaries. Proton NMR [45] and thermally simulated luminescence [24] techniques have also been used to study the interaction of HTS with water.

The HTS powder is highly susceptible [19] to degradation by reaction with the moisture in the ambient atmosphere. But at 30% relative humidity, no adverse effect on the characteristics of the powder was detected [19] by XRD and SEM. However, a TEM study [8] has shown that when HTS samples are exposed to low levels of humidity, crystallographic defects associated with moisture attack develop long before any degradation products are detected by XRD. The rate of surface degradation is enhanced by increasing the relative humidity and temperature. The early stage of the degradation of HTS in air consists of two modes as shown [20] by high resolution TEM. One is the formation of amorphous and polycrystalline phases due to the reaction with water vapors and the other is the formation of planar defects which are introduced parallel to the (001) plane between Ba-O and Ba-O layers even in dry air. The polycrystalline phase is formed after the formation of the amorphous phase.

The HTS powder exposed to water vapor at 26, 120, and 200 ^{o}C showed [26] two desorption peaks in the temperature programmed desorption spectra recorded using a quadrupole mass spectrometer. The one at lower temperature is due to chemisorbed water and the high-temperature one is from reacted amorphous hydroxide phase. The degradation of $YBa_2Cu_3O_{7-x}$ showed [28] the following dependence: wet steam (condensed thin film of water) > bulk water >> dry steam.

When exposed to 78% relative humidity, the fraction of the HTS phase decreased [27] parabolically with time and completely decomposed into $BaCO_3$, Y_2BaCuO_5, and CuO after six months. However, at a relative humidity of 51% or less, the powders remain superconducting even after six months which is somewhat surprising in light of the results of others. HTS powders kept at non-zero relative humidity showed surface reaction with water

and agglomeration. This would inhibit the sintering of these powders and would make the achievement of high sintered densities difficult. The fraction of the superconducting phase decreased exponentially [16] with time on exposure to 98% relative humidity at 20 $^{\circ}$C.

Phase pure HTS is found [18] to be more stable in moisture than the multiphase material. The tetragonal material is reported [34] to be more resistant to corrosion in water than the one having the orthorhombic structure. The presence of Cu^{3+} in the latter is probably the driving force for rapid reaction with water. Surprisingly, Pham et al [28] observed an increase in the surface degradation of the HTS in water with the extent of oxygen deficiency. In contrast, the reactivity of $YBa_2Cu_3O_{7-x}$ in water vapor was found [6,14] to be relatively insensitive to the value of x. At p_{H2O} = 2.7 kPa, the HTS decomposed extensively by reacting with water at room temperature and 140 $^{\circ}$C. At p_{H2O} = 270 Pa, the reaction was controlled by the diffusion, probably of OH^-, in $YBa_2Cu_3O_{7-x}$. Temperature dependence of diffusion coefficient, D, in the range of ~100 to 160 $^{\circ}$C is given by:

$$D_{OH^-} (cm^2/s) = 1.26 \times 10^{-11} \exp[-58.4(kJ/mol)/RT] \qquad (3)$$

However, no definite evidence was presented to support the fact that this indeed is the diffusion of OH^- in $YBa_2Cu_3O_{7-x}$. Diffusion coefficient of water in the HTS has been reported [41] to be ~(4-6) $\times 10^{-9}$ cm^2/s at 25 $^{\circ}$C.

Dynamic fatigue of a homogeneous, high density HTS in atmospheres containing water vapors has been observed [25]. The single crystals of HTS are reported [11] to be susceptible to moisture-enhanced crack propagation.

The above results indicate that the $YBa_2Cu_3O_{7-x}$ HTS in the form of powder, bulk or films is highly unstable in the presence of water or moisture. However, the superconducting $YBa_2Cu_3O_{7-x}$ phase can be regenerated [40] by reannealing the water-reacted material at 930 $^{\circ}$C for 6h.

