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Synthesis of copper/chromium oxide composites by a chemical processing method

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Abstract The aim of this paper is to synthesize a copper/chromium oxide composite material. The use of a chemical processing method like the Pechini method is the best approach to control the chemistry and the microstructure. Nevertheless, the standard Pechini method has to be modified to obtain this specific type of composite. In this work, we have adapted two steps. Firstly we have eliminated the step involving ethylene glycol and secondly a reduction step has been added at the end. The new method is now capable of obtaining a Cu/Cr_2O_3 composite with specific stoichiometric ratios and a grain size ranging from 0.1 to 1 μm. We have used chemical and microstructural analyses to validate this work.

Introduction

Cu/Al_2O_3 composite materials are used for their excellent room and high temperature strengths and high conductivity. These composites are generally made by an internal oxidation method [1, 2] but the main disadvantage of this process is that it is difficult to obtain a complete oxidation of Al. Incomplete oxidation leaves behind pure Al that in turn decreases the electrical conductivity of the composite. In order to solve this problem, Liang et al. [3] used Cr instead of Al to prepare a Cu/Cr_2O_3 composite by the same process involving internal oxidation. The use of a Cu/Cr_2O_3 composite instead of Cu/Al_2O_3 enhances not only its electrical conductivity but also its mechanical properties. However, the internal oxidation process produces a composite with micrometric grain size and residual pure Cr in the matrix. In order to obtain a composite with a micro/nanometric grain size, we have synthesized a Cu/Cr_2O_3 composite using a chemical process derived from the Pechini method.

The Pechini method has been used in the past to synthesize rare-earth, complex oxides and spinel compounds [4–6]. In the original method, a polymeric resin is obtained through polyesterification of a metallic acid with ethylene glycol followed by calcination. The basic Pechini method has been modified to simplify the process and obtain copper/chromium oxide powder composites. In this paper, we present the modified Pechini method that can yield reproducible Cu/Cr_2O_3 composite materials with well-controlled stoichiometric ratios for laboratory scale specimens. In the new method, though the use of ethylene glycol is not needed, there is an additional reduction step to obtain the desired composite.

Experimental method

Synthesis

Figure 1 summarizes the steps involved in the synthesis of the copper/chromium oxide powders. It should be noted that the

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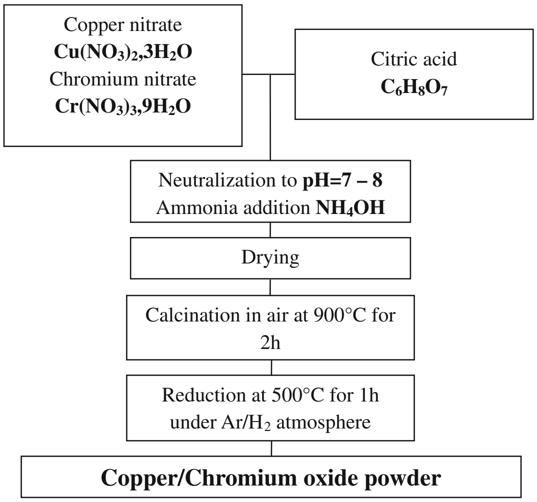


Fig. 1 Flow chart of the synthesis procedure for copper/chromium oxide powders

process route is different from the Pechini method in two different aspects. Firstly, the suggested method does not use any polyhydroxide alcohol, e.g., ethylene glycol. Secondly, the final single-phase product is obtained right after the calcination step in the original method whereas we add a reducing step in the new method. As shown in the flow chart (Fig. 1), copper nitrate and chromium nitrate are stoichiometrically mixed to obtain the desired volume of chromium oxide. This mixture is then dissolved in excess amount of a citric acid solution with a molar ratio of 1:5 $(n_{\mathrm{Cu}^{2+}}{:}n\mathrm{C_6H_8O_7})$. A clear solution is then produced by heating the mixture at 90 °C for 20 min. As the complexation reaction of cations by citric acid is improved at pH $\geq$ 7, the solution is neutralized by the addition of ammonia. The resulting solution is dried at 120 °C to enhance the complexation reaction rate. At the beginning of the drying process a black viscous solution appears and changes to a fragile solid black residue at the end of the process. This solid is then grounded and calcinated at 900 °C for 2 h in air to remove organic species. Finally, an annealing treatment under controlled atmosphere (Ar/H_2 with 5 vol.% of H_2) is carried out. This treatment reduces copper oxide to metallic copper to finally yield the copper matrix with a chromium oxide particle composite. The atomic concentration of chromium has been fixed at 1%.

