

# ISTRAŽIVANJE SINTEZE VISOKOTEMPERATURNE SUPRAVODLJIVE Y-BA-Cu-O KERAMIKE POSREDSTVOM KUGLIČNOG MLJEVENJA VISOKE ENERGIJE

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**KLJUČNE RIJEČI:** visokotemperaturna supravodljivost, Y-Ba-Cu-O keramika, supraprevodljiva keramika, kuglično mljevenje, tehnološki procesi, prijelaz u amorfnu stanje, istraživanje materijala, eksperimentalni rezultati

**SAŽETAK:** Smjesa prahova  $Y_2O_3$ - $BaCO_3$ - $CuO$ , u omjerima mase predodređenim za atomarni razmjer metalnih elemenata Y:Ba:Cu=1:2:3, podvrgnuta je mljevenju u kugličnome mlinu visoke energije. Na iznenađenje, čak ni jako produljeno mljevenje (do 202 sata) uz centrifugalnu akceleraciju kuglica od oko 10 g ( $g=9,81 \text{ ms}^{-2}$ ) ne uspijeva dokraja razporiti kristaliničnost bakrenog oksida, dok itrijev oksid i barijev karbonat prelaze u amorfnu stanje nakon 60-100 sati mljevenja. U radu se iznose putokazi mogućim objašnjenjima ove selektivne prijetvorbe u staklastu fazu.

## AN INVESTIGATION OF HIGH-ENERGY BALL-MILL PROCESSING OF A Y-Ba-Cu-O HIGH $T_c$ SUPERCONDUCTING CERAMIC SYSTEM

**KEY WORDS:** High temperature superconductivity, Y-Ba-Cu-O ceramics, superconducting ceramics, ball milling, technological processes, amorphisation, materials research, experimental results

**ABSTRACT:** A  $Y_2O_3$ - $BaCO_3$ - $CuO$  powder mixture with a mass ratio adjusted to fulfill Y:Ba:Cu = 1:2:3 stoichiometry was treated by means of the high-energy ball-mill equipment. It is slightly surprising that even after an enormously prolonged milling (up to 202 hours) and with a 10 g centrifugal acceleration of the milling balls the CuO component preserves its crystallinity, whereas yttria and barium carbonate undergo almost complete amorphization already after 60 to 100 hours of milling. The paper gives some hints about a possible explanation of the observed selective glassy transition.

### INTRODUCTION

Despite its quite recent discovery, it has become already a matter of common engineering knowledge that a key condition for large-scale application of cuprate based high  $T_c$  Y-Ba-Cu-O-type superconducting ceramics is a concentration of efforts on studying the possibility of a significant improvement in this type ceramics of bulk transport current density  $J_c$ . This, as well as other relevant critical parameters, are largely affected by various structural defects existing in synthesized materials as a consequence of a rather complex processing, usually consisting of both advanced powder-ceramic and conventional-post-synthesis heat treatments, as well as of promising newly-developed preparation procedures. The low values of the transport current density and the sensitivity of  $J_c$  to the magnetic field have been attributed to a number of extrinsic and intrinsic factors, but essentially to those which create inter- and intra-granular weak junctions. Naturally, these are caused primarily by various types of structural discontinuities that arise during processing, the most crucial of which are microcracks<sup>1</sup>. These also attack in a similar way mechanical properties, so that much of the undesirable mechanical behaviour of Y-Ba-Cu-O superconducting ceramics is not intrinsic but rather dominated by the presence of microcracks. For instance due to the adverse effect of micro-