3.2. CORROSION IN SOLUTIONS

The corrosion of $YBa_2Cu_3O_{7-x}$ HTS in various aqueous solutions including 0.2M HCl, 0.2M NaOH, 0.2M NaCl, and distilled water has been studied [34]. Reaction with HCl solution proceeds according to the following reaction:

$$YBa_2Cu_3O_7 + 13HCl \longrightarrow YCl_3 + 2BaCl_2 + 3CuCl_2 + 0.5H_2O + 0.5O_2 \qquad (4)$$
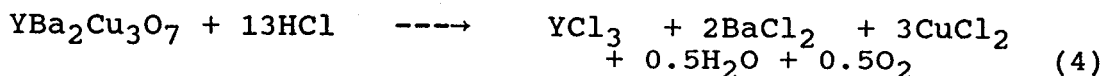
Measurement of the O_2 gas evolved can be used to determine the amount of Cu^{3+} in the HTS. In dilute HCl [9,10,34] and HNO_3 the HTS powder dissolves quickly. However, it develops a passivating layer in concentrated acid. Reaction of sintered HTS with NaOH solution was slower than that with either distilled water or acid. Reactions of the HTS powder with concentrated nitric and acetic acids and NH_4OH have also been investigated [46]. Reactivity of the HTS with concentrated or 10% solutions of various acids decreased [47] in the order HCl> HNO_3 >CH_3COOH >H_2SO_4.

The effect of pH on the chemical durability of $YBa_2Cu_3O_{7-x}$

HTS in aqueous solutions has been investigated [39] by determining the amount of each metal cation in the leachant. In a highly acidic solution of pH 1 at 20 °C, the HTS dissolves congruently. In a solution of pH 3, ion-exchanged water having pH 6.6, or NaOH solution of pH 13, barium ions dissolve preferentially whereas negligible amounts of yttrium and copper ions were leached out. The dissolution rates of barium and copper ions in the aqueous NH_4OH solution of pH 13 were much higher than those in the NaOH solution of the same pH. The higher dissolution rate of copper ions was due to the formation of $Cu(NH_3)_4^{2+}$ or $Cu(NH_3)_5^{2+}$ complex species stable at pH >12. The leaching rate of the cations gradually decreased with increase in pH above 3 and sharply increased as the acidity of the solution increased below pH 3.

Stability of $YBa_2Cu_3O_{7-x}$ in methanol-water mixtures containing 0 to 50 volume % methanol, 0.1M $BaCl_2$ and 0.01M $CaCl_2$ aqueous solutions, and 1.0M $NaNO_3$, 1.0M NaCl, 1.0M $Ca(NO_3)_2$, and 0.001 - 1.0M $CaCl_2$ solutions in 20 volume % methanol-water mixtures has also been studied [38]. In water, Ba leaches preferentially from the HTS, but in methanol-water mixtures the dissolution of Ba is greatly reduced. The dissolution of Ba was further decreased by the presence of $CaCl_2$ or NaCl in the 20 volume % methanol-water solution. In electrolytes such as 1M NaCl or 10M NaOH, the HTS showed [9] little reactivity at room temperature in one day and a slight reaction at 100 °C in 24 h. However, complete decomposition of the HTS was observed [9] at 300 °C and 10 KSI in a few days in 1M NaCl, 1M KCl, and 10M NaOH.

Leaching[31] of $YBa_2Cu_3O_{7-x}$ in 0.05M KI aqueous solution is highly incongruent. A significant amount of Ba dissolves quickly whereas Y and Cu hardly leach out. Leaching behavior of $YBa_2Cu_3O_{7-x}$ in aqueous solutions of $K_4[Fe(CN)_6]$, NaBr, KBr, and N,N,N',N'-tetramethyl-p-phenylene diamine hydrochloride has also been investigated [48].

