1838
doi:10.1017/S1431927611010063
Microsc. Microanal. 17 (Suppl 2), 2011

Nanoparticles by Mechanosynthesis in the Immiscible System Cu-Co

J.F. Angeles-Islas, D. Ramirez-Rosales, R. Zamorano-Ulloa, and H.A. Calderon.

Escuela Superior de Física y Matemáticas, IPN, Ed. 9 UPALM Zacatenco Mexico D.F. 07738.

Nanoparticles of different chemical composition have been synthesized by means of reactive mechanical milling. This technique allows the development of structures in metastable equilibrium and it is interesting to vary the composition in a thermodynamically restricted miscibility system such as Co-Cu and investigated the corresponding properties. Reactive milling has been performed by using metal chlorides and promote chemical reduction with Sodium to obtain metallic nanoparticles in NaCl. The milling is made in a high energy Spex mill and additional NaCl is added as a dispersant to inhibit possible agglomeration. Different mixtures of metallic chlorides have been used (5, 20, 50, 80 at.% Co) and including pure Cu and Co. Milling time has also varied from 2 to 40 h at room temperature. The as sintered powders have been characterized by different techniques (X-ray diffraction, calorimetry, and electron microscopy in high resolution mode to determine chemical composition, size and stability of the particles. EPR (electron paramagnetic resonance) and VSM (vibrating sample magnetometry) are used to measure the corresponding magnetic properties.

The as-milled powders contain nanoparticles with chemical compositions that follow the nominal compositions of the mixtures. Chemical analysis of powders report chemical ratios close to the nominally added ones. Little contamination is registered (Fe in small amounts). Figure 1 shows representative nanoparticles as imaged in high resolution electron microscopy for most of the chemical compositions under investigation. The interaction with the beam is characteristic of Co nanoparticles (Fig. 1a) but still sufficient contrast is achieved in the lattice image, most likely due to the aberration correction. The contrast is unaltered for other chemical compositions rich in Cu (Figs. 1b-1e) where particles with a relatively large sizes (2-7) nm are easily found together with nanoparticles with much smaller average sizes (1-2 nm, see Figs. 1b and 1c, for examples). The shapes of the larger nanoparticles are normally elliptical with a considerable number close to spherical as shown in Fig. 1. Most nanoparticles show a polycrystalline nature, most likely related to straining during synthesis. Apparently, the method is efficient to produce a solid solution of immiscible components that remains in metastable equilibrium for long times. The development of a solid solution has been tested by different techniques but the measurement of magnetic properties illustrates here the results. EPR shows patterns typical of solid solutions and completely different to those expected for paramagnetic Cu^{+2} or ferromagnetic Co. The measurements in Fig. 2 can additionally be completely explained on the basis of a behavior predicted by quantum mechanics [1]. The spectra show hyperfine lines produced by Co magnetic cores that can only be found in a solid solution. The number of lines is given by $L=2I+1$, I is the nuclear magnetic moment (3/2 for Co). This results in 4 hyperfine lines that overlap with a similar group of lines (covalent displacement) to give the observed six lines in the figure. The particles with smaller sizes (formed by instantaneous contact between powders and milling balls) presumably affect the magnetic properties of the powders making it possible to use such equations. The smaller particles are domains with extremely small sizes where any overlapping of electronic states is hindered explaining the observed behavior.

References

[1] J.F. Angeles-Islas, PhD Thesis, IPN 2010.

[2] This research has been supported by CONACYT (Grant 51833) and IPN (COFAA, SIP).

