# CHEMICAL BASED SYNTHESIS AND TEM CHARACTERIZATION OF NANOSCALE OXIDES PARTICLES.

Daniela Macedo (1), Gullermo Solórzano (1), Eduardo Brocchi (1). John Vander Sande (2). (1) Department of Material Science and Metallurgy - PUC-Rio de Janeiro, r. Marquês de São Vicente, 225, P.O. Box 38008 - Gávea, Rio de Janeiro, RJ, CEP 22453-900, Brazil. (2) Department of Materials,Science and Engineering, MIT, Cambridge, USA. Email: danielantc@bol.com.br

It has been clear the increasing importance of nanostructured materials in the present scientific and technological development. Due to their unique properties these materials can be used, whenever properly processed, in a wide spectrum number of applications. It is also well established that properties of materials can be severely altered by allowing them to reach a nano-strutured condition. In view of that, extensive studies have been carried out on a variety of materials such as alloys and different types of composites [1-4].

Recently, our group at the Department of Material Science and Metallurgy of Rio de Janeiro Catholic University has developed an alternative chemical-based synthesizing route to obtain nano-structured materials starting from nitrates. This approach can be applied to the production of oxides, metals or composites. In the last case, with a high level of homogeneity.

In the context of the investigation reported here, most of the experiments were carried out with samples of about 1g places in a 3cm diameter horizontal tube furnace at isothermic conditions in the range of 463 – 773 K using a established hydrogen flow of 100 $cm^3$. During the heating up of the furnace or for experiments with diluted hydrogen, it has been used argon as controlling atmosphere. The obtained material was then prepared to characterization by means of X-ray diffraction (XRD), scanning lecture microscopy (SEM) and transmission electron microscopy (TEM). The alloy before microstructural characterization by SEM was cold pressed and sintered at 1348 K. In the case of the composite, it was briquetted, sintered at the same temperature and annealed at 1173 K. Detailed TEM real-space observations were carried out with both the synthesized powder and consolidated materials, the instrument, a Jeol 2010, being operated at 200kV under diffraction contrast and phase modes. In addition, reciprocal space information was documented as diffraction patterns accompanying the images.

The oxides powder was analyzed by X-ray diffraction and the result is illustrated in Fig. 1. The average crystallite size was estimated from those diffraction patterns using the Rietveld method. The results indicated that the NiO crystallites were in the range of 20 nm. In order to measure more precisely this oxide particles size, TEM was extensively used. In Fig. 2, it is shown a bright-/dark-field pair of micrographs obtained under diffraction contrast mode and the corresponding selected area diffraction pattern (SADP) Fig 2c. Here, it is possible to directly measure the size distribution of particles of average 20nm, even smaller as 5 nm. These particles constitute single crystals and are defect-free as shown in Fig.3, corresponding to a high resolution TEM micrograph, obtained under phase contrast mode. Interesting to note, in this as-documented (no-processed) images of this small particles is their shape, either spherical or faceted.

The same procedure was applied for the CuO and co-formed oxides (CuO-NiO). The result for the CuO particles is shown in Fig. 4, also a bright-/dark-field pair and its SADP. It is observed that this synthesis temperature has yielded a larger particles size, which incorporated twin interfaces, better resolved in the dark-field image of Fig. 4b where the result of the shear transformation defines sharper interfaces. The result for the CuO-NiO (50 wt.%) system is shown in Fig.5. It can be seen that both oxides retained their identity as evident from the sharp separated peaks for CuO and NiO. The same trend was observed for the CuO- $Al_2O_3$ system. The particle size of the crystallites was identified as being in the range between 50 and 100 nm. Besides this, mixed oxide particles being significally larger when compared with the NiO particles, detailed TEM observations have shown that individual particles incorporate defects, as seen in the micrograph shown in the Fig.5, This feature is consistent with the even larger particle size of pure CuO oxide, where the observed average is about 200 nm (for the adopted synthesis procedure). Current studies are focusing in controlling their particles size and in identifying their degree of crystallinity by means of electron diffraction.

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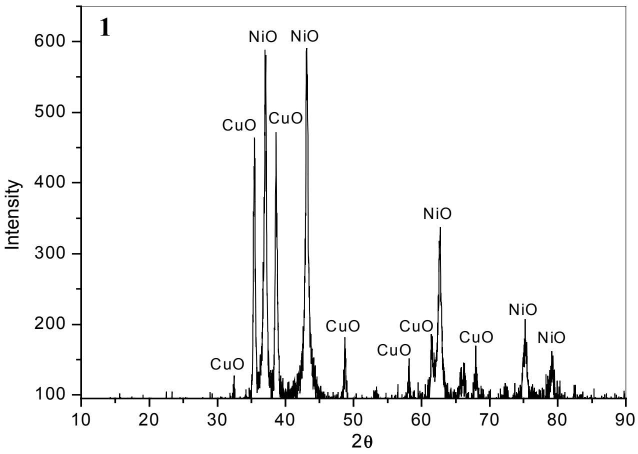
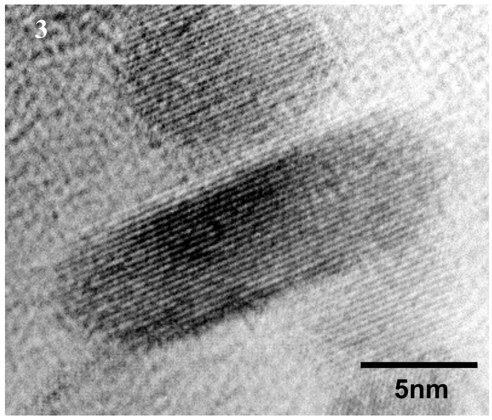
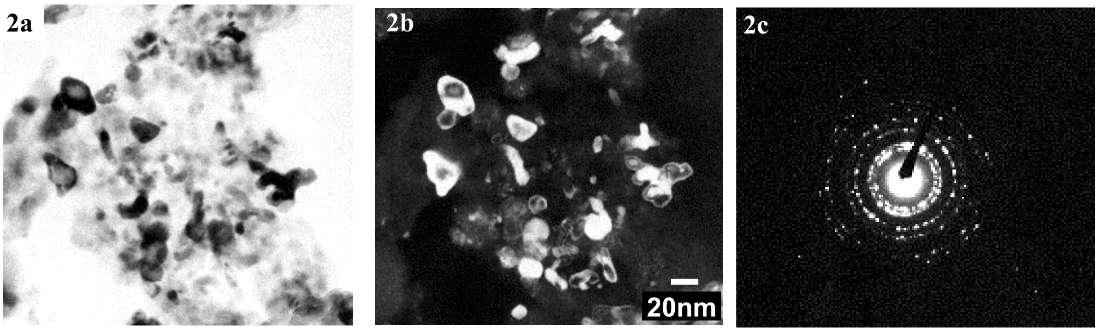
**References**