3.3. __STABILITY IN VARIOUS GASES__

Kinetics of CO_2 degradation of $YBa_2Cu_3O_{7-x}$ HTS powder has been investigated [49] using a nonisothermal technique. Below 900 °C, the overall reaction can be represented as:

$$YBa_2Cu_3O_{7-x} + 2CO_2 \longrightarrow \quad 1/2\ Y_2Cu_2O_5 + 2BaCO_3 + CuO$$
$$+ 1/2\ Cu_2O + (0.5 - x/2)O_2 \quad (5)$$
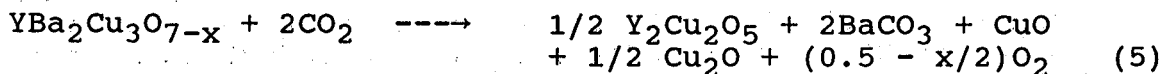
At higher temperatures, $BaCO_3$ and CuO react together to form $BaCuO_2$ according to the reaction:

$$BaCO_3 + CuO \longrightarrow \quad BaCuO_2 + CO_2 \quad (6)$$

The activation energy for carbonization was estimated to be 95.1 kJ/mol.

Formation of a barium oxycarbonate phase, having a nominal composition of $BaCO_{4.8}$, has been observed [50] in the grain boundaries of $YBa_2Cu_3O_{7-x}$ at temperatures >450 °C. The source of carbon in the grain boundary phase was the atmospheric CO_2. The reaction with CO_2 was not reversed by subsequent annealing in oxygen. For this reason, it was recommended that exposure of the HTS to the ambient atmosphere should be avoided at all stages.

Effects of heating $YBa_2Cu_3O_7$ to 1000 ^oC in various environments such as CO_2, CO, mixtures of CO_2 and O_2, wet O_2, and wet CO_2, has been studied [51] using TGA. In CO_2, a small weight loss caused by the loss of oxygen was observed, followed by a large weight gain up to ~950 ^oC after which the $BaCO_3$ formed started to decompose. In CO, the behavior was similar except that the O_2 loss was much more severe. In wet or dry CO_2, the HTS powder decomposed into a mixture of $BaCO_3$, $Y_2Cu_2O_5$, CuO, Cu_2O, and Y_2O_3. At higher oxygen concentrations, as in O_2 containing 10% CO_2, the reaction products were $BaCO_3$, $Y_2Cu_2O_5$, and CuO. Exposure of the HTS to 1% CO_2 in O_2 led only to broadening of the Bragg peaks of $YBa_2Cu_3O_{7-x}$. In CO the HTS decomposed into Cu, $BaCO_3$, and Y_2O_3. No new phases were formed when the HTS was exposed to wet or dry O_2 or to oxygen containing 0.1% CO_2. HTS specimens degraded by H_2O or CO_2 could be nearly regenerated by heat treatment above 900 ^oC in oxygen followed by annealing or slow cooling in O_2.

From UV photoelectron spectroscopy, $YBa_2Cu_3O_{7-x}$ was found [1] to be stable in O_2, but very reactive towards the adsorption of H_2O and CO_2. The effects of annealing $YBa_2Cu_3O_7$ in dry and wet O_2 (saturated with water at room temperature) at different temperatures between 200 and 930 ^oC on its superconducting behavior have been studied [2]. Substantial degradation of resistive behavior was observed on annealing in dry O_2, the effect being maximum at 500^oC. It was attributed to the formation of carbonate in the grain boundaries by the absorption of the contaminant CO_2 gas. Annealing at 930 ^oC restored the original superconducting behavior of the sample by decomposing the carbonate layer in the grain boundaries. Surprisingly, no degradation was observed on treatments in wet O_2 at 200 ^oC and above inspite of the detrimental effects of moisture reported by others at lower temperatures.

At temperatures below ~600 ^oC, $YBa_2Cu_3O_{7-x}$ powder is unstable [52] in the presence of NO_x and decomposes to form $Ba(NO_3)_2$.

