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Chemical etching technique for porous and fine-grain YBa2Cu307-x superconductors with or without silver addition

Guldem Guven
Lehigh University

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Chemical Etching Technique
For Porous and Fine-Grain
YBa2Cu3O7-x Super-
conductors With or Without
Silver Addition

DATE: May 31, 1992

CHEMICAL ETCHING TECHNIQUE

FOR POROUS AND FINE-GRAIN $YBa_2Cu_3O_{7-x}$

SUPERCONDUCTORS WITH OR WITHOUT SILVER ADDITION

by

Guldem Guven

A Thesis

Presented to the Graduate Committee

of Lehigh University

In candidacy for the degree of

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in

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Date

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Advisor in charge

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Chairman of Department

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I. ABSTRACT

In this study, a chemical etching technique of silver-doped and undoped YBa2Cu3O7-x superconductor was described. For this purpose, highly porous, (10% and 30% porosity) YBa2Cu3O7-x polycrystalline materials with grain size about 2 μm. were prepared. Some of these samples were doped with pure silver . The silver-doped and undoped samples were then chemically etched to determine the microstructural change. During the etching process, a number of chemical reagents such as hydrochloric , nitric, and sulphuric acids were used and their effects on microstructures of the samples were observed. To obtain clear etching figures of silver-doped and undoped YBa2Cu3O7-x superconducting materials, an optimum etching condition and procedure was determined. The porosity effect was also considered.

II. INTRODUCTION

The major discovery of Bednorz Muller's superconductivity in the La-Ba-Cu-O system [3] has led to the successive discoveries of high temperature superconductors with the transition temperatures above 90K [5] . A great deal of work focused on ceramic materials comprising Y-Ba-Cu-O compounds have been made, resulting in a rapid progress of the high temperature superconductors research on electrical properties, crystal structure and etc. [4].

The thermal etching process is one of the ways to show the microstructure of the Y-Ba-Cu-O superconductor. However, if the sample has a large number of porosities, new grains will be generated at the pore surface and the old grains will grow [5] , the microstructures change dramatically (Figure 1) . This is the reason why the conventional thermal etching technique can not be used.

The chemical etching technique has also been examined as another technique. A fine grain size structure has been shown with the convenient chemical etchant. The high porosity of the sample produces a larger area under the attack of the chemical etchant than the smoother area on a polished sample surface [4] .

The observation of such a fine microstructure with a grain size smaller than several microns cannot be done with an optical microscope. In this case of a sample with a grain size of 2 μ.m, a scanning electron microscope should be used for the observations. Thus in this study, a chemical etching technique with low accelaration voltage scanning electronmicroscopy was found to be appropriate.
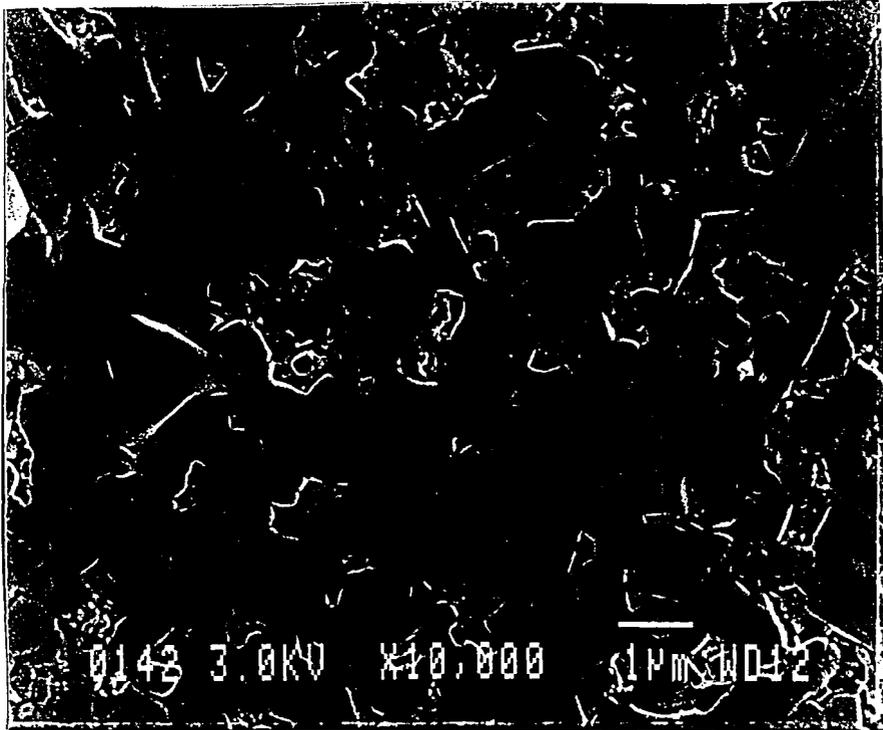
Figure 1   SEM micrograph of an YBa2Cu3O7-x sample of 73% density after thermal
etching at   850 °C for 2 hours.

