SYNTHESIS AND CHARACTERIZATION OF SURFACE MODIFIED COBALT AND COBALT ALLOYS OF CORE-SHELL NANOSTRUCTURE

Abstract

A simple, economic, viable and reproducible polyol process employing a cobalt hydrazine complex precursor is developed and applied to synthesize surface stabilized cobalt and cobalt alloys with the functional properties. The Co crystallites of an anisotropic shape of nanorods (caterpillar like structures) are grown with an average size of 300 nm in length and 40 nm in diameter by carrying out the reaction in a bomb digestion vessel, wherein the excess pressure induced by the gaseous products help in tuning the shape of growing crystallites. The structural characterization revealed that the crystallites predominantly form a metastable fcc-Co phase rather than an hcp-Co phase known of the bulk metal. An fcc \rightarrow hcp phase transformation occurs in increasing the crystallite size above a certain critical value. The experiments were carried out to prepare the cobalt also in the shapes of spheroids and dendrites which present similar magnetic behavior. The M_s value is grown-up regularly at room temperature with increasing the crystallite size layer.

The Co_{0.5}Pt_{0.5} alloy of small crystallites of two different sizes (8 and 30 nm) could be synthesized by simply varying the order of addition of the metal salt precursors in the reaction in a rheological carrier fluid. Smaller the size lower is the transformation temperature from an fcc \rightarrow fct L1₀ structure. A maximum $H_c = 7.781$ kOe is achieved along with M_r/M_s = 0.56 and $M_s = 40.23$ emu/g at room temperature in an 800 °C annealed sample (D = 40 nm) after the reaction scheme-2. Moreover, the Co_{0.5}Pt_{0.5} crystallites (D = 26 nm) annealed at 700 °C after the reaction scheme-1 have a markedly larger M_r/M_s = 0.66 but smaller $H_c = 6.501$ kOe and $M_s = 38.94$ emu/g.

A transmetallation reaction with a modified polyol process is applied in synthesizing Co_xCu_{100-x} (x = 10.7, 21.2, 31.6, 41.8, 51.9, 61.8, 76.4, 90.7) and Co_yAg_{100-y} (y = 20.6, 36.6, 48.5, 60.9, 72.2, 84.6, 94.7) with a core-shell structure. With an increase in the copper salt precursor, a marginal decrease in a Co-core size from 45 nm to 35 nm is observed in the Co_xCu_{100-x} series. An increase in a silver salt precursor under similar conditions results in a drastic decrease of the Co-core size from 45 nm to 8.5 nm. Detailed investigation of the displacement reactions of atomic Co by Cu^{2+} and Ag^+ ions reveal that the Ag^+ displaces Co atoms more efficiently than Cu^{2+} . Both the Co_xCu_{100-x} and Co_yAg_{100-y} core-shell crystallites exhibit a wide ferromagnetic hysteresis loop in the ideal single domains. A superparamagnetic behavior is observed in two specific compositions of $Co_{20.6}Ag_{79.4}$ and $Co_{36.6}Ag_{63.4}$, crystallites with a Co-core size of 8.5 nm. An optimal MR = 3.6% is achieved in an alloy $Co_{36.6}Ag_{63.4}$, and that is decreased to 2% in the $Co_{20.6}Ag_{79.4}$ sample. Both the samples have an average Co-core size of 8.5 nm, i.e., below the ideal single domain size. A reasonable MR value arises in a granular Co_xCu_{100-x} and Co_yAg_{100-y} core-shell structure in the case the core size lies below the ideal single domain size.