3.4. REACTIVITY WITH ORGANIC SOLVENTS

Only a few studies [46,53,54] are available concerning the reactivity of $YBa_2Cu_3O_{7-x}$ with organic solvents. No detrimental effect was observed [46] on $YBa_2Cu_3O_{7-x}$ powder when immersed in hexane, ethanol, isopropanol, or acetone at room temperature. At 100 ^oC the HTS powder undergoes surface reduction in these solvents, but can be regenerated by annealing in oxygen at 450 ^oC. After 220 h immersion of $YBa_2Cu_3O_{7-x}$ in organic solvents such as benzene, toluene, acetone, methanol, ethanol, isopropanol, or demethyl formamide, a minimal reaction was observed [54]. Nevertheless, the dissolution was incongruent indicating some reaction at the powder surface. This reaction could be due to the presence of dissolved water in the solvents which were not completely dried prior to the experiments. A white precipitate of $BaCO_3$ was formed on reaction of $YBa_2Cu_3O_{7-x}$ with CH_3OH followed by drying which was also ascribed [55] to the presence of absorbed moisture in methanol. No obvious reaction was observed [9] with CH_3OH in five days at room temperature or in one day at 100 ^oC. However, complete decomposition of the HTS occurred [9] after four days at 300 ^oC and 10 KSI in methanol as well as in methanol + 1M NaOH. At
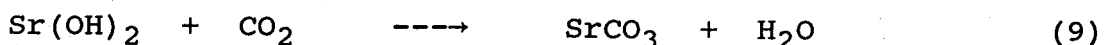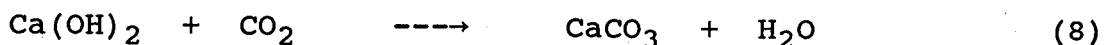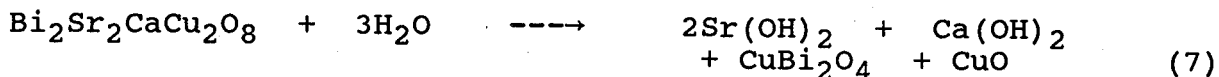
moderate temperatures, strong surface and interfacial reactions can occur [53] between the HTS and solvents such as acetone and hexane as well as organic polymers.

1,1,2 trifluorotrichloroethane (FC-113) is reported [19] to be nonreactive towards the HTS powder and recommended as a milling and storage medium for the HTS.
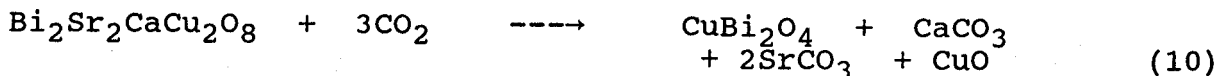
4. Bi- SYSTEM

Only a few reports have been published on the chemical reactivity of this HTS. In the very first paper published on the Bi- HTS, it was reported [56[that the superconducting phases, formed by heat treatment of the nominal $BiSrCaCu_2O_x$ composition, were extremely stable towards moisture and water. No change in superconducting characteristics was observed even after thermal cycling of the specimen between 4 K and room temperature or above. Degradation of superconducting properties of Bi-Sr-Ca-Cu-O thin films on (100) MgO substrate was observed [57] when soaked in water at 18 ^{O}C. From electron microprobe analysis it was determined that degradation was caused largely by leaching of Sr and Ca from the needlelike non-superconducting grains with off-stoichiometric composition. The platelike superconducting grains with stoichiometric composition were not affected by water. The amount of degradation depended strongly on the number of non-superconducting grains in the films.

