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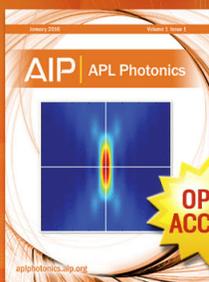
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High temperature x ray diffraction determination of the body-centered-cubic–face-centered-cubic transformation temperature in $(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ nanocomposites

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In situ high-temperature x ray diffraction and magnetization measurements were performed on a melt-spun $(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ amorphous alloy to follow its structural evolution. At 728 K, a bcc-FeNi phase was observed as the primary crystallization product followed by transformation to an fcc phase ~ 773 K. During cooling to room temperature, the fcc-to-bcc transformation was not observed, and the metastable fcc-NiFe phase was retained at room temperature. © 2012 American Institute of Physics. [doi:10.1063/1.3675990]

INTRODUCTION

Fe-Ni alloys have been extensively studied, due to their technologically important magnetic and mechanical properties. Moreover, it is known that Fe-based alloys prepared by rapid solidification techniques exhibit good soft magnetic properties^{1–3} and applicability in magnetic devices as motors, generators, transformers, sensors,¹ and, more recently, for magnetic refrigeration.^{4–6} Recently, the magnetocaloric effect⁷ (MCE) has spurred much research activity worldwide, with the objective to develop compositions exhibiting large magnetocaloric response.

There has been recent interest in the study of the metastable fcc γ -phase in the Fe-rich region of the Fe-Ni phase diagram,⁸ where extrapolation of the composition dependence of the Curie temperature for the stable γ -phase at high Ni concentrations suggest the possibility of a metastable γ -FeNi alloy with a low Curie point, suitable for applications near to room temperature.^{8,9} Thus, γ -FeNi alloys are interesting for magnetic applications, including self-regulated heating¹⁰ and MCE, because of the possibility to obtain compositions with tunable Curie temperature by changing the Fe/Ni ratio.

In our previous works,^{9,10} we demonstrated the production of the metastable fcc-FeNi phase by quenching the material from γ -phase field to room temperature and the applicability of these materials for, e.g., cancer thermotherapy. Other authors^{8,11,12} show that, in equilibrium for a Fe/Ni ratio 70/30, exist a two-phase field, and fcc and bcc phases coexist. We have shown it is possible to obtain a single γ -FeNi phase by high-energy mechanical alloying.⁶

Given the interest in the metastable γ -phase in the Fe-rich region of the Fe-Ni system for magnetocaloric applications, we have undertaken study of the alloys produced by primary nanocrystallization of amorphous

precursors. We describe studies of the structural phase evolution of melt-spun FeNiZrBCu amorphous alloy using *in situ* high-temperature x ray diffraction and magnetic measurements to understand the metastable phase evolution with time. The results described provide proof, in principle, for this as a viable processing route to produce metastable γ -FeNi nanostructures.

EXPERIMENTAL

$(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy ribbons were produced by melt-spinning technique, starting from high purity precursors arc-melted in an Ar atmosphere. The as-quenched structure was characterized by x ray diffraction using Cu K α radiation in a X'Pert PRO Multi Purpose Diffractometer. *In situ* high temperature x ray diffraction (XRD) patterns were also performed at 2 K/min. Samples were heated from room temperature up to 973 K in steps of 50 K and cooled to room temperature in steps of 100 K at 4 K/min. XRD patterns over a wider angular range have been taken, but for clarity, we show only those for which we use the integrated intensity to estimate the volume fractions of the fcc and bcc phases. We have applied a deconvolution procedure to fit the main reflection using pseudo-Voigt functions to represent each phase. We then used the area ratio to calculate the phase fraction of each contribution. Magnetization as a function of temperature was measured using a Lakeshore 7407 vibrating sample magnetometer (VSM). For this experiment, a temperature range from room temperature up to 1123 K and to 313 K and an applied magnetic field of 0.3 T were used.

RESULTS AND DISCUSSION

High temperature x ray diffraction (XRD) patterns are shown in Fig. 1(a). An amorphous structure is observed at room temperature for the as-cast sample. As temperature increases, XRD patterns show that the primary crystallization, α -FeNi crystals, occurs at ~ 673 K and the initial crystal

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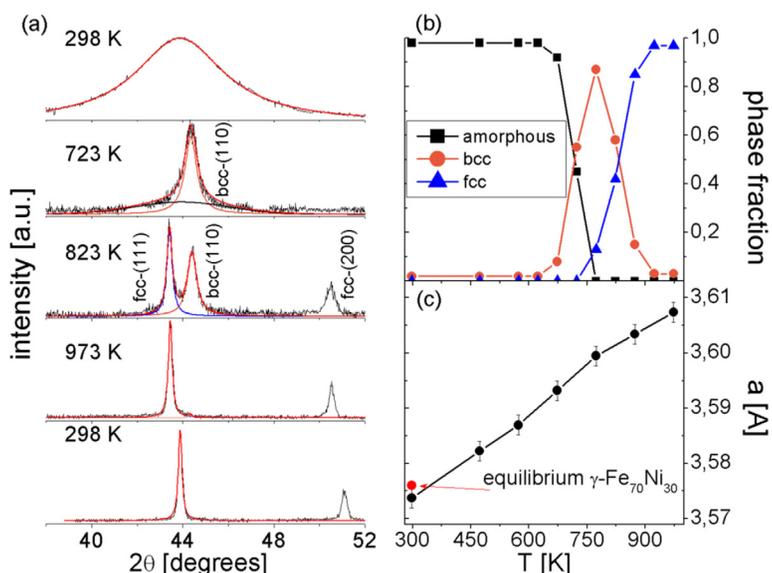


