

5-2010

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Published In

Journal of Applied Physics, 107, 9, 09A305.

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Metastable γ -FeNi nanostructures with tunable Curie temperature

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(Presented 19 January 2010; received 21 October 2009; accepted 1 December 2009; published online 15 April 2010)

We report on new metastable γ -FeNi nanoparticles produced by mechanical alloying of melt-spun ribbon using a high energy ball mill followed by a solution annealing treatment in the γ -phase region and water quenching in of the face-centered cubic γ -phase. In the Fe–Ni phase diagram there is a strong compositional dependence of the Curie temperature, T_c , on composition in the γ -phase. This work studies the stabilization of γ -phase nanostructures and the compositional tuning of T_c in Fe–Ni alloys which can have important ramifications on the self-regulated heating of magnetic nanoparticles in temperature ranges of interest for applications in polymer curing and cancer therapeutics. To date we have achieved Curie temperatures as low as 120 °C by this method.

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I. INTRODUCTION

Suppression of phase transformations in metastable nanostructures can be used to produce materials with properties that are not obtainable in equilibrium structures. Important recent examples of this can be found in the suppression of the nucleation of the stable γ -phase in Co–Fe-based nanocomposite systems produced from the primary nanocrystallization of amorphous precursors at compositions where the binary Fe–Co phase diagram would predict that the α -phases and γ -phases should coexist.^{1–3} In Fe–Ni-based nanocomposite systems, a similar phenomenon is observed in Fe-rich alloys⁴ where the nucleation of the equilibrium α -phase is suppressed in favor of the metastable γ -phase. This can also have profound effects on technical magnetic properties because on the Fe-rich side of the Fe–Ni phase diagram there is a strong compositional dependence of the Curie temperature, T_c , on composition in the γ -phase.⁵

In this work we describe the stabilization of γ -phase nanostructures in magnetic alloys produced by primary crystallization of amorphous precursors. We discuss the merits of the synthesis route on the compositional tuning of T_c which can have important ramifications on the self-regulated heating of magnetic nanoparticles⁶ in temperature ranges of interest for applications in polymer curing (~ 100 °C),⁷ cancer therapeutics (~ 42 °C), and the design of efficient magnetocaloric refrigerants.⁸

II. EXPERIMENTAL PROCEDURE

The method employed to synthesize a metastable γ -FeNi phase was mechanical alloying of $(\text{Fe}_{73}\text{Ni}_{27})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ melt-spun ribbon using a high energy ball mill followed by a solution annealing treatment in the γ -phase region and water quenching to stabilize the γ -phase. Mechanically milled $(\text{Fe}_{73}\text{Ni}_{27})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy ribbons are typically a metastable mix of the equilibrium α -Fe (bcc) and FeNi_3 (fcc)

phases. To stabilize the metastable γ -FeNi phase, with a desirable T_c , solution annealing in the γ -phase region followed by quenching is necessary. Figure 1 illustrates the Fe–Ni binary phase diagram⁹ with information on the compositional dependence of the Curie temperature, $T_c(X_{\text{Ni}})$. This $T_c(X_{\text{Ni}})$ behavior for the γ -phase can be extrapolated to metastable regions of the Fe–Ni phase diagram where desired T_c 's near 100 °C are predicted to occur near the 27% Ni composition. However, since the extrapolated $T_c(X_{\text{Ni}})$ curve is steep in this region of the phase diagram, a deviation in the stoichiometry of only a few atomic percent can result in a large change in the T_c of the alloy.

High energy ball milling for 24 h was used to synthesize nanopowders from $(\text{Fe}_{73}\text{Ni}_{27})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ melt-spun ribbon. Powder samples were removed after 12, 16, 20, and 24 h for phase and particle size analysis. The heat generated from the constant grinding of the steel balls (about 300 °C) against the powder causes these powders crystallize and form a two-phase mixture of 36.51% fcc FeNi_3 and 63.49% bcc α -Fe, as predicted from the Fe–Ni binary phase diagram.

