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The synthesis and characterization of nickel–copper alloy nanoparticles with a narrow size distribution using sol–gel synthesis

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ABSTRACT

Nickel–copper (NiCu) alloy magnetic nanoparticles with a narrow size distribution were prepared by reducing a Ni, Cu-oxide mixture in a silica matrix, obtained with a sol–gel method. In order to obtain the NiCu nanoparticles, the silica matrix was treated with an etching solution in an argon atmosphere. By selecting the nominal NiCu alloy composition of 67.5:32.5, a Curie temperature close to 65 °C was achieved. The nanoparticles were superparamagnetic with a magnetization of 8 emu/g at 293 K and exhibited a significant heating ability in an alternating magnetic field. The simplicity of the synthesis allows the preparation of NiCu alloy nanoparticles on a large scale. The method could also be used for the preparation of other mixed-alloy nanoparticles.

1. Introduction

The NiCu alloy has been extensively studied for different purposes, as catalysts [1–3] for electrochemical deposition [4] and multilayers [5]. However, there is now a lot of interest in its use in hyperthermia since it meets all the necessary requirements for the application of Self-regulating Magnetic Hyperthermia (SRMH). Recently, we reported the synthesis of NiCu alloy nanoparticles, where we put the emphasis on adjusting the Curie temperature by varying the chemical composition [6]. At this stage the key requirement was to prepare nanoparticles with a controlled Curie temperature and exhibiting a narrow size distribution in order to make the best of the nanoparticles' relaxation and to improve the specific absorption rate (SAR) of the magnetic nanoparticles. However, the preparation of nanoparticles with a controlled Curie temperature using a chemical method that excludes any mechanical treatment [7] is problematic since for thermodynamic reasons the homogeneity of the magnetic particles cannot be easily achieved at room temperature [8]. The particles' composition must be subsequently homogenized at high temperatures. Under these conditions the particles' homogeneity and the grain morphology are not compatible and tend to exclude each other.

The purpose of this investigation was the synthesis of mixed-alloy nanoparticles at high temperature, which instantaneously ensures the chemical homogeneity of the synthesized particles and leads to a monodispersed nanoparticle size in a silica matrix, which can afterwards be chemically removed. On the other hand, it is also important that the synthesis allows the production of nanoparticles on a large scale.

2. Experimental

The $Ni_{1-x}Cu_x/SiO_2$ samples were prepared according to a previously reported procedure [9] with some modification. Briefly, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and citric acid were dissolved in deionized water (D.I.). After 15 min, under vigorous stirring, absolute ethanol and TEOS were added to the solution. The vigorous stirring was continued until the two phase systems were converted into a single homogenous phase solution. For the Ni:Cu ratio of 67.5:32.5 the molar ratios of all the components were Ni:Cu:CA:TEOS:D.I.:ethanol =0.675:0.325:1.1:2.9:40.6:11.6. First, the sol was dried for 3 days at room temperature. Afterwards, the gel was calcinated in air at 500 °C for 24 h. The as-prepared powder was the nickel and copper oxides in the SiO_2 matrix. The next step was a reduction of the product in a

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H_2/Ar atmosphere for 24 h at 850 °C, to obtain the final product of $Ni_{1-x}Cu_x$ nanoparticles in a SiO_2 matrix. This SiO_2 matrix was then removed with the etching solution (1 M NaOH/3 wt% hydrazine hydrate) under stirring for 24 h in an argon atmosphere. After 24 h the $Ni_{67.5}Cu_{32.5}$ nanoparticles were collected using centrifugation. After that the product was washed with the etching solution and ethanol several times and finally re-dispersed in absolute ethanol (sample marked as S1EH). The nanoparticle size was inspected with TEM (JEOL 2010F). The XRD measurement was made on a D5005 diffractometer (Bruker Siemens). The success of etching the SiO_2 matrix was investigated with FTIR IRAffinity-1 (Shimadzu) and TEM. The Curie temperature was determined using thermal demagnetization with a modified thermogravimetric analysis on a TGA/SDTA 851 (Mettler Toledo). The magnetic properties of the nanoparticles were investigated with a Lake Shore 7307 vibrating-sample magnetometer and with a Quantum Design MPMS-XL-5 SQUID magnetometer. The magnetic heating-effect measurements of the etched powdered sample were performed in a conventionally built system that generates an alternating magnetic field with a nominal field strength of $H=4.2$ kA/m and four different frequencies [10].