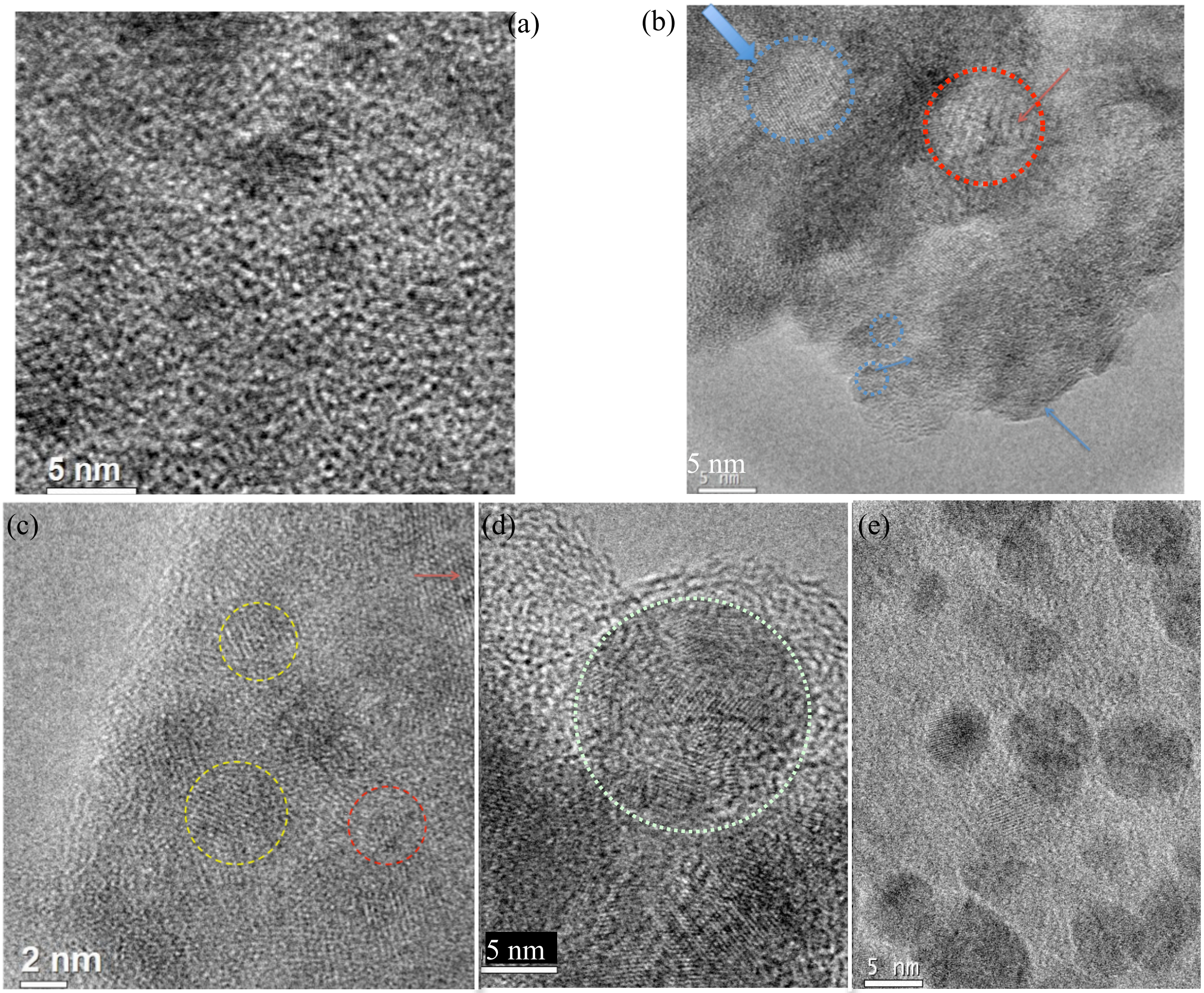

Figure 1. Nanoparticles as function of composition. (a) Pure Co, (b)- (c) 5 at-.% Co, (d) 20 at. % Co and (e) 50 at. % Co. Different synthesized particles sizes after 20 h of milling at room temperature in an excess NaCl environment. Arrows point at different particle sizes.

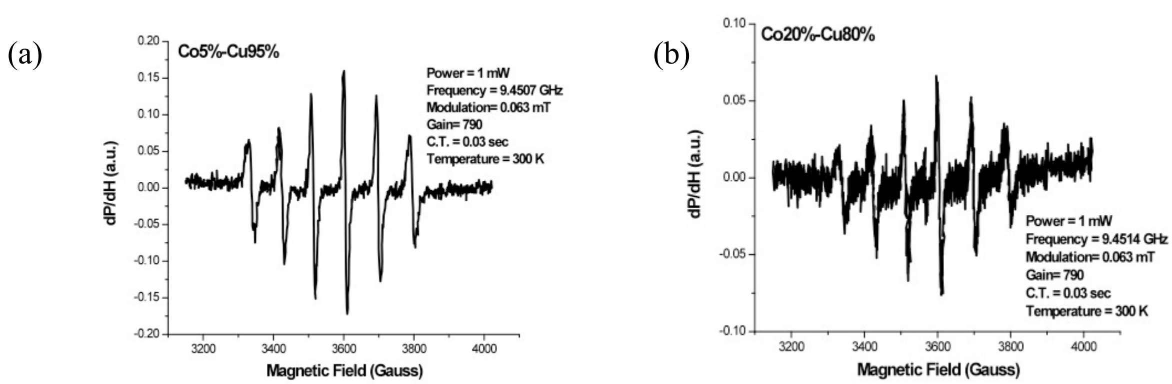

Figure 2. Magnetic measurements by EPR. (a) Cu-5 at.% Co and (b) Cu-20 at.% Co nanoparticles after milling for 40 h.

https://doi.org/10.1017/S1431927611010063 Published online by Cambridge University Press