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Effect of pH value and calcination temperature on synthesis and characteristics of Cu−Ni nano-alloys

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Abstract: Cu−Ni nano-alloys were prepared using precursors synthesized by the citrate-gel method. The effects of initial solution pH value and calcination temperature on the composition, crystalline structure, purity, morphology, homogeneity and grain size of Cu−Ni nanoparticles were investigated. Both the parameters significantly affect the crystalline structure, composition and grain size. Cu−Ni alloys prepared at pH value of 1 do not contain impurities, and their compositions are $Cu_{0.42}Ni_{0.58}$, $Cu_{0.45}Ni_{0.55}$ and $Cu_{0.52}Ni_{0.48}$ reduced at 300, 400 and 500 °C, respectively. The grain size grows with the increase of calcination temperature for the precursor prepared at pH values of 1.6 and 3. The Ni content of the alloys gradually increases with the increase of calcination temperature at pH value of 3.

Key words: nanostructured Cu−Ni alloys; chemical synthesis; physicochemical characteristics; pH value; calcination temperature

1 Introduction

Cu−Ni nano-alloys are utilized in a number of technologically important areas. Magnetic and nonmagnetic layered structures, such as Cu and Ni multi-layers, reveal giant magnetoresistance effects (GME). For this reason, they are used in the manufacturing processes of sensors for magnetic data recording and for monitoring the position of machine components [1]. Cu−Ni alloys coatings, which are electrochemically and thermally prepared, are used in the conversion of solar energy into a source of renewable energy, since they have a high solar absorbance and a low thermal emittance [2]. Similarly, Cu−Ni nano-powders present excellent catalytic properties which can be used in the dehydrogenation of cyclohexanol [3] and decomposition of methane [4]. Other applications include the use of Cu−Ni alloy seeds in hyperthermia applications aimed at the treatment of tumors [5] and in health care environments [6].

Recent studies have shown that the properties of materials depend on particle shape, surface area, homogeneity and degree of particle crystallinity. These characteristics are closely related to the preparation technique, therefore, a large number of chemical methods intended for preparing nanoparticles have been developed, such as sol−gel, hydrothermal and precipitation techniques, emulsion method [7,8].

The citric acid assisted sol−gel combustion process has been used for the preparation of nanocrystalline multi-component powders with desirable properties, such as lower crystallite size, controlled stoichiometry, narrow particle size distribution. In this process, citric acid is generally used as a chelating agent of metal cations. The polymerizing ability of the citric acid is effectively utilized for the formation of a colloidal solution, in which metal ions are uniformly distributed [9,10].

Combustion reactions are frequently applied for the preparation of different oxides. However, there are a limited number of publications referring to the effects of pH value and calcination temperature on the synthesis of Cu−Ni nano-alloys using precursors prepared by the citrate-gel method [11].

Different studies on the synthesis of materials using the citrate-gel method have been aimed at testing the influence of certain variables, such as the ratio between metallic ions, the ratio of acid citric to metallic ions, the pH value of the initial solution and the calcination temperature of the precursors, on the final products.

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CANNAS et al [12,13] studied the influence of various parameters which included the initial solution composition, the solution pH value, the gel formation method and the combustion temperature on the formation reaction of precursors prepared by the citrate-gel method. LIU et al [14] showed that the initial solution pH value and the molar ratio between the citric acid and metallic ions affected the homogeneity of the metal−citrate complexes, thus affecting the behavior during gel combustion and synthesized phases composition.

The solution pH value exerts a significant influence on citric acid ionization and on the type of complexes formed between citric acid and metal [15]. It has also been proved that the solution pH value of precursors significantly affected the gel morphology and porosity when the latter underwent a drying process [16]. In addition, the pH value has been proved to have an effect on the size of the material grain [8,17] and on the formation temperature of the materials [18].