cracks which have a very low aspect (width to length) ratio, the theoretical static bulk modulus of  $YBa_2Cu_3O_{7-x}$  mixed oxide becomes lower at least by a factor of five<sup>2</sup>. The critical transport current density decrease is even more pronounced, reaching several orders of magnitude. The actual source of the elongate microcracks population is the huge anisotropy of the thermal contraction which takes place during the martensitic transformation<sup>3</sup> of the high-temperature, pseudo-perovskite tetragonal (T)  $YBa_2Cu_3O_{6.4-6.5}$  lattice into the low-temperature orthorhombic (O)  $YBa_2Cu_3O_{6.8-7.0}$  variant at about 850 K<sup>4,5</sup>. From the difference in oxygen content of T and O phases it is evident that transformation progresses along with oxygenation. The tetragonal phase takes up oxygen from the ambient atmosphere as the material cools, due to the preferential occupancy of oxygen sites in the direction of the b-axis of the orthorhombic allotrope, this leading to the crack-causing misfit between the thermal expansion coefficients along the c- and the b-axes by a factor of four. The oxygen uptake is claimed<sup>6</sup> to be substantially rapid, and influenced by pressure and temperature, as well as by porosity, grain-size and compositional and phase (in) homogeneity.

Numerous technological procedures have been developed for overcoming the crack-forming tendency. There is some sense in the idea to pre-oxygenize the tetrago-

nal phase by means of prolonged heating at high temperatures (e.g. about 1000 K), in order to ensure an overall compositional homogeneity as a prerequisite for a smooth domino-like<sup>7</sup> succession of small atomic moves characteristic for the martensitic lattice change. Another favourable prospect for eliminating weak links is a combination of melting and subsequent directional solidification<sup>8,9</sup> to obtain textured, coarse-grained crack-formation suppressing structures. By applying this method the transport current density has been pushed up to above  $10^4$  A/cm<sup>2</sup> at 77 K and in zero magnetic field as compared to several hundred A/cm<sup>2</sup> units for samples without texture. Even more impressive results have been announced quite recently by Yamamoto et al.<sup>10,11</sup>. Using the rapid quenching technique followed by directional annealing treatment, the authors claimed for  $J_c$  the sensational value of  $4.3 \cdot 10^4$  A/cm<sup>2</sup> as measured at 77 K and in magnetic field of 1.06 T.

It has been recognized for a long time that in creating materials with predetermined properties the powder-metallurgy route offers considerable advantages in comparison to other techniques. Instead of conventional procedures of post-processing and tailoring the materials' properties by means of cold and hot working or by various surface treatments, this method makes possible direct access to the very origin of consolidated products by influencing their characteristics in their embryonal powder state. As the initial step of the consolidation process, ball-milling was adopted in powder metallurgy a long time ago and was recognized as a uniquely efficient method for the optimization of powder properties by means of comminution and uttermost homogenization of the powder mass. A variant of high-energy ball-milling was first applied by Benjamin and Voilin<sup>12</sup> as early as in 1929 when they were preparing a powdered precursor for an oxide strengthened nickel-base alloy. Ermakov et al.<sup>13</sup> and Koch et al.<sup>14</sup> revived this technique a decade ago with the idea to start producing amorphous powders from elemental metal-powder mixtures (mechanical alloying - MA), or from compound powders (mechanical grinding - MG). A series of interesting research projects based on MA/MG processing have been carried out since then, including the preparation of nanocrystalline powders with their fabulous statistical atomic structure<sup>15</sup>. Quite recently, the palette of various alloying, comminuting and amorphizing effects resulting from the MA/MG method has been enriched by an additional one: selective oxydation, as observed in MA/MG treatment of powder mixtures of the Ga-Sb binary<sup>16,17</sup>.

With respect to the application of the MA/MG procedure for the preparation of Y-Ba-Cu-O superconducting ceramics, one should mention the pioneer work of several authors<sup>18,19</sup> who suggested a special method for circumventing the inherent ceramic brittleness interfering by production of Y-Ba-Cu-O wires and other shaped materials. In short, one starts with the synthesis of ductile metallic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> precursor by applying the high-energy ball milling to the respective elemental metal powder mixture. The obtained product is easily swaged and

