Synthesis and Characterization of Metallic Nanoparticles of Cu, Co and Cu-Co by Reactive Milling.

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ABSTRACT

Nanoparticles have been produced by reactive ball milling. Cu, Co and alloyed Cu- 10 at. % Co particles have been obtained by milling metallic chlorides with pure sodium having NaCl in excess. Sodium chloride is also a product of the reduction reaction and it is used both to protect particles from oxidation and to prevent particle coalescence. A volume fraction of approximately 3 % is obtained in 3 or 8 h of milling. Characterization of the produced nanoparticles is made by electron microscopy, X-ray diffraction and calorimetry. Particles in all cases have sizes around 7 nm. A mixture of Co and Cu chlorides reacting with Na gives rise to alloyed Cu-Co nanoparticles. Such particles have spherical shapes and consist of a non equilibrium solid solution which can be decomposed into Cu and Co by thermal treatment as expected from the corresponding equilibrium phase diagram.

Keywords: nanoparticles, reactive milling, alloying, phase separation.

(1) INTRODUCTION

Properties of nanosized materials are highly dependent on the nanocrystal size, size dispersity, structure, defects and composition [e.g. 1]. Interest in the fabrication of metallic nanoparticles arises from their unique properties, useful in a variety of applications, including magnetic storage arrays, quantum electronics and plasmonic waveguides [2]. In addition, metallic nanoparticles can be used as catalysts for the growth of semiconductor nanowires and carbon nanotubes [3].

The preparation of nanosized materials with a desired size is important to investigate and utilize their size-dependent properties. However control of their composition is especially important as well. Currently most experimental methods in use are aimed to prepare nanoparticles of pure materials. For example important configurations such as the core shell are prepared by means of soft chemistry methods in several stages. However such a configuration is likely to be produced by applying other techniques and basic principles of materials science. The use of systems without solid solubility is one of them. Mechanical milling is known to produce metastable solid solutions [4] of otherwise immiscible elements such as Cu and Co or Au and Co. Such solutions can be decomposed by thermal treatment producing dispersion of precipitates in a metallic matrix. In the case of Cu and Co, dispersions of precipitated particles can be developed at temperatures as low as 150 °C [5]. Thus production of alloyed Cu – Co nanoparticles i.e., solid solutions of two immiscible elements, can be used to produce a dispersion of precipitates in a very small volume. Naturally at a relatively high temperature such a system of particles has the tendency to coarsen and form a single domain i.e. to develop a core shell structure. A nanoparticle is a very small domain and diffusion can be expected to take place over rather small distances, thus reaching the end of the coarsening process. But many other parameters of the process are still unknown in order to predict a definite behavior. However controlling the composition of nanoparticles can help to investigate them and develop a simpler method of synthesis. Summarizing this investigation deals with the production of nanoparticles with a controlled composition. Such a system can be used to produce core shell particles.

(2) EXPERIMENTAL PROCEDURE

Metallic nanoparticles are produced by reactive milling according to the following chemical reaction of reduction:

$$MCl_2 + 2Na \rightarrow M + 2NaCl \qquad [1]$$

The metallic chloride MCl_2 in the present case has been either Cu, Co or a mixture of Cu and Co. NaCl has been added in excess to the as received powders before milling in order to achieve a dispersion of the reaction products and effectively produce nanoparticles. Powders are used in all cases with a fine particle size (around –100 mesh) except for the case of Na, where the largest pieces could reach 1 mm in size. Table 1 summarizes the different milling conditions in use. A single volume fraction of nanoparticles f_v has been produced in a planetary mill i.e., 3 %. This is achieved by simply adjusting the amount of NaCl before milling, the maximum f_v that can be produced by this method is limited by reaction (1) to approximately 10 %. The reaction is conducted in an inert Ar atmosphere with 320 rpm for 3 or 8 h (pure and alloyed particles, respectively) and by using stainless steel balls (10 mm in diameter) in a ball:mass weight ratio of 3:1.