Thermogravimetric, chemical, and microstructural characterizations

One of our objectives is to obtain a composite as pure as possible. This objective is achieved by understanding the relationship between the calcination and reduction steps and the chemical composition of the final composite. Furthermore, this analysis is used to optimize the processes themselves. As a first step, thermogravimetric analyses (TGA) of the calcination step are carried out to optimize the annealing parameters (temperature and time). After the drying step, TGA is conducted on the powder for temperatures ranging from room temperature (RT) to 1000 °C in air. X-ray diffraction (XRD) patterns are obtained from a Philips PW1820, PANalytical X'Pert using Cu Kα radiation ($\lambda = 1.5418$ Å). XRD is used to study the structural evolution during the calcination step. The morphology of the powders is studied by scanning electron microscopy (SEM) using a JEOL 6700F equipped with a field emission gun. The distribution of particle size, after the reduction step, is obtained using a Malvern 2000 laser analyser. The powder is dispersed in water using ultrasonication and the particle size distribution is measured using laser diffraction. This method relies on the fact that diffraction angle is inversely proportional to particle size.

The composite powders are then densified using uniaxial hot pressing at 650 °C and 20 MPa for 20 min, under Ar/H_2 (5% H_2) atmosphere. The chemical composition of the consolidated powders is then determined using electron probe microanalyses (EPMA) with a CAMECA SX 100 equipped with wavelength dispersive spectrometry (WDS); the accelerating voltage is 20 keV. EPMA is mainly used to study the distribution of chromium and oxygen inside the copper matrix. A JEOL 2000 FX transmission electron microscope (TEM) is also used to analyze the microstructure and the crystalline structure of the consolidated powders.

Results and discussions

The primary purpose of the modified Pechini method is to obtain copper/chromium oxide composites free of any contaminants. The calcination step is used to remove all the organic residues, and it is important to assure that all the process parameters are optimized for this removal, which acts as a strict constraint. During the reduction step, copper oxide powder is reduced to metallic copper powder while the chromium oxide particles remain unaffected. XRD and EPMA are used to ascertain that copper oxide is completely converted to metallic copper.

Optimization of the calcining conditions

Temperature and time of the calcination step are optimized using TGA. XRD is also performed to analyze the crystalline structure of the annealed powders. Figure 2a shows that most of the organic compounds are removed between RT and 600 °C. However, in Fig. 2b, which represents a zoom of Fig. 2a between 600 and 1000 °C, a small mass loss can still be observed. This mass loss is linked to the final decomposition of the organic precurssors. Considering the slope of the mass loss, a temperature of 900 °C has been chosen to

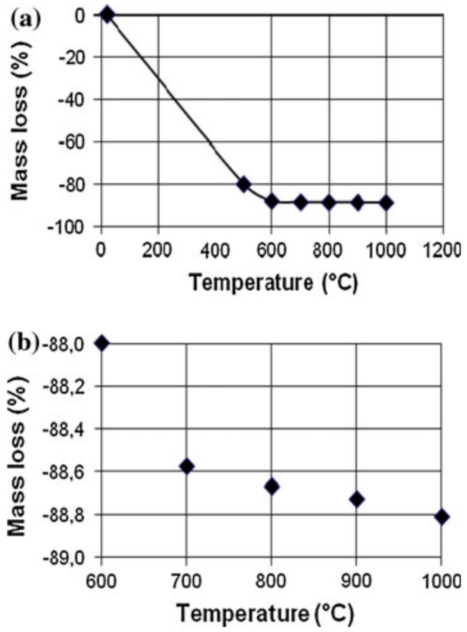


Fig. 2 **a** TGA curves of a copper–chromium oxide powder, **b** zoom between 700 and 1000 °C