wound to an assembling-ready shape. The oxidation of such an end-form at about 1170 K is just an additional step in production with no adverse mechanical effects. Batalla and Zwarts<sup>19</sup> believe the high-energy ball milling of elemental powders to offer a viable route for the production of superconducting ceramics for engineering purposes which would result in a final product consisting of single-phased material. Though actually promising from the wire-technology point of view, this rather optimistic claim fails to answer the question of cracking on cooling, thus leaving the crucial problem of low  $J_c$  value widely open. Nevertheless, the respective drawback should not encourage to complete abandonment of the underlying MA/MG technique. Leaving aside the wire-technological aspect, the use of high-energy ball-milling may well be recommended from the standpoint of the grain size related crack-generation intensity. The critical grain-size value for the suppression of microcracking in Y-Ba-Cu-O ceramics has been calculated, according to various models, to be 0.5  $\mu\text{m}$ <sup>20</sup>, 1.0<sup>21</sup>, or 3.4  $\mu\text{m}$ <sup>22</sup>, whereas experimental observations<sup>4</sup> have been focused on a range between 1 and 2  $\mu\text{m}$ . According to Chu and Dunn<sup>6</sup>, a small grain-size of about 1  $\mu\text{m}$  or less is necessary to prevent microcracking induced by the reoxygation due to the tetragonal to orthorhombic transition. On the other side, fine-grained materials themselves are desirable because of their mechanical properties. Moreover, in accordance with the basic powder-metallurgic experience, well dispersed powders readily sinter to higher densities and at comparatively low temperatures. For example, one-micron grained phase-pure structure of a nearly amorphous spray-dried nitrate powder mixture precursor was sintered to relatively high-density YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> ceramics at a temperature as low as 1120 K<sup>4</sup>. Unfortunately, it is true that the measured critical current density of 350 A/cm<sup>2</sup> of this sample was a rather low value. This is, however, to be ascribed to an early closure of interconnected pores in a well densified structure which hinders the access of oxygen to the interior of the sample. This results in a poor oxygenation which seriously affects the transport current property, as convincingly argued elsewhere<sup>8</sup>. Hence, this apparent weak side of fine-grained samples may be generally disregarded as a marginal phenomenon, or, preferably, may be even exploited as a prospective means for lowering the sintering temperature by modifying the sintering cycle in order to ensure a more complete oxygation.

In any case, direct mechanical alloying of precursor oxide or other compound powder mixtures intended to obtain YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> ceramics seems to offer an advantageous alternative in comparison to indirect route issuing from pure metallic precursors, from the view both of energy consumption and the transport properties of the prepared products. It is precisely the aim of this paper to report on the results of experiments which were designed to introduce the application of high-energy ball milling as a preparation procedure for the fabrication of high quality Y-Ba-Cu-O high  $T_c$  superconducting bulk ceramics.

## EXPERIMENTAL

In our experiment we used a 10 g ( $g=9.81 \text{ ms}^{-2}$ ) centrifugal acceleration ball-mill machine with an agate bowl having a volume of about  $110 \text{ cm}^3$  and a rather intricate internal geometry (Fig. 1). Initially designed for use with a single 25 mm diameter agate ball, the bowl was supplied with a previously optimized<sup>23</sup> milling body consisting of twelve hardmetal balls 10-16 mm in diameter.

As the starting material we chose a standard 99.99 % pure oxide-carbonate powder mixture of a weight ratio  $\text{Y}_2\text{O}_3:\text{BaCO}_3:\text{CuO} = 1513:5289:3198$ , as needed to satisfy the  $\text{Y}:\text{Ba}:\text{Cu}=1:2:3$  elemental stoichiometry. A total charge mass of 4 grams (charge to balls weight ratio 1:40) was milled in air for a total of 202 hours. At scheduled time intervals (5 mins, 20 mins, 30 mins, 1 hr, 2 hrs, 4 hrs, 8 hrs, 16 hrs, 24 hrs, 32 hrs, 40 hrs, 60 hrs, 100 hrs, 120 hrs, 132 hrs, 148 hrs, 160 hrs, 175 hrs, and 202 hrs) representative small powder samples were extracted from the bowl in order to be examined. X-ray diffraction powder photographs of the samples were taken using a 114.6 mm diameter Siemens-type Debye-Scherrer camera and Ni-filtered Cu radiation. The size and shape of the powder particles, which before examination had been coated with gold using the cathode sputtering method, were observed by means of a 25 kV Cambridge Stereo Scan 600-type scanning electron microscope.