III. LITERATURE SURVEY

a) CHEMICAL ETCHING

For many materials, the microstructure is revealed only by an appropriate etchant. In most cases, a polished specimen will not exhibit its microstructure because incident light is uniformly reflected. Producing of image contrast is required for the observation of microstructure [2] . There are many ways of obtaining contrast. These methods are; chemical and physical etching. Standard chemical etching solutions are most commonly used to produce 'etched' conditions for the structure examination. Etching is basically a controlled corrosion process resulting from electrolytic action between surface areas of different potential [1] . The chemical solutions used for etching have been developed primarily by trial and error with the knowledge of corrosion behavior of the material. Etching occurs by electrolytic action at structural variations on the sample surface. Electrolytic activity results from local physical or chemical heterogenities which cause some features anodic and others cathodic under specific etching conditions. Chemical etchants produce metallographic contrast either by crystal faceting (that is, grain etch at different rates because of variation in their crystallographic orientation) which produces steps at grain boundaries and reflectivity differences or by grain boundary etching, which produces grooves. Selective phase dissolution is more difficult to obtain, since it requires a preferential chemical attack. Selective etching can be obtained by roughening of the phase interest or by preferential staining of the phase.

Established chemical etchants have certain common features. Chemical etchants usually have three main components; a corrosive agent such as hydrochloric, sulfuric, phosphoric, and acetic acid, a modifier such as alcohol or glycerin that reduces ionization, and an oxidizer such as hydrogen peroxide, Fe^{3+}, or Cu^{2+}. In some etchants

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one component serves two of these functions, such as nitric acid in nital. Etching involves controlled dissolution. The oxidizer provides this control by absorbing electrons. Small changes in the oxidizing power of a reagent can change the dissolution rate. Since the dissolved oxygen in tap water will increase the dissolution rate, it is always best to use distilled water in preparing etchants.

With pure metals and single-phase alloys, a potential is produced between differently oriented grains, between grain boundaries and grain interiors, between impurity phases and the matrix, or at concentration gradients in the single-phase alloys. With two-phase or multiphased alloys, potential differences are also present between phases of different composition. These potential differences are used to produce controlled dissolution.

Microstructure is revealed by selective dissolution of the structure, starting at the surface and proceeding inward. Differences in the rate of attack reveal the structure. In two-phase alloys, the potential of one phase is higher than that of the other phase. During the etching, the more electropositive anodic phase is attacked while the electronegative cathodic phase is much less attacked. As the potential difference between the two phases increases, the etching time must be carefully controlled to avoid overetching.

The unetched cathodic phase will appear bright, especially if its size is large. The anodic phase is recessed below the original plane of polish and can appear to have a rough surface depending on the etchant and the alloy composition. Surface roughness will make the anodic constituent appear dark under bright illumination.