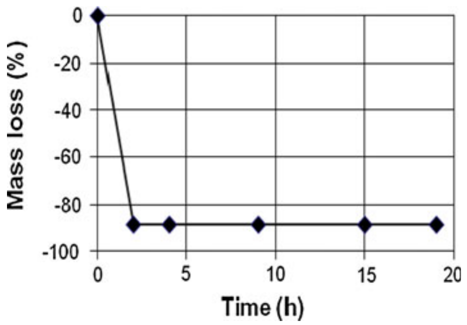


Fig. 3 Evolution of the copper–chromium oxide powder mass loss with the annealing time at 900 °C

investigate the isotherm evolution of the sample mass. This evolution is presented in Fig. 3. Based on these analyses, the optimized annealing treatment conditions are: 900 °C for 2 h in air. XRD patterns of the powders before and after calcination are shown, respectively in Figs. 4 and 5. It has to be mentioned that for both figures the Al peaks are related to the sample holder. Before the calcination step, only the presence of amorphous compounds can be observed (Fig. 4). This broad peak is attributed to amorphous copper and chromium oxides and to other residues (C, O, N). XRD patterns can be visualized in Fig. 5 for two sets of powders annealed at 600 and 900 °C for 2 h. At 600 °C, crystalline peaks of cupric oxide (CuO, $C2/c$ space group) and cuprous oxide (Cu_2O, $Pn\bar{3}m$ space group) can be indexed associated with small amounts of amorphous species (bump present at low 2θ angle). This structural analysis confirms the presence of organic residues after 600 °C, as observed by TGA. At 900 °C, crystalline peak of CuO is only observed by XRD. This oxide corresponds to the most thermodynamically stable copper oxide at that pressure and temperature. No more organic residue is observed. In all XRD patterns, crystalline chromium oxide peaks are never observed. Indeed, the limit of detection by XRD of crystalline phase is very close to the average atomic percent ratio of Cr present in our powders.

Determination of the reduction conditions

The aim of this step is to reduce the copper oxide (CuO and Cu_2O) to obtain the Cu/Cr_2O_3 composite. The reduction parameters (temperature and pressure) must be adjusted so as to reduce only the copper oxide. We use the thermodynamic equations for each metal/oxide pair to draw the Ellingham diagram of Cu/Cu_2O, Cu_2O/CuO, Cr/Cr_2O_3, and H_2/H_2O versus the partial pressure of oxygen $p(O_2)$.