Table 1. Milling conditions

M	MCl_2 (g)	Excess NaCl (g)	Na (g)
Cu	11.2	30	3.8
Co	11	30	4
Co + Cu	1.2 + 11.17	33.26	4.25

(3) RESULTS AND DISCUSSION

Cu and Co nanoparticles can be obtained after only 3 h of milling at 320 rpm. Figure 1 shows the X ray diffraction pattern of powders milled for the production of Co nanoparticles. In the same figure the peak positions corresponding to Co (fcc, JCPD 15-0806) and NaCl (JCPD 05-0628) are also given. Longer milling times produce identical results with a slight variation in the final size and agglomeration of the powder. Increasing the energy of the milling process (higher rpm) induces the formation of Co with the hcp structure. In the case of Cu, higher milling energies affect only the agglomeration of powders.

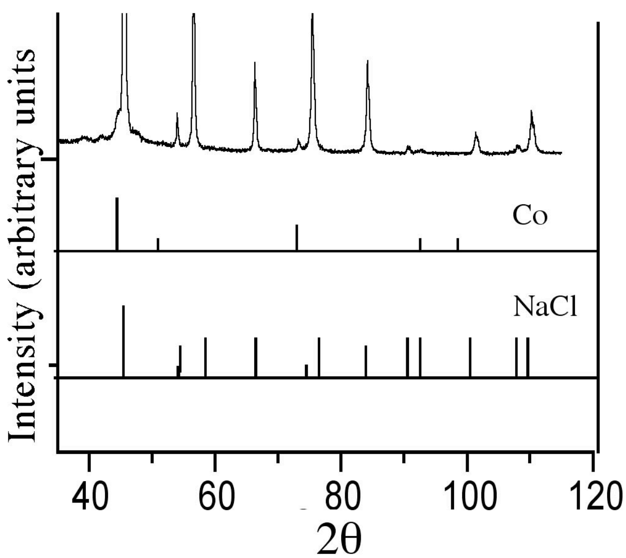

Figure 1. X ray diffraction pattern for powders milled for 3 h for the production of Co nanoparticles. The lines indicate expected peak positions.

Figure 2 shows the diffraction pattern obtained for the production of Cu – 10 at.% Co nanoparticles. The milling time in this case increases to 8 h, the figure also provides the expected peak positions for Cu and NaCl. Apparently the Cu structure is preserved but there is a slight difference between the experimental and expected peak positions for Cu (see dotted lines) due most likely to the presence of a small amount of Co in solid solution. The small amount of $CoCl_2$ added to the milled mixture would hardly allow detection by X ray diffraction but the peak displacement indicates that the expected solid solution has been formed. It is known that Co and Cu can form unstable solid solutions in the whole composition range if mechanically milled [6].

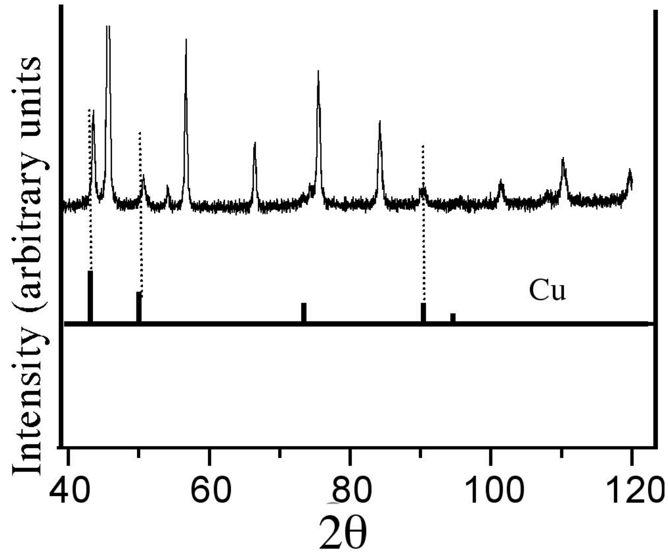

Figure 2. X ray diffraction pattern for powders milled for 8 h for the the production of Cu – 10 at. % Co alloyed nano-particles. Vertical dotted lines are added to show peak position disagreement.