Etching of single-phase pure metals and alloys takes place without the aid of the large potential differences. The potential differences between the grain boundaries and grain interiors are small and exert less influence on etch response. Impurities that segregate to the grain boundaries can significantly change the etch response. In single-phase metals and alloys a particular etchant can either attack the grain boundary or preferentially dissolve differently oriented grains (faceting), which produce grain contrast etching.

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Many chemical etchants are mixtures of acids with a solvent such as water. During the etching, atoms on the anodic surface are transferred to the etching solution as cations. However, before these atoms are transferred to the solution, they are adsorbed on to the metal surface:

$$M_{lattice} \rightarrow M_{ad.}$$
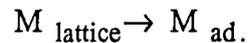
these atoms are mobile and are transferred to the etching solution as follows:

$$M_{ad.} \rightarrow M_{aq.}^{n+} + ne^{-}$$
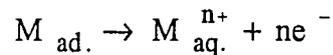
The water molecules become bound to the metal cation by ion dipole forces, and the metal cation is hydrated . Finally, the cation is removed from the surface into the solution after hydration is completed. The metal being etched does not always react with the etchant to produce hydration. Instead, complexly bounds ions or relatively insoluble metal compounds may be formed and precipitated onto the metal surface.

In general, the composition of chemical etchant is not critical. The success of an etchant can be effected by the order in which the chemicals are mixed, by changes due to aging, or by the purity of the chemicals. Most chemical etchants contain a solvent used to dissolve the etching agent. Chemical additions can influence ionization or decomposition of an active agent. In some cases, a concentrated acid or a mixture of two acids are used for etching . Each etchant is used to etch different metal, the etch components can have different roles with different metals.

b) HIGH Tc SUPERCONDUCTORS

Microstructure such as grain size, defect structure etc. has profound effects on the properties of materials. Given the extreme complexity in the crystal chemistry of the high Tc oxide superconductors, studies of microstructural phenomena are not only very interesting but also important to the understanding of many physical measurements in this new class of materials.

The perovskite superconductors have the highest critical temperatures of many materials studied at the present [3 , 4] . They may also have enormous critical magnetic fields . Since 1911,when Kamerlingh Onnes discovered superconductivity in mercury at 4.2K, the highest observed values of Tc gradually moved upward by the work of B.T. Matthias, J.K. Hulm, J.E. Kunzler, T.H. Geballe and others. In 1973, J.R. Gavaler observed that sputtered films of Nb3Ge began to superconducting at 22.3K [12] , and this was increased to 23.2K by L.R. Testardi et al. In 1986 , J.G. Bednorz and K.A. Muller observed that a lanthanum barium copper oxide began its superconducting transition as it was cooled below 35K [3]. C.W. Chu observed that YBa2Cu3O7-x has superconductivity with Tc a few degrees above 90K [3] .

Oxide superconductors can be divided into three classes. Class 0 materials are compounds such as LiTi2O4 [5] which has a transition temperature of 13.7K, and BaPb1-xBixO3 [6] which has a transition temperature of 13K. These materials do not have high values of Tc. The class1 materials are related to La-Ba-Cu-O. These materials have K2NiF4 crystal structure. Its transition temperature does not exceed 40K. The class 2 materials exhibit superconductivity above the liquid nitrogen temperature, in the range of 90K, and have the chemical formula MBa2Cu3O7-x, where the metal M is Y or any of the rare earth elements except Ce, Pr, or Tb [4 - 6] .

The class 1 superconductors possess layered perovskite structure. The distorted oxygen defect perovskite structure is a characteristic of the class 2 oxide superconductors .A common feature of both of these structures is a two-dimensional copper oxygen plane which is believed to be relevant to the conduction process. An important aspect of class 2 materials is the matter of oxygen vacancies. The oxygen vacancies of the top and bottom copper oxygen planes on opposite ends of the unit cell are believed to be organized in chains along the b axis rather than as planes parallel to the a-b plane.