Variations [58] in electrical conductivity and pH with time of the solution obtained by reacting the 2212 HTS powder with water at 0 ^{O}C and room temperature (25 $\pm$ 5 ^{O}C) are shown in Fig. 4. Both pH and conductivity of the solution rapidly increase with time indicating a fast reaction between 2212 and water. The reaction rate is slower at 0 ^{O}C, as expected. The following mechanism has been proposed [58] for the reaction of 2212 phase with water:

$$Bi_2Sr_2CaCu_2O_8 + 3H_2O \longrightarrow 2Sr(OH)_2 + Ca(OH)_2 + CuBi_2O_4 + CuO \qquad (7)$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (8)$$

$$Sr(OH)_2 + CO_2 \longrightarrow SrCO_3 + H_2O \qquad (9)$$

The overall reaction may be written as:

$$Bi_2Sr_2CaCu_2O_8 + 3CO_2 \longrightarrow CuBi_2O_4 + CaCO_3 + 2SrCO_3 + CuO \qquad (10)$$

It is interesting to compare reactions (1) and (7). In reaction (1), there is evolution of O_2 and the formal valence of copper changes from +2.3 to +2 whereas the valence of copper remains unchanged and there is no O_2 evolved in reaction (7).

Corrosion of 2212 HTS with various aqueous solutions has also been studied [55]. In 2M HCl, O_2 gas is slowly evolved and a brown precipitate, probably of Bi_2O_4 or Bi_2O_5, is formed which later on dissolves back according to the reaction:

$$Bi_2O_5 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O + O_2 \qquad (11)$$

The rate of O_2 evolution was much faster in 2M HCl than in

distilled water. The reaction rate constant for leaching of a sintered pellet in 10% HCl was found [55] to be less than one-half of that for $YBa_2Cu_3O_{7-x}$. No reaction was observed with methanol or 2M NaCl aqueous solution. The reaction with 2M NaOH was stronger with 2212 than with $YBa_2Cu_3O_{7-x}$. A dark blue solution and a brown solid, probably Bi_2O_4 which is insoluble in NaOH solution, were formed. The blue solution is probably due to the formation of $NaBiO_3$ which is soluble in NaOH and may form a complex with Cu^{2+}.
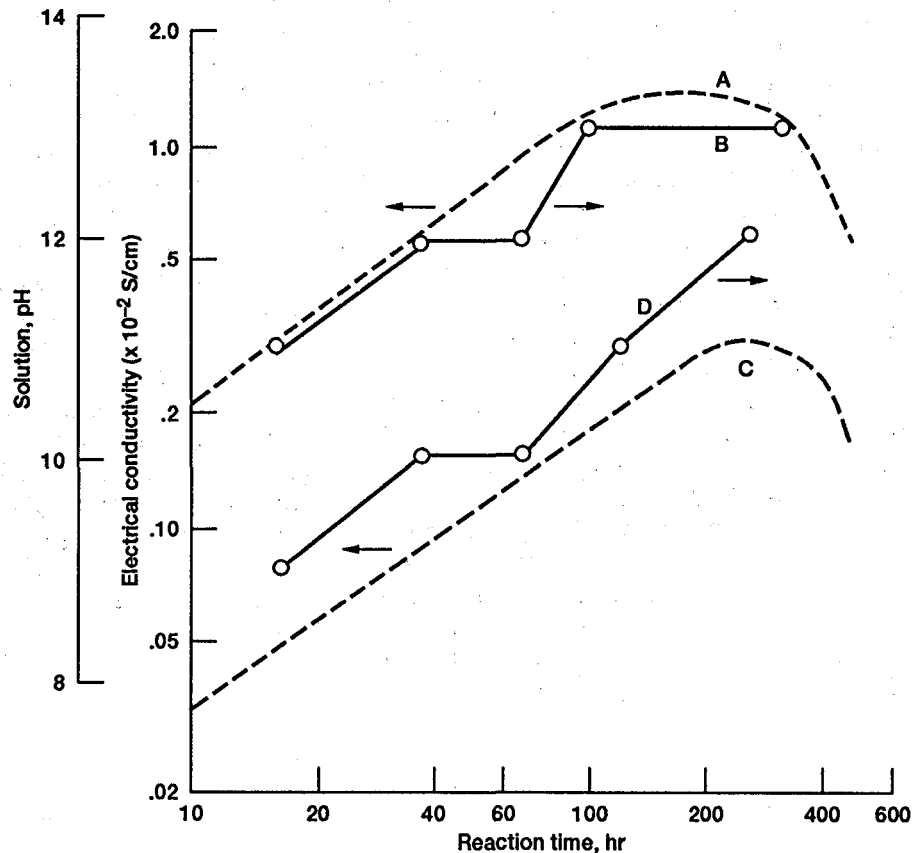