Fig. 4 X-ray diffraction pattern before calcination

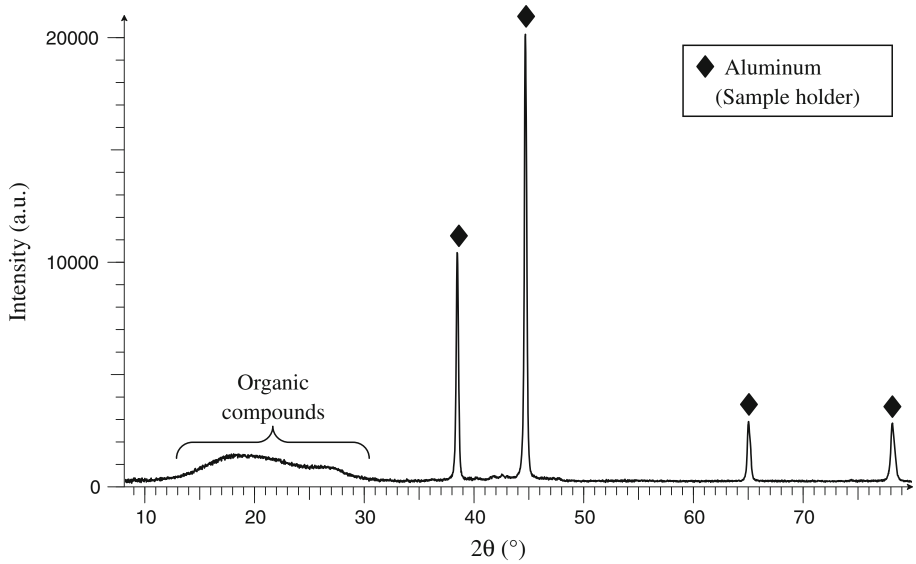


Fig. 5 X-ray diffraction pattern after calcination in air at 600 and 900 °C

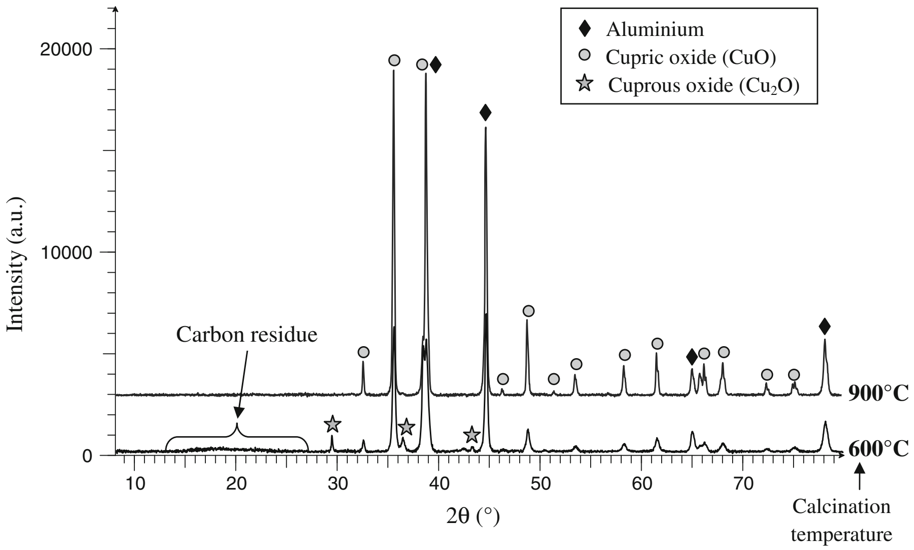


Table 1 Enthalpy and entropy of various metal/oxide pairs

Reactions	$\Delta_f H^\circ_{298\,K}$ (kJ mol^{-1})	$\Delta_f S^\circ_{298\,K}$ (J mol^{-1} K^{-1})
$2Cr(s) + 3/2O_2(g) \rightarrow Cr_2O_3(s)$	−1128	257
$2Cu(s) + 1/2O_2(g) \rightarrow Cu_2O(s)$	−163	67
$1/2Cu_2O(s) + 1/2O_2(g) \rightarrow CuO(s)$	−156	276
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$	−245	52

Determination of the metal/oxide (M/M_aO_b) equation

The metal oxidation reaction is described as follows:

$$a\mathrm{M} + \frac{b}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{M}_a\mathrm{O}_b \left(\Delta_f G^\circ\right)$$

Using the free Gibbs energy of reaction at equilibrium $\Delta_r G = 0$, we can write:

$$p(\mathrm{O}_2)^{\mathrm{eq}} = \exp\left(\frac{2}{b} \times \frac{\Delta_r G^\circ}{RT}\right)$$

Determination of the H_2/H_2O equation

Dihydrogen with oxygen is described as follows:

$$\mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{H}_2\mathrm{O} \left(\Delta_f G^\circ_1\right)$$

Using the free Gibbs energy of reaction at equilibrium $\Delta_r G = 0$, we can write:

$$p(\mathrm{O}_2)^{\mathrm{eq}} = \left[\frac{p(\mathrm{H}_2\mathrm{O})}{p(\mathrm{H}_2\mathrm{O})} \times \exp\left(\frac{\Delta_r G^\circ_1}{RT}\right)\right]^2$$

The $p(H_2O)/p(H_2)$ ratio corresponds to the experimental gas pressure ratio used. In our case, it was a mixture of

Fig. 6 Oxygen pressure variation with temperature for different metal/oxide pairs

