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Microstructural and Magnetic Properties of Core-Shell Ni-Ce Nanocomposite Particles Assemblies

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ABSTRACT

Novel magnetic core-shell Ni-Ce nanocomposite particles (15-50 nm) are presented. SEM observation indicates a strongly ferromagnetic interacting order with chain-like features among Ni-Ce nanocomposite particle assemblies. Typical HREM image demonstrates that many planar defects (i. e. stacking faults) exist in large Ni core zone (10-45 nm); the innermost NiCe alloy and outermost NiO oxide exist in the thin shell layers (3-5 nm). Nano-diffraction patterns show an indication of well-defined spots characteristic and confirm the nature of this core-shell nanocomposite particles. Superparamagnetic relaxation behavior above average blocking temperature ($T_B = 170K$) for Ni-Ce nanocomposite particles assemblies have been exhibited, this superparamagnetic behavior is found to be modified by interparticle interactions, which depending on the applied field; size distribution and coupling with the strong interparticle interaction. In addition, an antiferromagnetic order occurs with a Néel temperature T_N of about 11K due to Ce ion magnetic order function. A spin-flop transition is also observed below T_N at a certain applied field and low temperature.

INTRODUCTION

Magnetic nanoparticles have been an active subject of intense research due to their unique magnetic properties that are appealing from both scientific and technological points of view [1-3]. Specifically, metallic (Fe, Co, Ni, etc) [3-6] and oxide (γ - Fe_2O_3 , etc) [4] magnetic nanoparticles have attracted considerable attention as high-density magnetic storage media because a high coercive force and a high saturation magnetization can be achieved. Recently, experimental evidences for low temperature superparamagnetism relaxation [7] and the ordering of spin-glass like behavior [4, 8] in some single domain magnetic particles (i.e. γ - Fe_2O_3) had also been of significant interest. In this study, novel Ni-Ce nanocomposite particles coated with NiCe alloy and NiO oxide shell layers were prepared. Their unique microstructure features and superparamagnetic order properties will be reported here.

EXPERIMENTAL

The Ni-Ce particle nanocomposite were prepared by the plasma-metal reaction technique [9]. A JEOL-4000EX high-resolution transmission electron microscope (*HRTEM*) was used to determine the detailed core-shell phase and average grain size of the particle. It also allows recording selected area electron nano-diffraction patterns. A Phillips XL30 scanning electron microscope (*SEM*) equipped with X-ray energy-dispersive analysis (*EDX*) system, was employed to provide the morphology of particles and chemical analysis. The magnetization measurements were performed by using SQUID magnetometer in the temperature range from 2 to 300K at different applied magnetic fields. Measurements were performed by the zero-field-cooling (ZFC) and the field-cooling (FC) methods. From the curves of M vs T (ZFC and FC cases). The average blocking temperature (T_B) was obtained, which is defined as the maximum of the ZFC curve.

RESULTS AND DISCUSSION

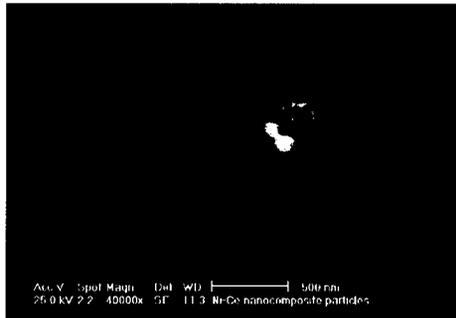


Figure 1. SEM morphology of Ni-Ce nanocomposite particles

SEM image (figure 1) clearly indicates that these particles exhibit strong a tendency of forming chain-like features with negligible shape anisotropy. This chain-like behavior can be attributed to a strong ferromagnetic interaction, and the tendency of reducing the specific surface energy of the system among Ni-Ce nanocomposite particle assemblies.

From the typical HREM image (figure 2) of this Ni-Ce nanocomposite particle, very clear lattice images of core-shell type structure are observed. Each particle consists of a large core and a thin outer shell. In addition, many structural defects are observed, such as stacking faults. Most particles are covered with *ca.* 3-5nm thick crystalline phase, which has some discontinuities (as shown by the arrow of figure 2). This indicates that the shell phases are polycrystalline. The outermost layer spacing is 0.24nm, this value corresponds with that of NiO (111) plane, and in the innermost layers spacing of 0.278nm and 0.219nm have been indicated, which correspond to

NiCe (111) and Ni₂Ce (311) planes, respectively. Nano-diffraction patterns (figure 3) show well-defined rings and spots characteristic of nanocomposite grained materials, where some crystal relationships among orthorhombic [111] of NiCe and cubic [311] of Ni₂Ce, face-center crystal [222] of NiO, cubic [111] of nickel can be identified. These features are due to the core-shell nature of the particles. It is worth noticing that, stacking faults exists in the nickel core region give rise to distortions in the particle crystal surface that lead to the diffuse scattering in the Nano-diffraction patterns.