Figure 3 show a conventional transmission electron microscope (TEM) image in bright field (Fig. 3a) of the as milled powders (3 h) for the Co nanoparticles. The powder dispersion and size can be seen. The corresponding diffraction pattern (Fig. 4) shows that only rings corresponding to the fcc phase of Co and NaCl are obtained. In this case sample preparation for TEM requires dilution of the powders in methanol. This reduces the amount of NaCl in the finally investigated sample.

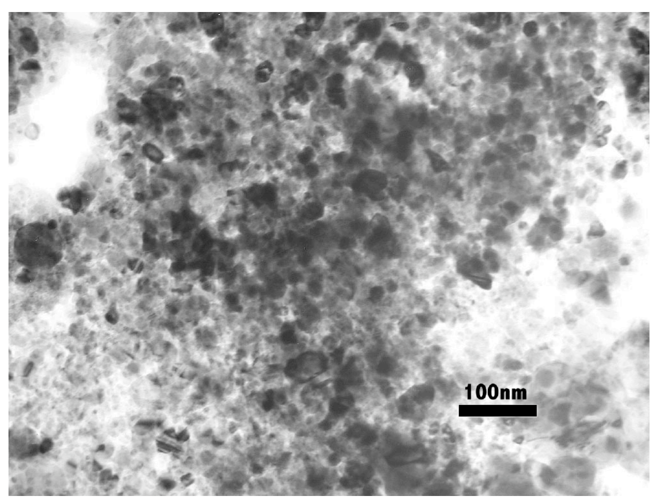

Figure 3. TEM bright field image of $CoCl_2$ powders milled for 3 h together with Na and NaCl.

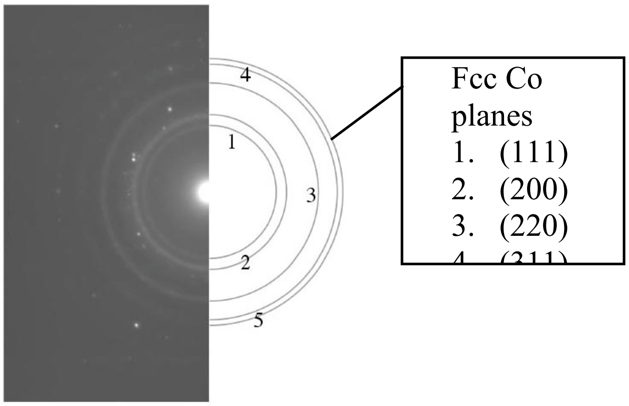

Figure 4. Diffraction pattern of as milled powders for the synthesis of Co nanoparticles.

Figure 5 shows the TEM bright field image of as milled powders for the mixture containing $CuCl_2$ and $CoCl_2$ in proportions to obtain Cu – 10 at.% Co nanoparticles. Oxides or other contamination products cannot be found, only powder particles ranging from some nm to approximately 50 nm. This is probably also a consequence of sample preparation since methanol dissolves partly the protective NaCl. The corresponding diffraction pattern is shown in Fig. 6 and contains rings that can be used to identified the structure of Cu. The precision of electron diffraction is lower that that of X rays and a position displacement due to the presence of Co is difficult to note.