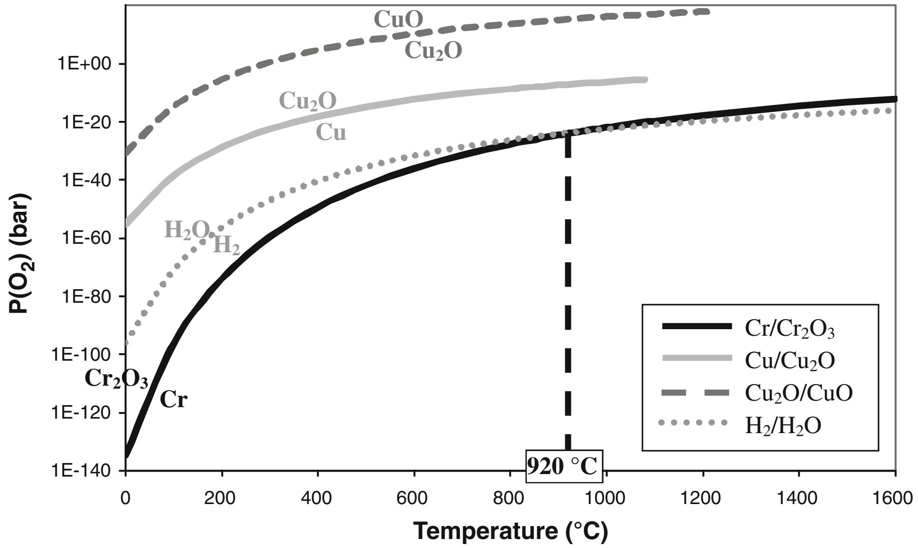
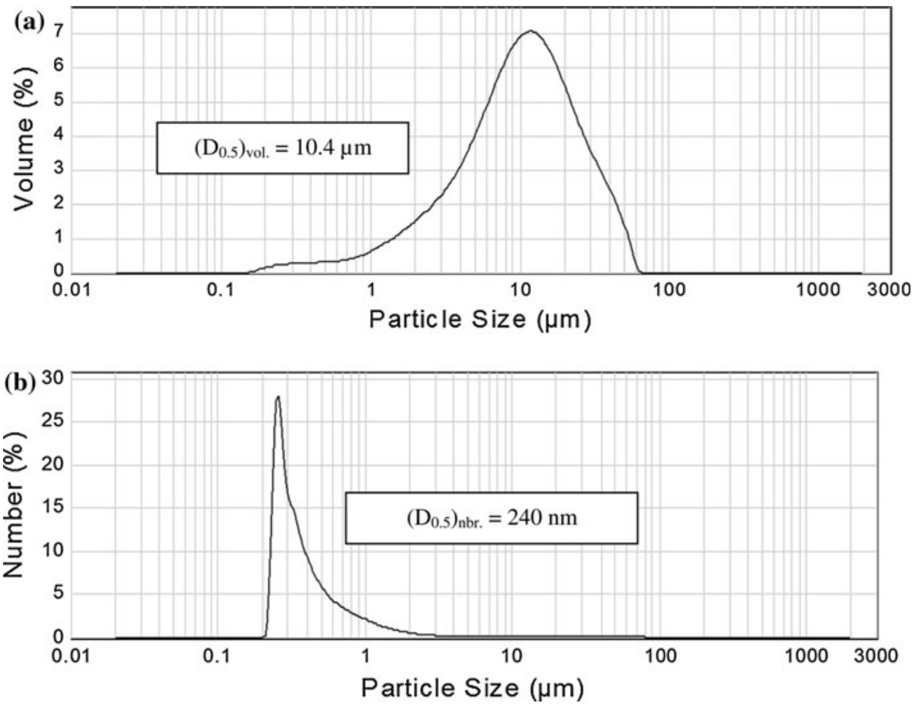


Fig. 7 Particle size distribution **a** in volume and **b** in number for the copper/chromium oxide powder