To facilitate the transformation into the metastable

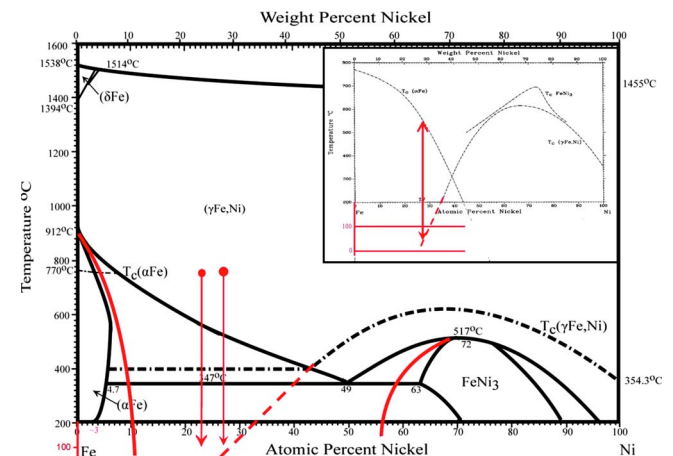


FIG. 1. (Color online) Fe–Ni phase diagram with T_c -composition curves and vertical lines showing composition choice for a T_c of 100 °C.

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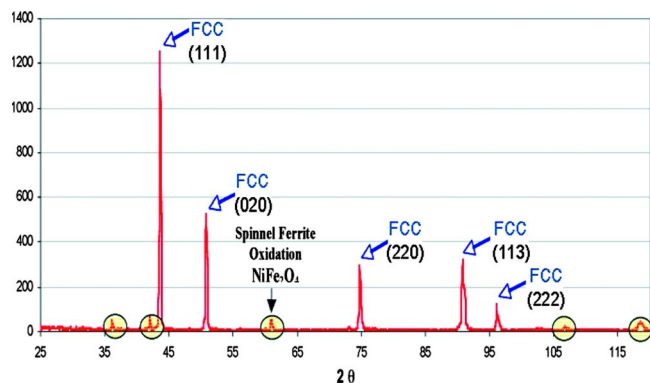


FIG. 2. (Color online) XRD pattern for $\text{Fe}_{73}\text{Ni}_{27}$ nanoparticles after annealing and water quenching to obtain the fcc γ -phase.

phase, the particles were encapsulated in a quartz glass tube which was evacuated and refilled with Ar gas to prevent oxidation of the Fe–Ni powder. The $(\text{Fe}_{73}\text{Ni}_{27})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ powder was then annealed to 700 °C, in the γ -phase region, for 2 h followed by water quenching to retain the metastable fcc γ -FeNi phase. This rapid cooling ensures that the particles do not have sufficient diffusion time required for phase separation into the equilibrium phases.

High-temperature vibrating-sample magnetometry was used to measure Curie temperatures on heating the metastable γ - $\text{Fe}_{73}\text{Ni}_{27}$ nanopowders from room temperature to 600 °C. An average heating rate of 5 °C/min in the temperature range of interest was employed.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) shows that after annealing and quenching the $\text{Fe}_{73}\text{Ni}_{27}$ nanoparticles, the mixture of bcc α -Fe and fcc FeNi₃ phases were transformed into solely fcc γ -phase; indicated by the presence of only fcc peaks (Fig. 2). This shows that a nearly single γ -phase $\text{Fe}_{73}\text{Ni}_{27}$ nanoparticles are present. The additional small peaks matched to known XRD patterns for a spinel ferrite oxide (NiFe_2O_4) present on the sample after the high energy mechanical milling process. A Scherrer's analysis¹⁰ of line broadening in XRD patterns estimated a mean particle size of ~ 10 nm.

Transmission electron microscopy (TEM) was carried out on a JEOL 2000EX microscope with operating voltage of 200 keV. Nanoparticles were dispersed in absolute ethanol and deposited on a carbon-coated copper grid. TEM was used to examine the morphology of the nanoparticles and selected area electron diffraction (SAED) was used to identify present crystalline phases. Mean particle size was determined to be 20 nm from a sampling of approximately 100 nanoparticles [Fig. 3(a)]. The SAED pattern confirms the presence of the fcc γ -phase [Fig. 3(b)], where the position and relative intensities of diffracted rings match well with theoretical values for fcc Fe–Ni alloys.

