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In-situ Scanning Transmission Electron Microscopy Annealing Studies of $Ni_{1-x}Cr_x$ Nanocluster and Correlation with Magnetic Properties

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Metallic nanostructures show unique physical and chemical properties compared to their bulk counterparts due to their high surface area to volume ratio. For instance, magnetic nanoclusters (NCs) show superparamagnetic behavior only when they are below a certain critical size [1]. In addition, intrinsic magnetic properties such as the Curie temperature (T_c), saturation magnetization (M_s), and coercivity are mainly determined by the crystal structure, stoichiometry, and morphology of the NCs. In particular, the T_c of $Ni_{1-x}Cr_x$ NCs drops sharply with increasing Cr concentration [2]. This feature is very attractive and provides a way to tune the T_c of $Ni_{1-x}Cr_x$ NCs between temperatures of 314 and 319 K. One important application of this special feature is localized hyperthermia [3]. Hyperthermia is a method used to treat a variety of tumors by increasing the temperature of the body. Cancer cells are more susceptible to high temperatures (314-319 K) than normal tissue cells, which can survive temperatures up to 333 K. Thus, magnetic NCs in an alternating magnetic field can be used to induce heating of specific regions of the body [2].

To optimize this heating effect, further understanding of growth parameters is needed to control the size, size distribution, nanocluster density, chemical composition, and morphology of magnetic NCs. Transmission electron microscopy (TEM) is a powerful tool to study all these properties at the nanoscale. Furthermore, environmental TEM (E-TEM) offers the advantage to study the annealing effects on the as-grown magnetic nanoclusters and follow the structural and compositional changes *in-situ.*

In this work, we report the correlation between structural and magnetic properties of $Ni_{1-x}Cr_x$ NCs that were prepared by modified magnetron sputtering system. Magnetic NCs were deposited on Si substrates for magnetic measurements and on Si_3N_4 membrane window grids for TEM analysis and *in-situ* heating studies. The magnetic properties were measured using a Quantum Design Physical Property Measurement System (PPMS) after correcting for the diamagnetic contribution of the Si substrate. TEM and STEM analysis were performed using a Cs-corrected E-TEM (FEI Titan^{TM} 80-300kV) operated at 300 kV. The *in-situ* heating studies were performed in STEM mode using a single tilt heating holder (Gatan^{TM}). Additionally, energy dispersive X-Ray analysis was done in order to confirm the average composition of the nanoclusters, and electron energy loss spectroscopy (EELS) elemental mapping was performed to elucidate the structural changes of the nanoclusters during annealing.

Our results show that the as-grown $Ni_{1-x}Cr_x$ NCs present an average size of 6 nm (± 3nm) at room temperature (RT) (Fig. 1A). Annealing the sample up to 550 ºC and cooling down to RT, produced bigger NCs, due to coalescence, resulting in an average size of 11 nm (± 7nm) (Fig. 1B). EDX shows that before and after annealing the average composition is maintained at Ni~95% and Cr~5%. Fig. 1C shows the difference in the magnetic behavior of the as-grown NCs (blue) and the annealed NCs (green). The as-grown NCs show a Ni-core and a NiCrOx shell (Fig. 2), while the annealed nanoclusters show a Ni core and a CrOx shell (Fig. 3). The combination of size increase as well as the rearrangement of the CrOx atoms to the surface generates a drastic change in the magnetic behavior of the NCs. An explanation for this phenomena as well as the loss of the superparamagnetic behavior of the nanoclusters will be presented.