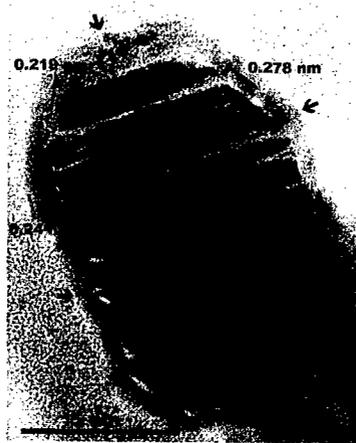


Figure 2. HREM image of Ni-Ce nanocomposite particles with innermost CeNi compounds (lattice spacing, 0.278nm and 0.219nm, for CeNi and CeNi₂, respectively) and outermost NiO layer (lattice spacing, 0.24nm) shell structures. Also planar defects, i.e. stacking faults, as showed in arrows.

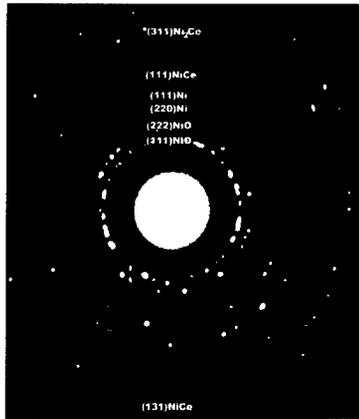


Figure 3. Nano-diffraction patterns of Ni-Ce nanocomposite particles, indicating the crystal relationship among orthorhombic [111] of NiCe and cubic [311] of Ni₂Ce, face-center crystal [222] of NiO, cubic [111] of nickel.

The variations of zero-field-cooled (ZFC) and field-cooled (FC) magnetization with temperature at different applied magnetic field (from 500Gs to 1Tesla) between 2 and 300K are shown in figure 4 (a, b, c, d).

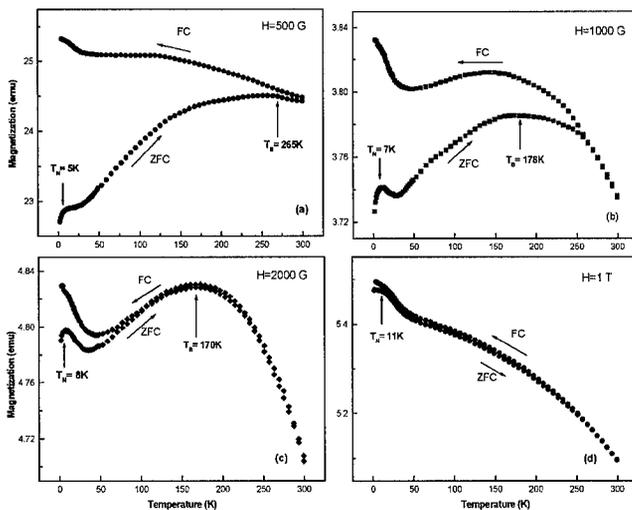


Figure 4 (a, b, c, d). Magnetization as function of temperature for Ni-Ce nanoparticles

Figure 4 (a, b, c, d) shows the typical blocking behavior of superparamagnetic nanoparticles, the Ni-Ce nanoparticles show a different magnetization process when the sample is cooled below the blocking temperature with an applied magnetic field [10]. The ZFC magnetization curves have a broad maximum at about 170K, such a maximum is also a characteristic feature of superparamagnetic relaxation and blocking behavior. Actually, the broad maximum of $\chi_{ZFC}(T)$ suggests a broad distribution of grain sizes of the particle assemblies. The most prominent feature is that the blocking temperature varies as the strength of applied magnetic field changes. This indicates that, such superparamagnetic behavior can be modified by the applied field and the size distribution [11]. SEM images also indicates a strong interparticle interaction among those particle assemblies, and as we know, superparamagnetic properties could be modified by such like dipole-dipole interaction effect [12]. Those effects suggest that our Ni-Ce nanocomposite particles could be considered interaction dominated rather than being pure superparamagnetic ensembles according to the Néel-Brown model.

On the other hand, as shown in the figure 4, the magnetization for Ni-Ce nanoparticles exhibit a sharp maximum around Néel temperature $T_N = 5-11$ K suggesting an antiferromagnetic transition. This can be attributed to the appearance of magnetic ordering of Ce ions [13] in the thin shell layer of Ni-Ce nanocomposite particles. At low temperature, the magnetization of Ni-Ce nanocomposite particles exhibits complicated behavior (see figure 4 (a, b, c, d), which

suggests that a spin-flip occurs below T_N in the antiferromagnetic state of this Ni-Ce nanocomposite particle assemblies

CONCLUSION

A new type of magnetic core-shell Ni-Ce nanocomposite particle (15-50 nm) have been prepared. SEM morphology and HREM image indicate these are typical large cores and thin shell nanocomposite particles with many microstructure defects. Nano-diffraction patterns confirm the nature of these core-shell nanocomposite particles. Modified superparamagnetic behavior above average blocking temperature ($T_B = 170\text{K}$) for Ni-Ce nanocomposite particles assemblies have been exhibited, this superparamagnetic behavior is affected by the strong interparticle interaction. In particular, a spin-flip transition and the antiferromagnetically order with a Néel temperature T_N of about 11K was observed at low temperature for Ni-Ce nanocomposite particle assemblies.

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