Figure 4 shows magnetization versus temperature, M versus T , plots where the Curie temperatures, T_c , were estimated by squaring the reduced magnetization and extrapolating to $m=M/M_s=0$. A Curie temperature of 120 °C for the γ -phase $\text{Fe}_{73}\text{Ni}_{27}$ nanoparticles is observed upon heating of the alloy from room temperature to 200 °C. Figure 4 also

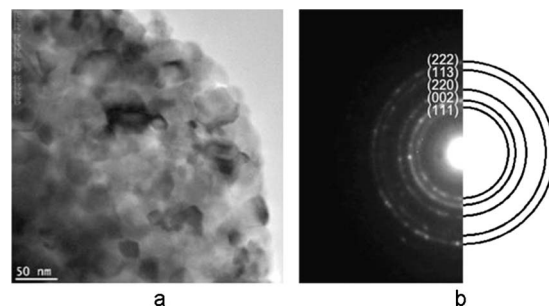


FIG. 3. (a) TEM bright field image of mechanically milled FeNi nanoparticles and (b) SAED pattern.

shows the transformation of the metastable fcc γ -phase back into the higher Curie temperature bcc α -Fe phase upon heating to 600 °C. The bcc α -Fe phase is shown to have a Curie temperature around 550 °C. We note the good agreement of the experimentally estimated values of T_c with the values predicted from the $T_{c(\gamma\text{-Fe,Ni})}$ dotted lines in Fig. 1 for the $\text{Fe}_{73}\text{Ni}_{27}$ composition used.

The compositional tuning of T_c in these magnetic nanoparticles have important application in the radio frequency (rf) magnetic heating to cure diglycidyl ether of bisphenol-A based epoxy resins at 120 °C for use in high-performance protective coatings, structural adhesives, and low-stress integrated circuit encapsulants.¹¹ In addition, further reduction in T_c may be of use to target other applications such as cancer therapeutics ($T_c \sim 42$ °C) and magnetocaloric refrigeration ($T_c \sim 25$ °C).

IV. CONCLUSION

It has been shown here that the stabilization of γ -phase $\text{Fe}_{73}\text{Ni}_{27}$ nanopowder is possible through solution annealing in the γ -phase region followed by immediate water quenching. This fcc γ -phase is shown to have a lower Curie temperature ($T_c=120$ °C) than the equilibrium bcc α -Fe phase ($T_c=550$ °C) for the $\text{Fe}_{73}\text{Ni}_{27}$ composition. Once in the γ -phase, the T_c of the particles can be tailored by varying the Ni concentration in the alloy for use in applications such as polymer curing and cancer therapeutics.

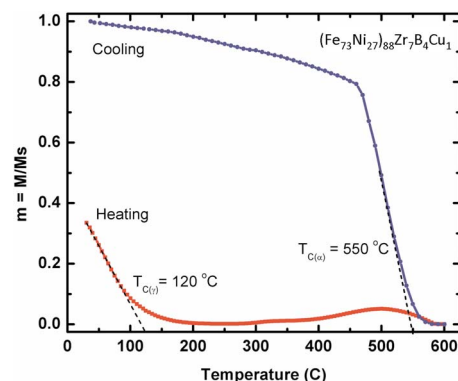


FIG. 4. (Color online) Reduced moment (m) vs temperature curve measured for metastable γ -phase $\text{Fe}_{73}\text{Ni}_{27}$ nanopowder illustrating the transformation back into the higher Curie temperature bcc α -Fe phase upon heating to 600 °C.

ACKNOWLEDGMENTS

K.J.M. and M.E.M. acknowledge support from STTR Proposal “Novel Management of Transducer Heat and Non-linearity” Topic No.: N08-T020 under Contract No. N00014-08-M-0313. K.J.M. and M.E.M. gratefully acknowledge helpful discussions with Professor O’Handley, Dr. Jiankang Huang, Jesse Simon, and Yiming Liu. “The Wise never forget a help received.”

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