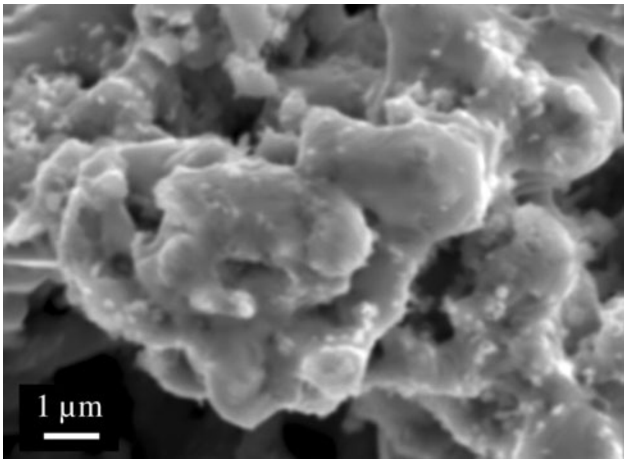
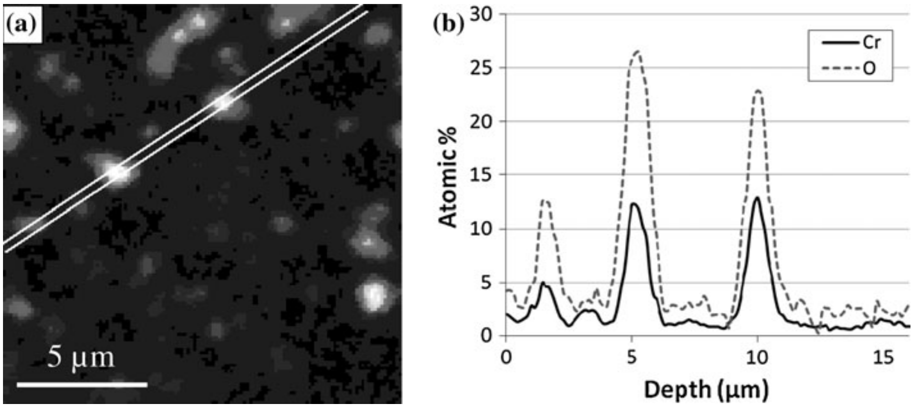


Fig. 8 SEM micrograph of the copper/chromium oxide powder

Ar/H_2 with 5 vol.% of H_2 and a $p(H_2O) = 5$ ppm so that the $p(H_2O)/p(H_2)$ ratio equals 1×10^{-4}. Using the previous equations and the data in Table 1, we can plot on Fig. 6 the oxygen pressure variation versus temperature for the following metal/oxide pairs: CuO/Cu_2O, Cu_2O/Cu, H_2O/H_2, and Cr_2O_3/Cr. Figure 6 shows that to obtain a powder with metallic copper and chromium oxide particles, the reduction step needs a temperature lower than 920 °C. The copper oxide reduction parameters are well known and depend on the thermodynamic and kinetics of the reaction. The reduction of copper oxide in copper is achieved at a temperature of 500 °C for 1 h under a controlled atmosphere of Ar/H_2 (5 vol.%). After the reduction step, irrespective of the calcination temperature (600 or 900 °C), it is found that all of the copper oxides, CuO and Cu_2O, are reduced to metallic copper.

Fig. 9 EPMA mapping of chromium on the copper/chromium oxide powder after densification with the position of the line profile. Atomic concentrations of chromium and oxygen versus the position along the line profile