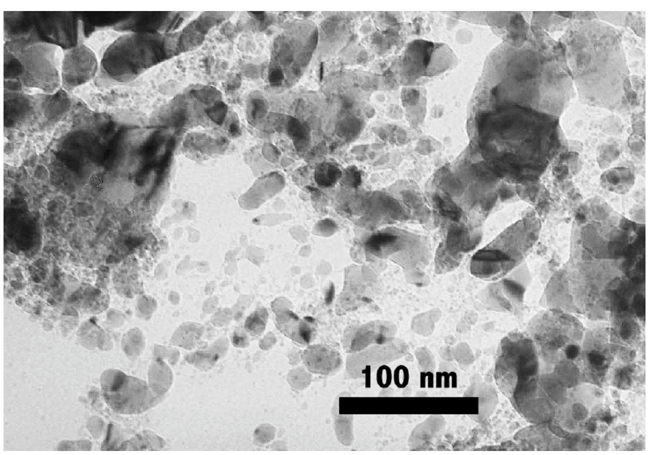

Figure 5. TEM bright field image of $CoCl_2$ and $CuCl_2$ powders milled for 8 h in the presence of Na and NaCl.

The nanoparticles can be seen only in high resoltion mode by transmission electron microscopy (HREM). A typical image is shown in Figure 7 where the lattice lines can be clearly imaged and identify the metallic nanoparticles. The sample in this case corresponds to the powders milled for 8 h to obtain alloyed nanoparticles with the targeted composition of Cu – 10 at.% Co. More research is necessary to clearly determine the nanoparticle composition but the images show the presence of a single lattice structure in agreement with X ray and electron diffraction. The nanoparticles are supported on a normal C thin film and show still some NaCl surrounding them but the imaging condition (negative defocus) has been selected to favor viewing the nanoparticles. In some cases nanoparticles form part of agglomerated arrays but some clear cases of independent particles can be also seen (e.g. arrow in Fig. 7).

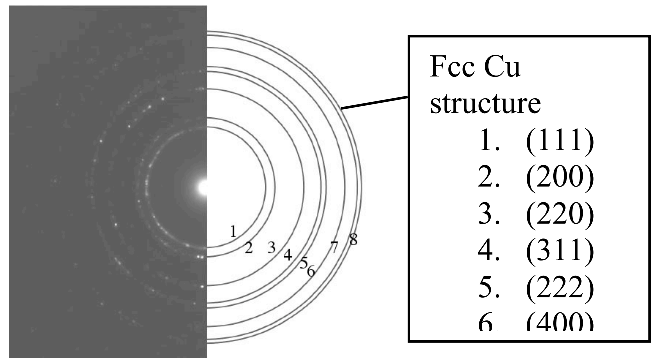

Figure 6. Diffraction pattern of as milled powders for the synthesis of Cu- 10 at. % Co particles.

Circles have been added to Figure 7 as a guide. Approximately 132 particles have been measured with an average diameter of 7 nm and a standard deviation of ± 2.7 nm.

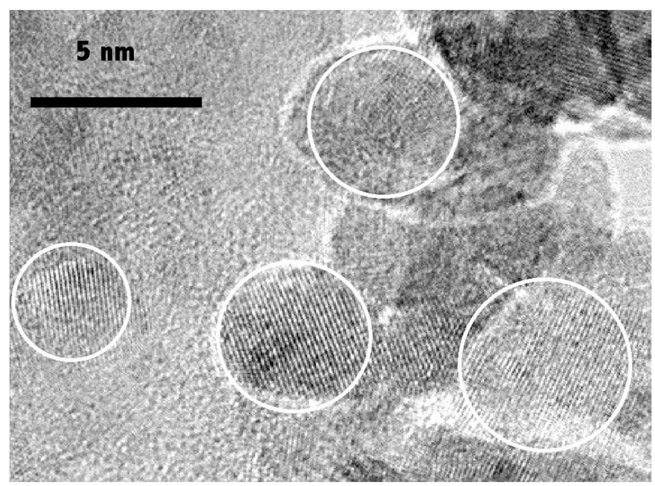

Figure 7. (HREM) image of the as milled powders containing alloyed Cu – 10 at. % Co nanoparticles. Circles indicate the lattice images of nanoparticles.