The new superconductors have three fundamental properties: large Tc, short coherence length, and large spatial anisotropy. These properties open the way for many new applications.

c) STRUCTURE OF YBa2Cu3O7-x

YBa2Cu3O7-x has both planes and chains of Cu and O . A great deal of work has focused on the roles of these planes and chains in the yttrium compounds. It is known that the planes play the major role in generating superconductivity, while the chains act as electron reservoirs which can be filled or emptied either by changing the oxygen stoichiometry or by other types of doping. If the number of oxygen atoms per formula unit is reduced to 6.5 or 6.7, the yttrium compound's Tc falls to 55K or 60K [3] . There is a tendency for oxygen atom vacancies to occupy a single chain, and the YBa2Cu3O7-x compounds with 0<x<1 tend to have ordered arrays of completely oxygen depleted chains (Figure 2) . The Y compounds with approximately seven oxygen atoms per formula unit are orthorhombic, and almost always exhibit twinning. It was speculated

that the twin planes in these Y Ba2Cu3O7-x samples are a source of high temperature superconductivity. However, the Raman effect data on untwinned sample show the presence of superconductivity .

d) MECHANICAL BEHAVIOR OF HIGH TEMPERATURE SUPERCONDUCTORS

Adaptation of ceramic oxide superconductors to both large scale energy or micro-scale electronic applications will be contingent on the resolution of several technical issues. The development of bulk and thin film materials and material processes with practical critical properties equivalent to or exceeding NbTi but at higher currents and field strengths is very important . Bulk polycrystalline superconductor materials are either very brittle or friable. They generally have low strength.

Bulk YBa2Cu3O7-x can be sintered at high temperatures to increase density and strength, but the resultant microstructure may yield a reduced critical current density (Jc) value [9] . The low strength, low fracture-toughness and brittleness of the superconducting ceramic provides a challenge, i.e., how to improve the mechanical and fracture properties of this material without diluting the bulk superconducting properties. Hence it is of great interest to improve the mechanical properties of the superconducting ceramic by changing the standard processing conditions or by using metal fillers, fibers and polymers.

An investigating the pore distribution within the ceramic, Blendell et. al [10] have identified three kinds of pores: pores trapped inside grains, pores on two or more grain junctions, and larger pores due to poor packing. The pores on the boundary are small and are mostly due to grain junctions.

High temperature superconducting is highly anisotropic in nature and the anisotropy is noticed in thermal expansion coefficients, elastic moduli and current densities [11]. The thermal anisotropy produces a 1.2% volumetric strain and linear strains of 0.308%, 0.423% and 0.423% in the a, b and c crystallographic directions for a 220 °C temperature variation. Microscopically the material has to accomodate the high strain arising from the operating conditions. For a grain-oriented superconductor, the large thermal strains result in cracking both during processing and under the operating conditions.
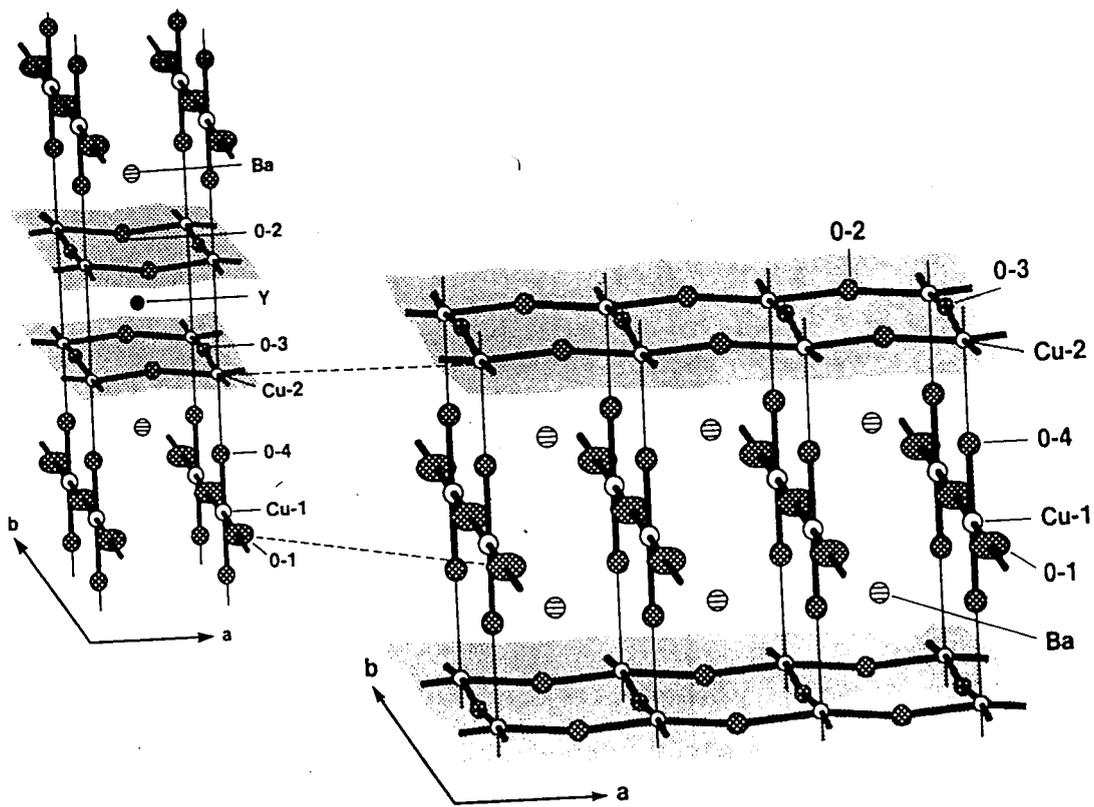
Figure 2 The structure of YBa2Cu3O7-x