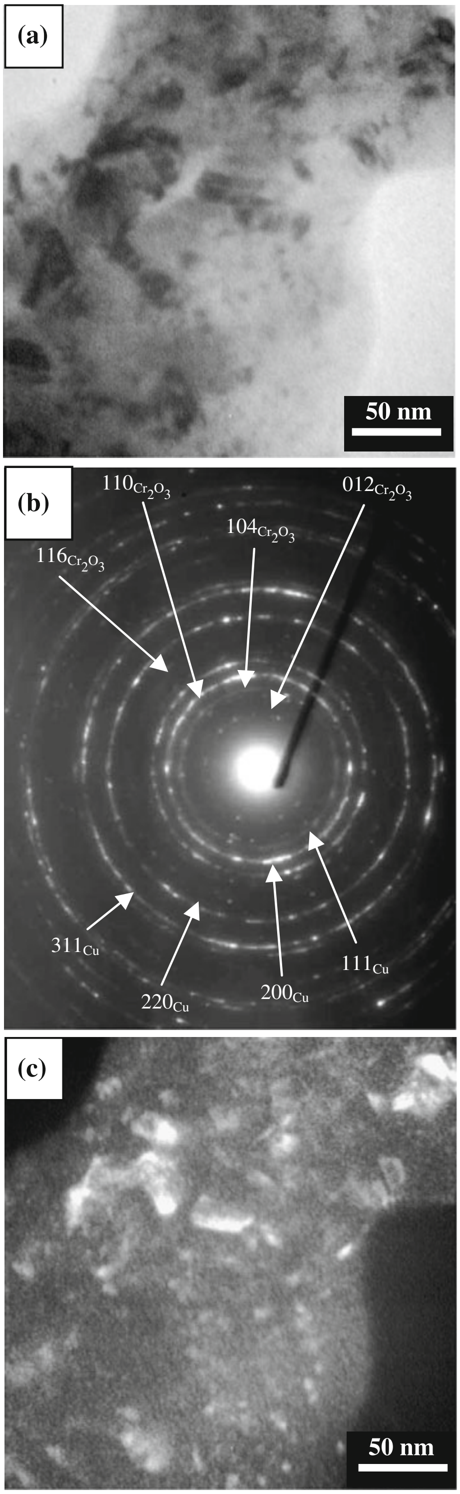


Fig. 10 Transmission electron microscopy analyses of a copper/chromium oxide sample. **a** Bright micrograph, **b** diffraction pattern, **c** dark micrograph with a part of the *ring* {012} Cr_2O_3 of the diffraction pattern (**b**)

Morphology characteristics of the composite powders

Particle size distribution analyses, performed on the final Cu/Cr_2O_3 powders, show a volumic distribution of sizes with a median value D_{50} of 10.4 µm and two different populations (Fig. 7a). The first one ranges from 1 to 70 µm and the second from 0.1 to 1 µm. A better description of the smaller particles is obtained from the distribution analysis by number (Fig. 7b): it shows a population centered around 240 nm. Figure 8 presents a typical SEM micrograph of the powder. Two types of particles are observed: one nanometric and the other micrometric. The nanometric particles seem to stay on the surface of the micrometric ones.

Chemical properties of the powder: EPMA analyses

Figure 9a shows the WDS-EPMA mapping of chromium for densified Cu/Cr_2O_3 materials. In this figure, the gray scale represents the concentration of chromium, black being no chromium (0 at.%), white the maximal concentration (14 at.%), and the gray in the matrix corresponding to a concentration inferior to 0.5 at.%. On the same polished surface, a line profile of Cu, Cr, and O (Fig. 9b), is performed along the line marked on Fig. 9a. The line profile has been obtained by averaging the pixels in between the two plotted lines. Figure 9a shows that the Cr is not homogeneously distributed inside the Cu matrix. However, chromium containing particles (with size ranges from 0.1 to 1 µm) seem to be very well dispersed inside the Cu matrix. From Fig. 9b, and therefore from the line profile represented in Fig. 9a, the atomic concentration of Cu, Cr, and O versus the analysis position in the line is also plotted. Copper profile cannot be observed on that figure due to the fact that the maximum atomic percent plotted is 40%. Three particles are crossed by the line profile. It can be observed that there is an increase of both Cr and O concentration in these three particles. The ratio between Cr and O is close to 2/3 which corresponds to a Cr_2O_3 chromium oxide.

Transmission electron microscopy characterization

Figure 10a shows a typical TEM bright field micrograph of the powder calcinated at 900 °C and reduced at 500 °C for 1 h. The black and white levels observed on this micrograph are mainly linked to the thickness, the chemistry and the crystallographic orientation of the grains. It should be noted from this typical observation that metallic copper and chromium oxide grains cannot be distinguished. Electron diffraction pattern is obtained from that area (Fig. 10b). It shows a ring-like morphology which is characteristic of polycrystalline grains with sizes much smaller than the diffraction diaphragm used to obtained that pattern (10 μm). The indexation of the diffraction rings are obtained using a pure copper structure ($Fm\bar{3}m$ space group) and a chromium oxide structure ($R\bar{3}c$ space group). This analysis confirms the EPMA results. A dark field micrograph using a section of the {012} Cr_2O_3 diffraction ring is shown in Fig. 10c. From that micrograph, we can observe the distribution and the nanometric size (between 5 and 30 nm) of Cr_2O_3 grains, which appear in white.

Conclusions

A Cu/Cr_2O_3 composite has been synthesized using a chemical process by modifying the well-known Pechini method. Various analyses have been used to optimize the process parameters. We have determined that a calcination step at 900 °C for 2 h in air and a reduction step at 500 °C for 1 h under controlled atmosphere need to be used to obtain a Cu/Cr_2O_3 composite material with a micro/nanometric grain size and without any residue. In contrast with the internal oxidation process, our chemical method produces a composite with nanometric grains on the surface of the micrometric ones. Another advantage of our process is the lower temperature used. While internal oxidation process requires a temperature range of 950–1100 °C, for our process a temperature of 900 °C is sufficient.

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