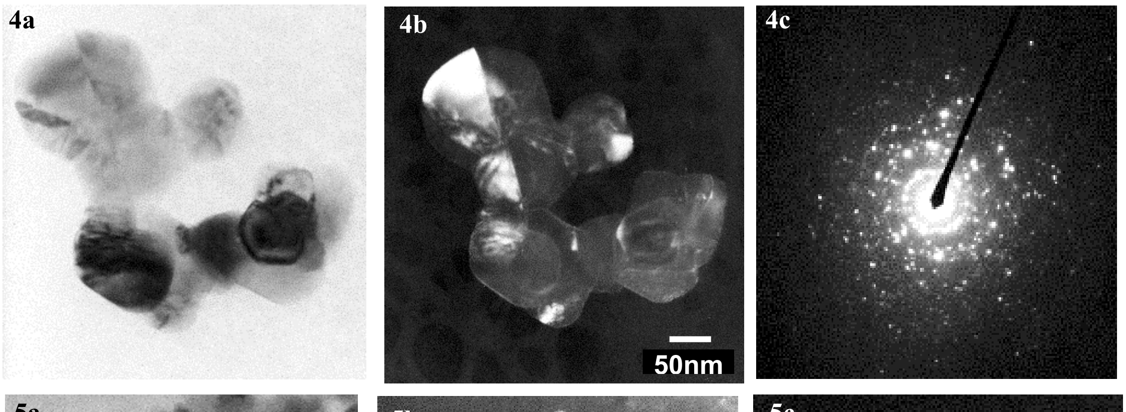
[1] P. Yin, D.L. Chung, J. Mater. Sci. (1997) 32, 2873.
[2] E. Rodeghiero, O. Tse, J. Chisaki, E. Giannelis, Mater. Sci. Eng. A (1995) 195, 151.
[3] T. Sekino, T. Nakajma, S. Veda, K. Niihara, J. Am. Ceram. Soc. (1997) 80, 1139.

[4] M. Lieberthal, W. Kaplan, Mater. Sci. Eng. A (2001) 302, 83.



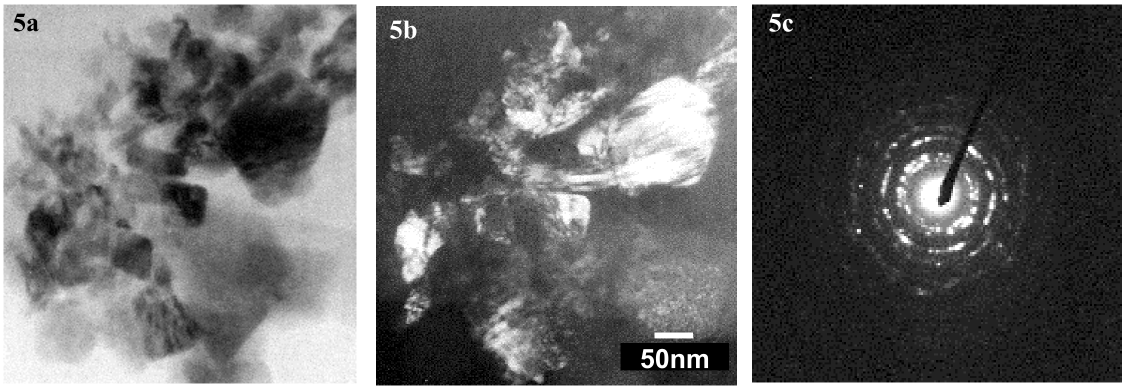




**Figure 1 -** XRD diffractogram of Ni-Cu co-formed oxides
**Figure 2 -** High resolution TEM images of individual defect-free NiO particles.
**Figure 3 -** A bright-field (a), centered dark-field (b) images and diffraction pattern (c) of NiO nano-particles.
**Figure 4 -** A bright-field (a), centered dark-field (b) images and diffraction pattern (c) of CuO nano-particles
**Figure 5 -** A bright-field (a), centered dark-field (b) images and diffraction pattern (c) of NiO-CuO co-formed nano-particles