IV. EXPERIMENTAL PROCEDURE

For the present experiment the commercial $YBa_2Cu_3O_{7-x}$ powders (super amic Y123 by supplied the Rhone Poulenc Inc.) were used. The compacts were sintered with or without silver (supplied by Johnson Matthey, with 99.9% purity). A number of samples with different densities and grain size were prepared [Table 1] .

Sintered and oxygen annealed samples were cut and mounted in epoxy. After grinding from 120 to 600 SiC papers, the samples were polished with diamond paste and 0.05 μ alumina.The polished samples were then etched by dipping and stirring into the etching solution at room temperature.

Nitric acid of 0.3% to 2% concentration, hydrochloric acid of 0.5% concentration, 2% Nital, and sulfuric acid of 0.5% concentration were used as etching solutions. They were prepared by mixing the concentrated acids with dionized water.

The etched samples were washed under the flowing tap water for 30 sec.. Then, it was washed with alcohol spraying and dried by stream of warm air. For microstructural observations a JSM-6300F electron microscope was used.

Table 1.   YBa2Cu3O7-x   samples with or without silver used for
etching tests

Ag %	Bulk Density (%)	Sample ID	Sintering	GS
0	72	YI04	S875A6H	0.5
0	89	YI21	S915X6H	--
25	91	YI06	S875A6H	0.9
25	93	YI24	S895X6H	1.0
0	--	YI23	S895X6H	--

S875A6H : sintered at 875 °C in air for 6 hours.

GS: grain size

V. RESULTS AND DISCUSSION

Chemical etching experiments have been carried out to exhibit fine-grain structures of $YBa_2Cu_3O_{7-x}$ containing silver.

Table 2. shows the result of etching for four types of samples for different solutions were used . In most cases, the etching rate increased with increasing porosity. Since pore surfaces would produce a larger area of reaction, the 0.5% HCl etchant was found to be good for etching the undoped $YBa_2Cu_3O_{7-x}$ material, but not good for the silver-doped one. This is because that HCl reacts with silver and the insoluble AgCl particles deposit on the surface of silver grains.

The 0.5% HNO_3 solution is good for silver-doped and undoped $YBa_2Cu_3O_{7-x}$ material. A convenient etching time is four seconds. In this case, the silver-doped sample yields some reaction products with HNO_3, but these particles can be removed by scrubbing the surface with enough pressure during washing with water. Figure 3 and 4 show the microstructures of the samples with 25 vol. % silver with and without scrubbing.