Fig. 4. Variations in solution electrical conductivity (curves a, c) and pH (curves b, d) with time during the reaction of 1.36 g powder of 2212 HTS with 50 ml water; at room temperature: (a) and (b), and at 0 °C : (c) and (d). (From Jin et al [58]).

Degradation of both the 80 K and the 110 K superconducting phases present in $Bi_{1.4}Pb_{0.6}Sr_2Ca_2Cu_3O_x$ by reaction with boiling water has been followed [59] by measuring the changes in magnetic susceptibility and electrical resistivity as a function of time. The 110 K phase deteriorated at a much faster rate than the 80 K phase. The high-T_c phase in the (Bi,Pb)-Sr-Ca-Cu-O system is destroyed [60] on exposure to the humid environment but can easily be regenerated by annealing in air at 845 °C.

From a comparative study [55] on the chemical stability of 2212 and $YBa_2Cu_3O_{7-x}$ in various solutions and solvents, 2212 was in general more stable, except in strongly basic solutions, owing to the amphoteric nature of Bi.

Reaction with water of high-T_c Bi(Pb)-Sr-Ca-Cu-O/Ag superconducting microcomposites containing 24-80 weight %

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silver, produced by oxidation of metallic precursor alloys, has been investigated [61]. HTS samples containing ⁻80 wt.% Ag showed no change in T_c and J_c even after immersion under water for 104 days. In specimens with low silver content the 2223 HTS phase was surprisingly reported [61] to be inert towards water. But, some nonsuperconducting Ca-rich oxide phase reacted with water and disrupted the contact between the superconducting grains, resulting in a large drop in J_c.

5. ETCHANTS FOR HTS FILMS

A number of aqueous [62-64] (H_3PO_4, HNO_3, HCl, and HCl + H_3PO_4) and non-aqueous [65-67] (Feliox-115/CH_3OH, Br/ C_2H_5OH, I/C_2H_5OH, HF/C_2H_5OH, and HCl/C_2H_5OH) chemical solutions have been employed as etchants in patterning of the HTS thin films. An aqueous solution of ethylenediamine tetra acetic acid has also been suggested [68] as an etchant.

6. PASSIVATION AND PROTECTION OF HTS

Practical application of HTS depends on developing techniques for passivating exposed surfaces and depositing nonreactive overlayers. Some attempts [69,70] have been made to protect the 123 HTS from degradation.

The effects of depositing metal and semiconductor atoms such as Al, Ti, Fe, Cu, Pd, Ag, La, Au, In, Bi, Ge, Si on to clean HTS surfaces has been investigated [71-77]. Ag and Au were the only nonreactive elements, although Ag induces some disruption and Bi may be considered mildly reactive. However, the reactivity of HTS with metal and semiconductor overlayers can be reduced by providing activated oxygen during deposition. A hermetically sealed layer of Ag, Al, Au, Cu, In, SiO_2, or SiO_3N_4 over the HTS surface has been suggested [78] to protect the HTS against the atmosphere.

The addition of 5 - 10 weight % of Ag_2O during processing seems [79] to retard the deterioration of $YBa_2Cu_3O_{7-x}$ HTS by water. The Ag-doped HTS retained superconductivity even after one hour immersion in boiling water. From EPMA and XRD analysis, it was suggested that Ag deposited on the crystallite surfaces during processing prevents water diffusion into the superconducting crystallites. The corrosion kinetics of the composite ($YBa_2Cu_3O_{7-x}$ + 25 weight % Ag) towards water are reported [43] to be considerably reduced. The moisture- and water-induced degradation of Y-Ba-Cu-O superconducting films deposited at high temperatures using layer structures was greatly reduced [69,80] when a silver barrier layer was included in the starting structures.