Determination of the chemical composition of the individual alloyed nanoparticles is still under investigation. Direct chemical analysis by established techniques renders still unsatisfactory results due to the small volume of the nanoparticles. However chemical analysis of larger volumes produces results that indicate that alloying has taken place. Figure 8 shows a spectrum for the sample containing alloyed particles and obtained by energy dispersion spectroscopy (EDS) in a field emission scanning electron microscope (FEG-SEM). The presence of Co and Cu is very clear. Quantitative analysis including substraction of the influence of NaCl renders values relatively close to the nominal composition (approximately 9 at. % Co). Although EDS analysis has normally a limited precision due to different operative parameters (X ray absorption, atomic number, fluorescence), the agreement is encouraging.

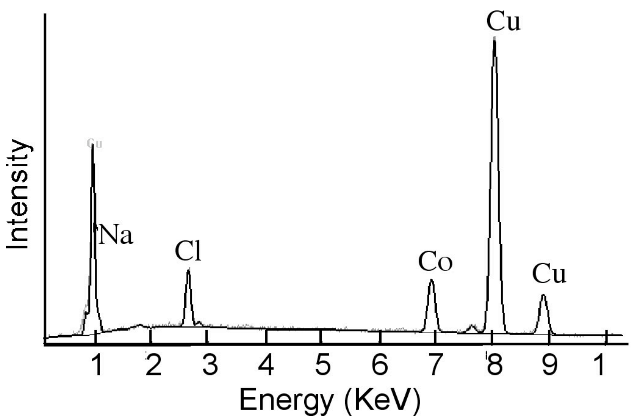

Figure 8. EDS spectrum of as milled powders for the synthesis of Cu / 10 at. % Co nanoparticles. Na and Cl lines are not uniquely identified by the system. They are selected as the most likely.

Differential scanning calorimetry (DSC) has been used to follow the phase transformation in the alloyed nanoparticles. The Cu-Co equilibrium diagram shows that there is a severely limited solubility of Co in Co and viceversa [ref]. Thus a reaction of precipitation or exsolution can be expected in case a metastable solid solution is formed during the reactive milling process in the present investigation. Figure 9 shows a typical example of such an experiment. The sample was carefully rinsed in methanol in order to increase the relative volume fraction of particles and consequently increasing the magnitude of the measured signal. Figure 9 shows that there is an exsolution reaction starting at around 225 ºC that can be interpreted as the well known phase separation in the Cu-Co system. The supersaturated solid solution formed during reactive milling, decomposes into a Cu matrix and Co particles as has been observed in conventional Cu-Co alloys [7].

4. CONCLUDING REMARKS

Alloyed and pure nanoparticles have been obtained by reactive milling in the Cu-Co system. Addition of NaCl helps dispersing and protecting the nanoparticles against oxidation. Electron microscopy and differential scanning calorimetry are used to characterize the alloyed particles and demonstrate that they consist of a single phase i.e., a supersaturated solid solution in metastable condition.

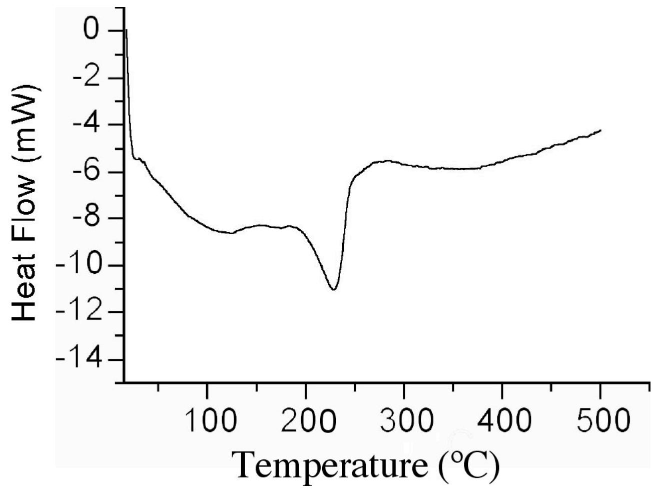

Figure 9. DSC response from a sample consisting of alloyed Cu – 10 at. % Co nanoparticles

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