Although the 2% Nital gives a clean etched surface, strange patterns were generated during etching for 15 sec. It is then not good for etching the $YBa_2Cu_3O_{7-x}$ material. Also for the silver-doped sample silver chloride was detected by the EDX analysis, whereas it was not found in undoped sample after etching. Since no chlorine ion was present either in nitric acid or in the sample, it must have been introduced from one of the two possible sources. One was from the tap water which was used for washing. The other was from the epoxide mount which contained a small amount of chlorine. The

former was less likely because the time was not long enough to allow the considerable reaction during washing at room temperature. Since the chlorine was not detected from the same sample etched with the nitric acid, the alcohol in the nital may have played a role. It was suggested that the chlorine ions in the epoxide were dissolved in the nital during etching and reacted with silver to produce silver chloride. The H_2SO_4 solution gave a surface coated with reaction products. Thus, this is not a good etchant for the doped and undoped $YBa_2Cu_3O_7-x$ material.

An etching technique is important as well as the selection of etching solution to obtain well etched surfaces. When the sample was dipped into the etching solution, it was necessary to stir the sample to prevent deposition of reaction products on the sample surface. Removing the residual etchant from the surface was also important. For this purpose, rinsing with alcohol or water was tried. It is known that, $YBa_2Cu_3O_7-x$
is very sensitive to water. But, at room temperature it is not possible to accelerate the reaction between the $YBa_2Cu_3O_7-x$ and water. Also washing with alcohol only would give small crystallites of a rectangular shape. These crystallites were water soluble and could be removed with water. Therefore water is a convenient agent for washing after etching. Alcohol can be used after water washing. It gives a final clean microstructure. But, clean and pure (>95%) alcohol must be used for the final washing. The sample had to be dried quickly with a stream of dry air. Otherwise, some water-droplet marks would be left on the surface.

During etching, a fresh etchant should be used for every sample to prevent the deposition of dissolved ions. It was determined that etching the sample with a concentrated acid for a short time will give a cleaner surface than a longer time etching with a dilute acid. Here the HNO_3 solution with 0.3 % concentration gives the best etched surface. The optimum time is 4 sec. Under these conditions, a slightly etched

surface can be observed under the electron beam with a low acceleration voltage (1-5kV) . The grain boundary contrast of YBa2Cu3O7-x sample with 30% and 10% porosity and fine grain size can be achieved by this technique (Figure 5 , 6) .

The recommended procedure for etching is established as follows : Dipping and stirring in 0.3% HNO3 for 4 sec.,scrubbing with cotton during washing in flowing water for 30 sec., final cleaning with alcohol, drying quickly with a stream of dry air. The observation of microstructures using scanning electron microscope was done under 3 kV acceleration voltage, 10 mm. working distance and 5000 - 10000 times magnification.

Table 2. Results of etching experiments using various etchants for
YBa2Cu3O7-x samples with and without 25% vol. Ag

			0% Ag		25% Ag	
ETCHING CONDITION			YI04	YI21	YI06	YI24
NA	0.3%	4 sec.	good	good	good	good
NA	0.3%	11sec.	over	--	over	over
NT	2.0%	4 sec.	bad	bad	bad	bad
NT	2.0%	11sec.	bad	--	bad	bad
HC	0.5%	4 sec.	over	good	orange	orange
HC	0.5%	1 sec.	over	--	orange	pink
HS	0.5%	3 sec.	bad	bad	bad	yellow