FIG. 1. (Color online) (a) *In situ* high-temperature x ray diffraction for some temperatures. (b) Temperature dependence of the phase fraction evolution. (c) Lattice parameter of the fcc-FeNi phase as a function of temperature.

size is 15 nm, determined by Scherrer method.¹³ At 773 K, a small shoulder indexed as (111) fcc-FeNi is observed, in agreement with previous observations for a Fe₇₀Ni₃₀ system.¹⁴ At higher temperatures, we observe an increase in γ -FeNi phase fraction, as illustrated in Figs. 1(a) and 1(b). The crystal size of the γ -FeNi phase increases from 15 nm at 773 K up to 40 nm at 973 K. Note that the fcc phase appears after the amorphous phase has crystallized in bcc phase, indicating that the fcc phase transforms from the bcc phase.

Figure 2(a) shows a magnetization curve performed for the as-cast sample. The first magnetic transition observed is the ferromagnetic to paramagnetic transition for the amorphous phase at ~ 613 K. Above this temperature, the crystallization of α -FeNi crystals is seen to begin at ~ 728 K. This difference in the crystallization temperature of the α -FeNi crystals from both experiments could be ascribed to heating rate differences.

The kinetics of primary crystallization in similar Fe and Fe-Co based alloys has been characterized within the context

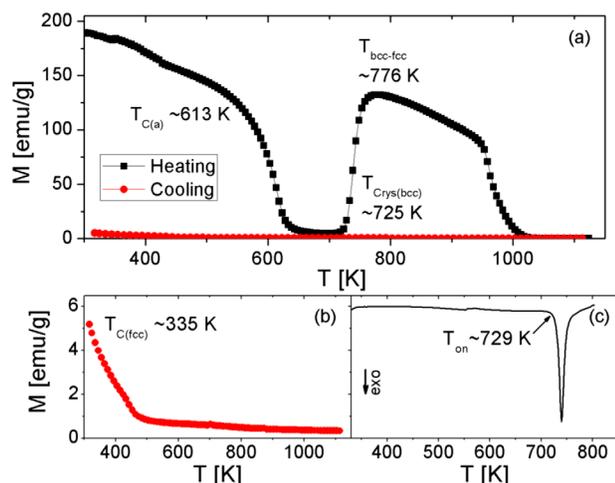


FIG. 2. (Color online) (a) Magnetization as a function of temperature at 0.3 T. (b) Magnetization curve for cooling process. (c) DSC scan for as-cast sample at 10 K/min.

of Johnson-Mehl-Avrami kinetics and will be the subject of future research for these materials.^{15,16} Kinetics studies indicate the importance of the time scale for experimental determination of a transition temperature. The lower crystallization temperature determinate from XRD as compared to that observed in magnetization data is explained by isothermal crystallization, due to the longer time required to record each pattern.¹⁷ Differential scanning calorimetry, DSC, scans for an as-cast sample (Fig. 2(c)), agree with the magnetic measurement. For higher temperatures, the bcc-fcc phase transformation at ~ 780 K is observed, in agreement with XRD data and the Fe-Ni phase diagram.¹⁸

After heating, XRD patterns and magnetic measurement were also recorded on cooling (Figs. 1(a), 2(a), and 2(b)). From XRD patterns, a monotonically decreasing lattice parameter of the γ -FeNi phase is observed, which is ascribed to lattice contraction¹⁹ (Fig. 1(c)). From the magnetization curve, an increase can be seen in magnetic moment at low temperatures, below 473 K, where the para-ferromagnetic transition of the fcc-FeNi phase is expected to take place.

Contrary to the expected behavior, the fcc-bcc phase transformation was not observed from both experiments. This is contrary to previous observations in ribbons of a similar, but more Fe-rich, composition (Fe₇₃Ni₂₇)₈₈Zr₇B₄Cu₁.¹⁰ This result shows that the diffusion-controlled structural ($\gamma \rightarrow \alpha + \text{FeNi}_3$) phase transformation was suppressed, extending the thermal stability of the γ -(Fe₇₀Ni₃₀) phase at room temperature with Ni content.

The extended stability of the γ -phase is still an open question. While prior published phase diagrams indicate a two-phase, $\alpha + \text{FeNi}_3$, field at room temperature and low Fe concentrations, more recent studies suggest a miscibility gap between the FeNi₃ and Fe-rich fcc-phase, which would be accompanied by spinodal decomposition, in which these phases partition in fine lamellar structures. The large, shared interfacial area enhances the stability of the fcc-phase.¹⁹ Moreover, the kinetics of spinodal decomposition would be enhanced in nanostructures.

CONCLUSIONS

We have studied the structural evolution of $(\text{Fe}_{70}\text{Ni}_{30})_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ amorphous composition. This material shows a primary crystallization of bcc-FeNi-type crystals at 673 K. The fcc-FeNi phase transforms from the bcc-FeNi crystals at 780 K and has an extended stability at low temperatures.

This enhanced stability of the fcc-FeNi phase to low temperatures is significant for enabling the use of this kind of composition for magnetic applications around room temperature, e.g., for magnetocaloric applications.

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