## RESULTS

In the course of milling there occurred spectacular colour changes. The first, from the pigeon-gray of the original mortarized oxide-carbonate mixture to a matte-black, took place between 20 and 30 mins of milling. The changes took place throughout the milled mass, regardless of the position of the powder in the bowl: on the wall, the cover, the balls, everywhere, indicating a high degree of homogeneity of the process. The second change to lilac-brown occurred between 1 and 2 hours of milling, and again was overall and complete. As neither of these changes were accompanied by observable x-ray diffraction pattern modifications, the underlying reactions should be regarded as essentially superficial. No abrupt colour change took place subsequently, except for continuing disappearance of the lilac shade in favour of a yellowish one.

The x-ray diffraction pattern changes are shown in Fig. 2. Fig. 2(a) shows the diffraction lines pattern of the initial powder mixture after mere 5 mins of homogenizing milling. Irrespective of some line intensity fading off, essentially the same pattern keeps maintained up to 32 hrs of milling (Fig. 2(b)). The first substantial change was observed after 60 hrs of milling. The respective powder photograph is represented in Fig. 2(c). Beside an emerging amorphous halo at low angles, from this figure one can observe still two strong, broadened CuO reflexions,

and a feeble, so far unidentified line at  $\approx 26.75^\circ$  indicating a d-spacing of about  $3.375^\circ\text{A}$ . This indicates an amorphization of the yttria and the barium-base compound, whether it was the starting carbonate or the nascent barium oxide deriving from its decomposition. In fact, we expected amorphous oxide to appear, if we started from our experience with the Ga-Sb system, according to which the energy input in ball-milling becomes equivalent to oxidizing temperature effects that occur at a minimum of  $840 \text{ K}$ <sup>16,17</sup>. On further milling to 100 hrs the pattern does not change substantially, except for the evident growing of intensity of the halo and unidentified line mentioned above Fig. 2 (d). Prolonged milling to 202 hrs by itself adds nothing dramatic. However, the continuous fading off of the unidentified line, together with a hardly observable further broadening of CuO reflexions, increases the prospect of a possible complete amorphization of the mixture after still longer milling times.

Scanning electron microscopy observation, unfortunately, did not reveal a great deal about the micromorphologic development. There is an evident difference between the apparent crystallinity of yttria as compared to barium carbonate and cuprous oxide, of which that of the latter two differs only slightly (Figs. 3(a), (b), (c)). The microphotographs taken after 2, 40 and 175 hrs of milling show a significant reduction of particle size (Figs. 3(d), (e), (f)), though there is little to see of the agglomerate substructure. Probably because of the inevitability of the sputtering operation these Figs, due to the gold coating, might not show the actual microstructure of the powder, while the use of higher magnifications is pointless because of the adverse effect they would exert on the intra-particle resolution. Also, from the micrographs (Figs. 3 (g), (h), (j)), it is evident that milling also has great local agglomerating countereffects, though these are atypical and show a tendency to lose intensity with continuing milling, to vanish practically after 60 hrs of milling.

## DISCUSSION AND CONCLUSIONS

Though spoiled by the low resolution power of the electron micrographs, presumably due to the sample preparation method applied, a positive comminution effect of the ball-milling as observed on the secondary particle size level (agglomerates) can not be seriously disputed. Former investigations of the metallic systems Al-Ni and Ni-Ti<sup>23</sup> have unambiguously shown that the primary particle size after 40 hrs of milling (for Ni-Al), or 122 hrs of milling (for Ni-Ti), is significantly reduced and enters the submicron-size region, despite the largely retarded agglomerate-size reduction. There is no provable reason to doubt that the respective effect takes place in the present case of brittle ceramics as well. Hence, as regards the surface free energy, a highly activated powder mixture, ready to sinter to high densities at relatively low temperatures within a comparatively short

time, may actually be expected to result from our experiment.