NA : nitric acid   HC : hydrochloric acid

HS : hydrosulfuric acid   NT : nital

orange, pink and yellow are of silver color
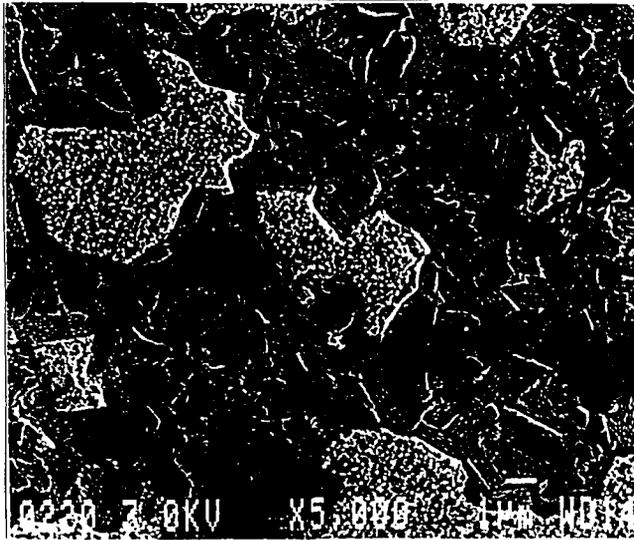
over : over-etched

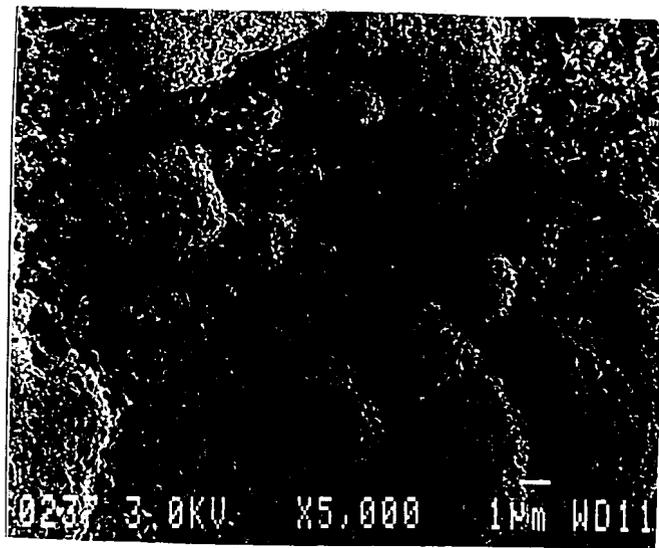Figure 3. An YBa2Cu3O7-x - 25% Ag sample etched with HNO3 and scrubbed with water.

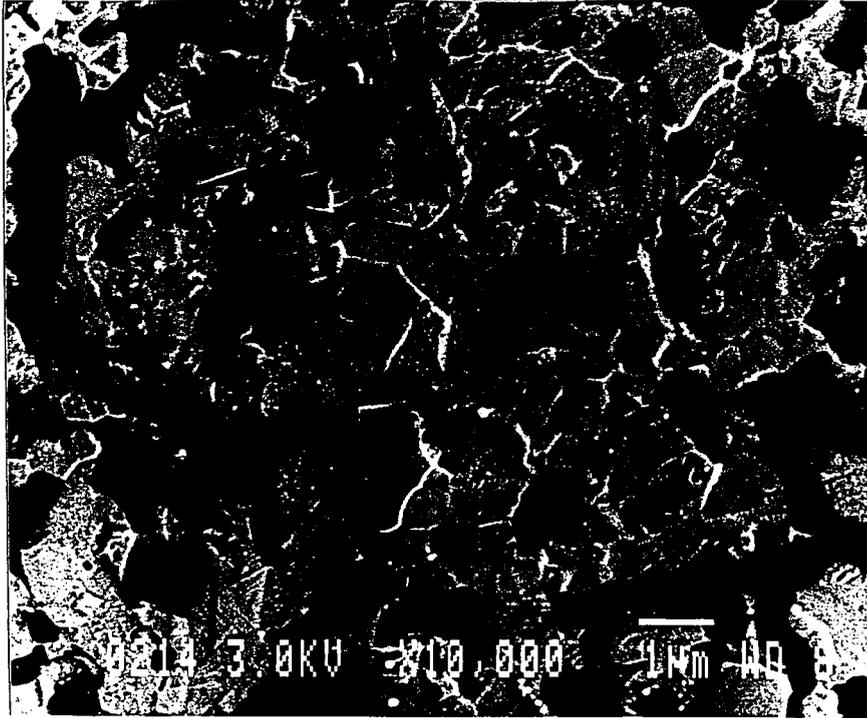Figure 4 . YBa2Cu3O7-x - 25 % Ag sample etched with HNO3 and water washing
without scrubbing.

