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Tuning the Curie temperature in γ -FeNi nanoparticles for magnetocaloric applications by controlling the oxidation kinetics

Huseyin Ucar,^{1,a)} John J. Ipus,² D. E. Laughlin,¹ and M. E. McHenry¹

¹Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA

²Dpto. Física de la Materia Condensada, ICMSE-CSIC, Universidad de Sevilla, Spain

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Mechanically alloyed Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ alloys were characterized in terms of their structural and magnetic properties. Previous studies showed that single phase FCC γ -FeNi alloys with \sim 26-30 at. % Ni have Curie temperatures, T_c , near room temperature. Having T_c near room temperatures along with large magnetization makes γ -FeNi alloys attractive for room temperature magnetocaloric cooling technologies. To obtain a single γ -phase, particles were solution annealed in the γ -phase field and water quenched. The preferential oxidation of Fe during ball milling was used as a means to tune the Curie temperature, T_c , of the alloy. Refrigeration capacities, RC_{FWHM} , of the Fe₇₀Ni₃₀ and the Fe₇₂Ni₂₈ alloys were calculated to be \approx 470 J/kg and 250 J/kg at 5 T, with peak temperatures \approx 363 K and \approx 333 K, respectively. The RC_{FWHM} for the Fe₇₀Ni₃₀ is higher than the previously reported Nanoperm (Fe₇₀Ni₃₀)₈₉Zr₇B₄ type alloy and on the same order of magnitude with other Fe-based alloys. The maximum magnetic entropy change values observed for the Fe₇₀Ni₃₀ and the Fe₇₂Ni₂₈ are 0.65 and 0.5 J kg⁻¹ K⁻¹, respectively, at a field of 5 T. These are smaller than those of rare earth magnetic refrigerants showing first order transformation behavior. The larger RC_{FWHM} value results mainly from the width of the magnetic entropy curve in these types of materials. We discuss the economic advantage of these rare earth free refrigerants.

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Soft magnetic γ -FeNi nanostructures are attractive candidates for magnetocaloric applications. They have low hysteresis losses and tunable Curie temperatures, T_c , with minor compositional changes. They also can be suspended in solutions thus providing versatility in applications. A relatively low magnetic entropy change of these alloys would yield a small adiabatic temperature change at a single temperature but tuning over the temperature to span a range of temperatures in a thermodynamic cycle can impact thermodynamic efficiency.

To produce γ -FeNi nanoparticles, one technique is mechanical alloying (MA) of powders using high energy ball milling followed by solution annealing treatment.

In MA, high energy ball milling generates heat due to grinding of steel balls against the powder which causes oxidation of nanoparticles. Here, we demonstrate the tunability of the T_c of γ -FeNi nanoparticles by controlling the oxidation kinetics during synthesis. In addition, we propose γ -FeNi alloys as an alternative to other magnetocaloric refrigerants operating near room temperature. Previous work on controlling oxidation kinetics and interfaces in the FeCo system for RF applications inspired us to tune the T_c of γ -FeNi metastable phase with similar processes.^{1,2}

Temperature increases during milling have been reported to be \sim 300 °C for the Fe-1.2% C system³ and \sim 180 °C for the Ni-Zr binary system.⁴ In another study, it was reported that 80% of the temperature rise during milling comes from the motor and bearings, while 20% is due to the friction between the balls and milling container and the presence of an exothermic reaction.⁵ The temperature rise in

Fe-Ni system is expected to be on the same order of magnitude with those cited alloy systems.

Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ alloys were produced by ball milling in a shaker mill (Spex 8000D) from elemental Fe, Ni powders under Ar atmosphere. The initial powder mass was 8 g and the ball to powder ratio was 10:1. After selected milling times as mechanically alloyed powder samples were taken out from the vials to characterize crystal structure by x-ray diffraction (XRD) using Cu K α radiation in an X'Pert PRO MPD diffractometer. In order to obtain a material with a single γ -FeNi phase, Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ powders were subsequently sealed in a quartz crucible with Ar atmosphere and annealed in the γ -phase region, 700 °C, and quenched in water to stabilize the metastable γ -FeNi phase. Besides the structure using x-ray diffractometer, magnetic properties of the γ -FeNi phase were studied using a Lakeshore 7407 vibrating sample magnetometer using a maximum applied field of 0.55 T at constant temperatures in the range of room temperature to 523 K. The magnetic entropy change due to the application of a magnetic field has been calculated using a numerical approximation to the equation

$$\Delta S_M = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

where ΔS_M is the magnetic entropy change, M is the magnetization, and T is the temperature. The partial derivative is replaced by finite differences and the integration is performed numerically from zero to the maximum value of the applied magnetic field.

In this study, RC_{FWHM} , defined as the product of the peak entropy change times the full width at half maximum (FWHM) of the peak ΔT , $RC_{FWHM} = |\Delta S_M^{pk}| \Delta T$ was used as

^{a)}Author to whom correspondence should be addressed. Electronic mail: hucar@andrew.cmu.edu.