The activity of the obtained powder is not limited to the mere surface energy (i.e. particle size) effect, but also manifests itself through the radical ordering decline of its compound components structure, that is through the amorphization of yttria and barium carbonate, as well as through the strongly perturbed crystallinity of CuO. As regards BaCO<sub>3</sub>, the observation of high-temperature oxydation effects in the Ga-Sb system<sup>16,17</sup> makes the concurrent decomposition of this compound into amorphous BaO during milling quite probable. So, presumably, we obtained a doubly-activated tripple-oxide mixture ready to sinter at low energy cost and without substantial cracking which might allow a high J<sub>c</sub> for high T<sub>c</sub> superconductive 1-2-3 bulk ceramics. These are the most provoking facts emerging from the results of the present work. Indeed, we are eagerly looking forward to the results of isothermal or directional sintering experiments which are underway. Also in progress are several more sophisticated characterization procedures aimed at obtaining more microstructural data regarding the milled powder.

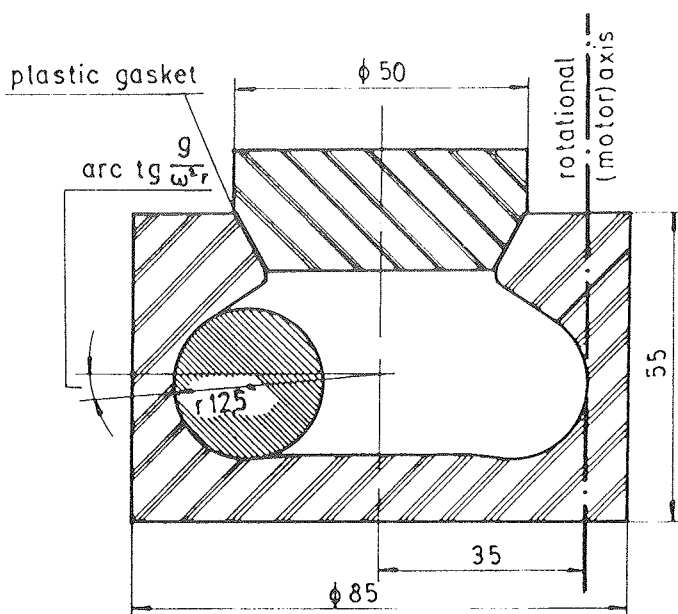


Fig. 1. Sketch of the container design

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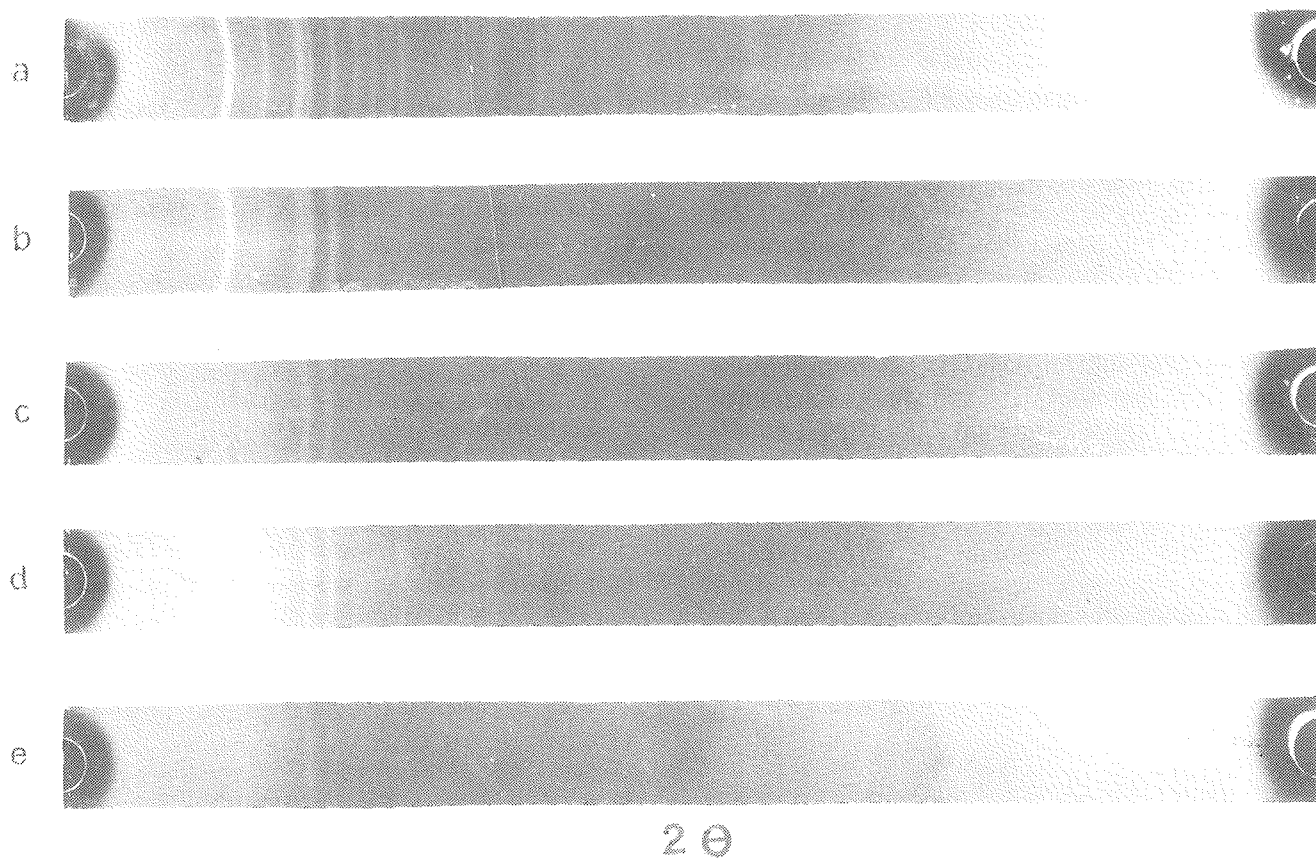
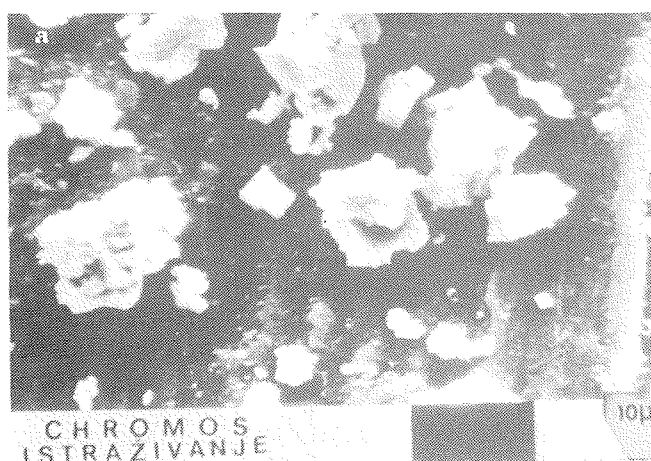
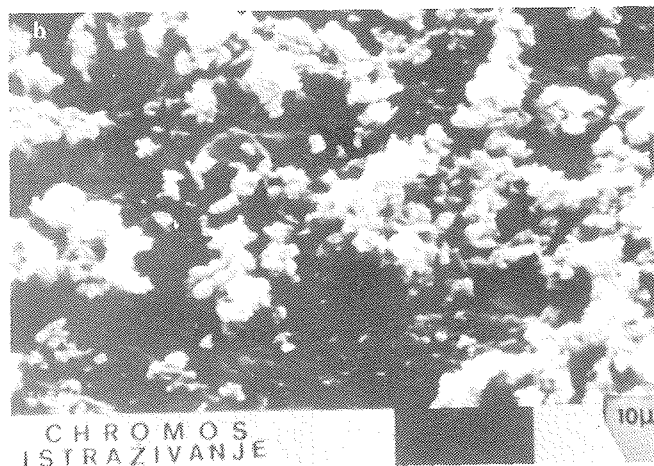


Fig. 2. X-ray powder diffraction photographs of samples milled: (a) 5 mins, (b) 32 hrs, (c) 60 hrs, (d) 100 hrs and (e) 175 hrs.



a)