Different authors have studied the effect of the calcination temperature on the characteristics of oxides and metallic oxides mixtures synthesized by the citrate-gel method. These authors have also observed that the calcination temperature significantly affected the grain size which growed as the calcination temperature increased [19−21]. CHEN et al [22] prepared cerium oxide nano-powders, and observed that the rise of calcination temperature (473−1273 K) and the length of thermal treatment increased the crystallinity and the average crystallite size of the nanocrystallites ranging from 12 nm to more than 47 nm. OH et al [23] demonstrated that the crystallite sizes and morphologies of Co_3O_4, CuO and NiO were influenced by calcination temperature. Based on the nano-thermodynamic theory, GUISBIERS et al [24] confirmed that mixed Cu−Ni nanoparticles were difficult to be synthesized at room temperature and required a substantial heat treatment. In addition, they concluded that it is possible to control the structure of the alloy by adjusting the synthesis temperature. The melting behavior of Cu−Ni nanoparticles was modeled with a thermodynamic approach reported by SHIRINYAN et al [25] and SOPOUSEK et al [26]. They predicted a depression of the solidus temperature, which was reported as size dependent.

This work focused on the systematic study of the influence exerted by pH value and calcination temperatures on the composition, crystalline structure, purity, morphology, homogeneity and grain size of Cu−Ni nanostructured alloys. These nano-alloys were prepared using precursors synthesized by the citrate-gel method, using solutions with different pH values. These precursors were later calcined at three different temperatures and reduced with H_2 diluted in N_2 to obtain Cu−Ni nano-powder alloys.

2 Calculation of species at equilibrium based on pH value

The acidity of the initial solution used to prepare the precursor of Cu and Ni oxides mixtures is very important due to the effect of this variable on the speciation and the complexing ability of citric acid. For this reason, and with the purpose of establishing the most appropriate working pH value for the synthesis of the Cu−Ni alloy, the theoretical calculation of equilibrium molar concentrations was performed on all species in the solution. Maple V ® 12 was the software used in the study, and the species considered for the analysis were the following:

1) Species of citric acid: H_3L, H_2L^-, HL^{2-} and L^{3-}.

2) Complexes of citric acid formed with Cu(II): $Cu(L)^-$, Cu(HL), $Cu(H_3L)^{2+}$ and $Cu(OH)^+$.

3) Complexes of citric acid formed with Ni(II): $Ni(L)^-$, Ni(HL), $Ni(H_2L)^+$ and $Ni(OH)^+$.

where L is the citrate anion $(C_6H_5O_7)^{3-}$.

The concentrations used were $n(Cu^{2+})$=0.315 mol/L, $n(Ni^{2+})$=0.341 mol/L and $n(H_3L)$=0.48 mol/L. The equilibrium constants used in the calculations were taken from bibliographic sources [27,28]. These theoretical results show that Cu^{2+} and Ni^{2+} mainly form $Cu(L)^-$ and $Ni(L)^-$, which are stable in the pH value range of 1−14. The rest of the complexes also formed but in very low concentrations. The previous experiments have shown that when NH_4OH was added to increase the pH value above 3, the solution precipitation took place, and thus the citrate-gel could not be obtained. In agreement with these theoretical and experimental results, the pH value influence was studied in the range of 1−3.

3 Experimental

3.1 Materials

Nickel nitrate ($Ni(NO_3)_2·6H_2O$) (Fluka), copper nitrate ($Cu(NO_3)_2·2.5H_2O$) (Rieldel–de Haën), ammonium hydroxide (Biopack), and citric acid (Anedra) were used. The gases employed were 99.999% pure N_2, a mixture of H_2 (5%) and N_2 and a mixture of O_2 (10%) and N_2. The gases were purified using adequate traps to retain water and oxygen.

3.2 Synthesis procedure

3.2.1 Preparation of precursor

Three precursors were prepared from solutions with the pH values of 1, 1.6 and 3, and with the molar ratio of Cu(II) ion to Ni(II) ion of 1:1. In all the cases, the molar ratio between citric acid and the sum of Cu(II) and Ni(II)