References:
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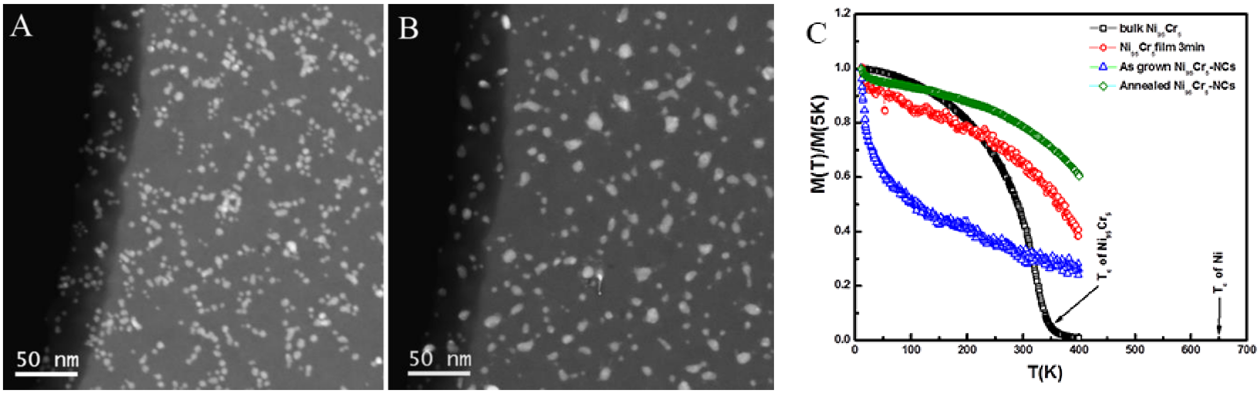

Figure 1. Annular dark field STEM images were adquired at 300kV. The images were taken at room temperature (A) before and (B) after annealing at 550 ºC. (A) Shows the as grown $Ni_{95}Cr_5$ NCs with an average size of 6nm. (B) Shows the same area as (A) after annealing the sample at 550 °C. The NCs undergo coalescence (e.g. red squares) and present a wider size distribution with an average size of 11 nm. (C) Normalized magnetization curves vs. temperature for the as-grown and annealed NCs, as well as for a $Ni_{95}Cr_5$ thin film and bulk $Ni_{95}Cr_5$ for comparison.

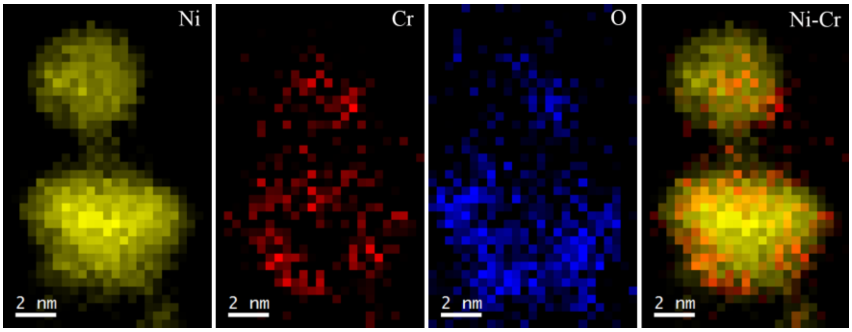

Figure 2. EELS elemental maps of two NCs before annealing. The NCs show Ni cores and NiCrOx shells. The oxidization is due to exposure to air during transportation of the sample.

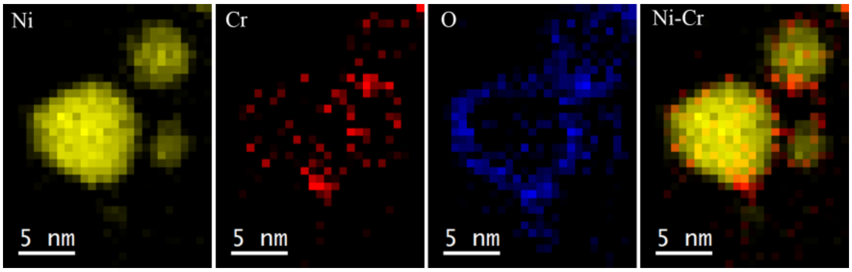

Figure 3. EELS elemental maps of two NCs after annealing at 550 ºC. There is a rearrangement of Ni from the shell to the core resulting in a shell that is mostly CrOx. The stability of the CrOx shell makes it difficult to be reduced at low temperatures in the absence of hydrogen.