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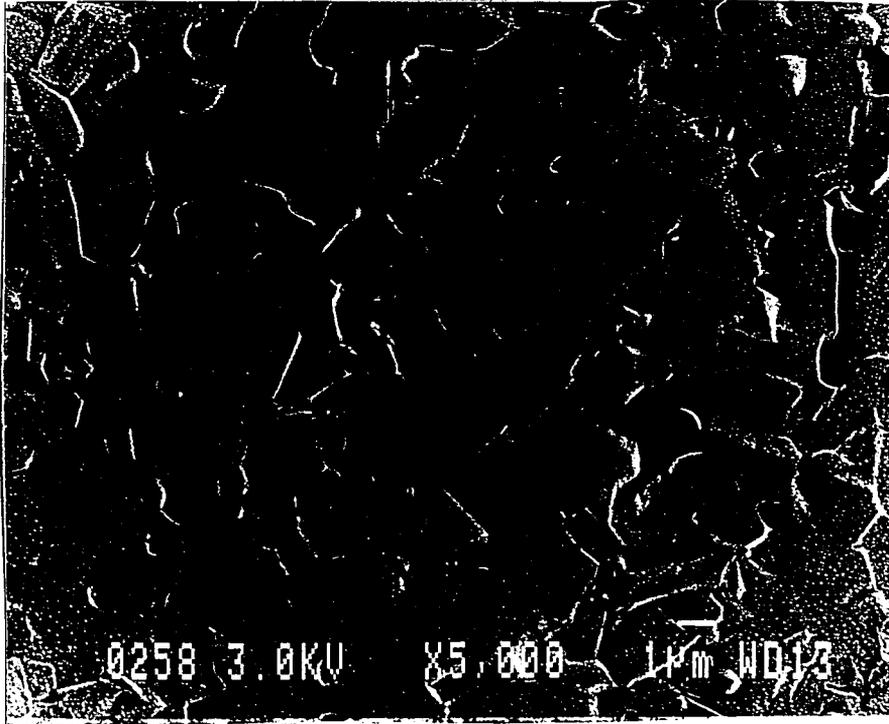Figure 5. An YBa2Cu3O7-x sample of 73% density etched with HNO3.

Figure 6. An YBa2Cu3O7-x sample of 89% density etched with HNO3.

VI. CONCLUSIONS

In this study, silver doped and undoped YBa2Cu3O7-x material with high porosity and fine grain size was studied. Etching condition and procedure were determined. From the experiments, 0.3% HNO3 solution was found to be convenient etchant to see the fine grain size. Etching time was determined as 4 sec.. HCl was also found to be good for etching of undoped YBa2Cu3O7-x material. Instead of optical microscope, scanning electron microscope was found to be appropriate for the observations.

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[12] Ginsberg, D. M. , "Physical Properties of High Tc Superconductors I ", 1st ed. , World Scientific Publishing   Co. ,Teaneck, 1989

VIII. VITA

Guldem Guven was born on February 24, 1966 in Denizli, Turkey. Her parents Nurettin and Birsen Utkan raised her in many cities of Turkey, mostly western Turkey. In 1983, she graduated from Ankara Cumhuriyet High School. From fall 1983 to spring 1989 she attended Middle East Technical University, in Ankara, Turkey and graduated with a B.S. in Chemical Engineering in July 1989. After she graduated, she won a scholarship from Turkish Ministry of Education and left her country on March 12, 1990 for a M.S. in Materials Science and Engineering in the U.S.

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