Passivation of HTS surfaces with CaF_2 and oxides of Bi, Al and Si has also been investigated [71,77]. The overlayers of CaF_2 deposited on $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_{2-x}Ca_{1+x}Cu_2O_{8+y}$ were found to be nonreactive. Deposition of Bi, Al, and Si in the presence of activated oxygen resulted in Bi-O, Al-O, and Si-O compounds which were much less reactive with $YBa_2Cu_3O_{7-x}$ than their respective elements.

Fluorine treatment [81] also seems to passivate the 123 HTS against hydrolysis in water or humid air. The fluoride passivating surface layers can be formed [65] using wet chemical techniques such as with HF in ethanol or by using gas phase reactants such as F_2 or XeF_2. The characteristics of $YBa_2Cu_3O_{7-x}$

HTS treated with HF [82,83] and HCl [84] have also been investigated. The HTS may also be protected [85] against attack from moisture by depositing on their surfaces thin passivating layers of iodides, sulfates, or sulfides.

A thermosetting epoxy coating on $YBa_2Cu_3O_7$ is reported [86] to inhibit its degradation from aqueous environments, provided that the coating is continuous and free from cracks and pin holes. A thin plastic coating, deposited using a solution of butadiene and styrene copolymer (SBSC) in CCl_4, is found [33,58] to be more effective than the epoxy in protecting the 123 and the 2212 superconductors against corrosion from moisture and water.

7. CONCLUSIONS

The $La_{1.8}Ba_{0.2}CuO_4$ HTS is unstable in the presence of H_2O, CO_2, and CO. The $YBa_2Cu_3O_{7-x}$ HTS is highly susceptible to attack from various chemicals and degrades even in the ambient atmosphere, particularly in high humidity. The rate of corrosion is rapid when it comes in contact with water. The degradation reactions of HTS are much slower, the lower the temperature and denser the material. It appears that the 123 HTS degraded by exposure to water or CO_2 could be nearly regenerated by heat treatment above 900 ^{o}C in oxygen followed by annealing or slow cooling in oxygen. 2212 HTS appears to be chemically more stable than the 123 HTS, except in strongly basic solutions. The Bi(Pb) Sr-Ca-Cu-O/Ag HTS microcomposites containing high silver content showed excellent resistance towards reaction with water.

8. RECOMMENDATIONS

Processing of $YBa_2Cu_3O_{7-x}$ HTS in purified oxygen, rather than in air, using high purity non-carbon containing starting materials is recommended. Exposure of this HTS to the ambient atmosphere should be avoided al all stages during processing and storage. For all practical applications, electronic devices made from these HTS should be protected with an impermeable coating of an appropriate material such as polymer, glass, or metal (silver, or gold) to prevent atmospheric degradation during use.

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13. ABSTRACT (Maximum 200 words)

A review of the available studies on the chemical stability of the high-temperature superconductors (HTS) in various environments has been made. The $La_{1.8}Ba_{0.2}CuO_4$ HTS is unstable in the presence of H_2O, CO_2, and CO. The $YBa_2Cu_3O_{7-x}$ superconductor is highly susceptible to degradation in different environments, especially water. The $La_{2-x}Ba_xCuO_4$ and Bi-Sr-Ca-Cu-O HTS are relatively less reactive than the $YBa_2Cu_3O_{7-x}$. Processing of $YBa_2Cu_3O_{7-x}$ HTS in purified oxygen, rather than in air, using high purity non-carbon containing starting materials is recommended. Exposure of this HTS to the ambient atmosphere should also be avoided at all stages during processing and storage. Devices and components made out of these oxide superconductors would have to be protected with an impermeable coating of a polymer, glass, or metal to avoid deterioration during use.

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