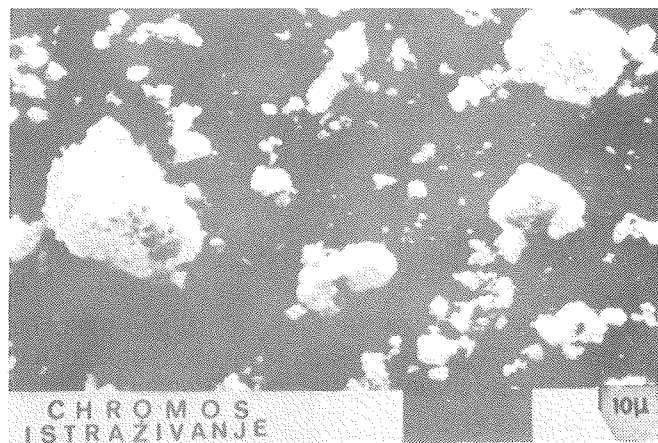
b)

Fig. 3. Scanning-electron micrographs of the powdered samples: (a), (b) and (c)- starting  $Y_2O_3$ ,  $BaCO_3$  and  $CuO$  component powders, respectively; samples extracted after 2 (d), 40 (e), 175 (f), 0.5 (g), 8 (h) and 40 (j) hours of milling.

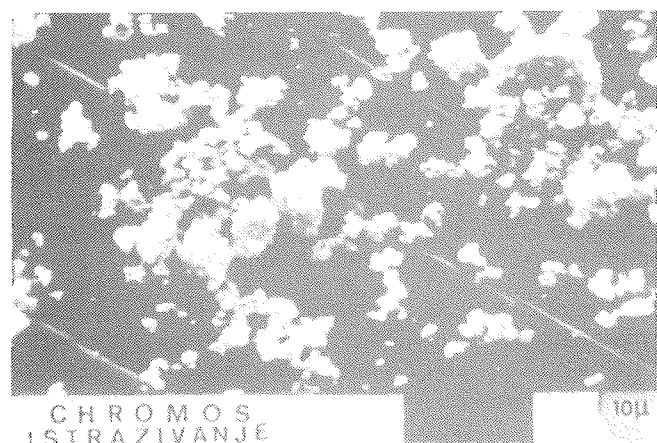




c)



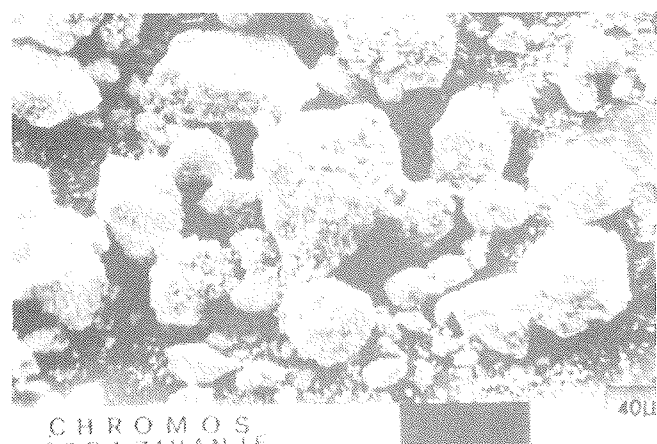
d)



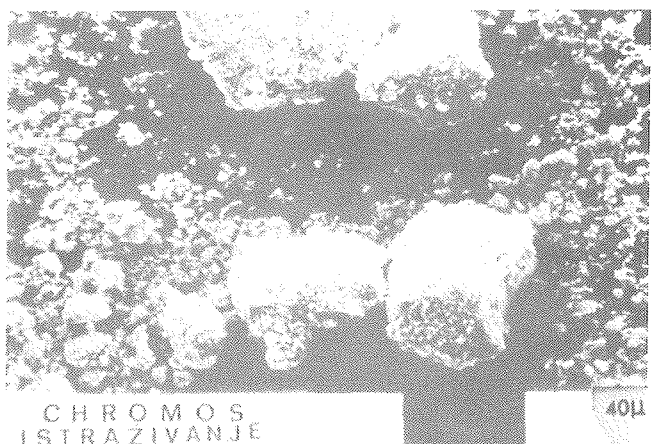
e)



f)



g)



h)



j)

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