3. Results and discussion

The composition of the synthesized alloy nanoparticles was selected to exhibit a Curie temperature close to 65 °C ($Ni_{67.5}Cu_{32.5}$). The as-prepared powder of nickel/copper oxides in a SiO_2 matrix was treated in a H_2/Ar atmosphere for 24 h at 850 °C (see experimental). During this step the nucleation of the alloy proceeds, i.e., the nuclei of the $Ni_{67.5}Cu_{32.5}$ alloy were formed and outgrown inside the SiO_2 matrix. In order to remove the silica matrix the etching solution was used in an argon atmosphere. Preliminary experiments led to the discovery of the proper etching solution with the composition 1 M NaOH/3 wt% hydrazine hydrate. The addition of hydrazine hydrate to the 1 M NaOH solution is a key factor, because without the addition of the hydrazine hydrate, copper oxide (Cu_2O) was detected, while the silica matrix remained on the nanoparticles (etching time 5 h). Fig. 1 shows the X-ray diffraction patterns (a) and the FTIR spectra (b) of the as-prepared sample in the SiO_2 matrix (S1), the etched S1 sample in the etching solution, with (S1EH) and without the hydrazine hydrate (S1E). The 2Θ diffraction angles in Fig. 1a correspond to the (111) and (200) planes of the NiCu alloy crystallites. The sample S1E in Fig. 1a shows the presence of copper oxide (Cu_2O), as mentioned before, and also the presence of silica (Fig. 1b; peak at 1026 cm^{-1}). The presence of Cu_2O after the etching was the reason that we used hydrazine hydrate in the etching solution. To remove all the silica matrix the etching time was prolonged to 24 h. In order to verify the success of etching the SiO_2 matrix from the $Ni_{67.5}Cu_{32.5}$/SiO_2 composite, the FTIR spectra was analyzed. The absence of characteristic bands at 802 cm^{-1} (Si–O bending) and 1080 cm^{-1} (Si–O–Si stretching) in the S1EH sample was confirmed, which indicated the successful etching of the SiO_2 matrix, so only $Ni_{67.5}Cu_{32.5}$ nanoparticles remained.

The final examination to see whether the silica matrix was completely removed was conducted using the TEM. Fig. 2 shows TEM images of the $Ni_{67.5}Cu_{32.5}$ nanoparticles before and after etching for 24 h. Fig. 2b shows that the SiO_2 matrix was washed away and only spherical nanoparticles of $Ni_{67.5}Cu_{32.5}$ with a narrow size distribution (Fig. 3c) remained. This sample, marked as S1EH, was used for further examinations. The magnetization of the $Ni_{67.5}Cu_{32.5}$ nanoparticle vs. the magnetic field at 293 K is shown in Fig. 3a. The results show that the hysteresis of the magnetic particles cannot be observed, while the magnetization does not saturate at 10 kOe. Fig. 3b shows zero-field/field cooling (ZFC/FC) curves, where the blocking temperature (T_B) can be obtained by identifying the maximum temperature in the ZFC curve, which is 135 K. Above this temperature the magnetic moment of the unblocked nanoparticles fluctuates due to thermal energy, which indicates a superparamagnetic behavior. The superparamagnetic behavior is also indicated by zero values for the coercivity and remanence on the magnetization curve. From the magnetization curve at 293 K, the particle size distribution (Fig. 3d), and the median nanoparticle diameter (d_0) with the standard deviation (σ) of the sample was determined [11]. The average estimated particle size was in agreement with that determined from the TEM images; however, with a smaller average particle size. This is in agreement with the fact that the magnetization data take into consideration only the magnetic phase, while the TEM image also "sees" the nonmagnetic part ("dead layer") of the particles, which is usually present on the particle surface [12].

The Curie temperature of sample S1EH was determined using thermal demagnetization with a modified thermogravimetric analysis (Fig. 4a). The Curie temperature was taken as the temperature where half of the weight increase ≡ loss of the magnetization was recorded during the course of the heating. The determined Curie temperature was 65 °C and is close to the temperature predicted for the nanoparticles' nominal composition [13].

Fig. 4b shows calorimetric measurements of the sample S1EH in an alternating magnetic field with field strength 4.2 kA/m and four different frequencies. The self-heating temperature curves converge to the limiting temperature and the difference between the steady-state temperatures decreases, although the frequency of the field increases. The steady-state temperature attained by the alloy nanoparticles at the highest field frequency is lower than the Curie temperature determined with the modified thermogravimetric method.

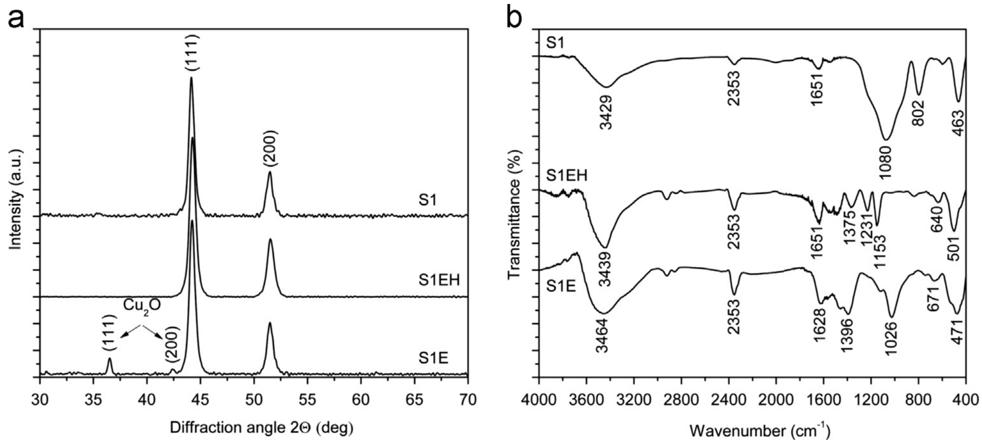

Fig. 1. X-ray diffraction patterns (a) and FTIR spectra (b) of as-prepared sample in SiO_2 matrix (S1), etched S1 sample in etching solution, with (S1EH) and without hydrazine hydrate (S1E).