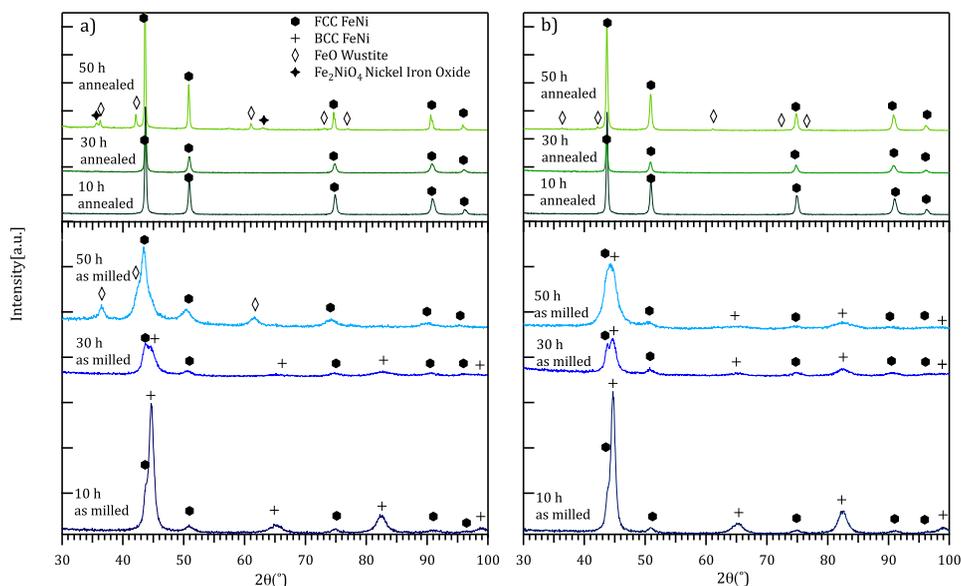


FIG. 1. X-ray diffraction patterns of 10, 30, 50 h as-milled powders and solution annealed powders at 700 °C for 1 h followed by quenching for (a) Fe₇₀Ni₃₀ and (b) Fe₇₂Ni₂₈.

a figure of merit. For materials that did not cover sufficient area around the peak, e.g., Fe₇₂Ni₂₈, RC_{FWHM} was estimated by extrapolating the experimental data to the temperatures required for this calculation.

Fig. 1 presents x-ray diffraction patterns from powders of both Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ alloys ball milled for 10, 30, 50 h and powders of these which were annealed in the γ -phase field followed by quenching. The diffraction patterns for 10 and 30 h milled Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ powders reveal both fcc and bcc phases and the fcc ratio is observed to increase with milling time for Fe₇₀Ni₃₀ while it is invariant for Fe₇₂Ni₂₈. While Fe₇₀Ni₃₀ exhibits only fcc peaks and additional oxide peaks that are indexed to FeO (wustite), Fe₇₂Ni₂₈ alloy is observed to retain both fcc and bcc phases after 50 h of milling. While wustite is observed for the two compositions after solution annealing the 50 h milled alloys, the γ -stabilized Fe₇₀Ni₃₀ exhibits NiFe₂O₄ (NiFe oxide) peaks in addition to the wustite. The lattice parameter of the wustite was found to be $a = 4.290 \pm 003 \text{ \AA}$ which agrees well with the results from JCPDS index of wustite.⁶

Even though the equilibrium phase diagram dictates the coexistence of bcc and fcc at low temperatures, the supersaturation of fcc γ -FeNi is obvious from 50 h ball milled powders.⁷ The two phase region is reported to narrow with milling intensity which is caused by the temperature dependence of the metastable equilibria.⁸ Here, we observe the narrowing of the two-phase field with milling time at increased temperature attributed to the additional dissolution of Fe in fcc FeNi.

The heat generated due to grinding of steel balls against the powder leads to oxidation of particles as is seen in the XRD patterns of 50 h as milled powders of Fe₇₀Ni₃₀ and γ -phase stabilized 50 h milled powders of both compositions. In the Fe–Ni system, there is a strong dependence of the Curie temperature, T_C , on composition in the γ -phase.⁹ Since wustite and nickel-iron oxides are Fe-rich, their formation depletes Fe from the core. This in turn changes the T_C of the system. Tuning the RC with the T_C can be accomplished with the formation of an oxide layer. In tuning the RC, exchange coupling of the 2-phase core/shell structure is exploited. This is analogous to disorder induced broadening of the transition due to distributed exchange interactions.^{10,11}

Magnetocaloric response is calculated using Eq. (1) using isothermal magnetization curves. Fig. 2 illustrates the magnetic entropy change, ΔS_m , for annealed γ -Fe₇₀Ni₃₀ and γ -Fe₇₂Ni₂₈ powders for a maximum applied field of 0.55 T.

The maximum magnetic entropy change values observed for annealed γ -Fe₇₀Ni₃₀ are 0.32, 0.22, and 0.17 J kg⁻¹ K⁻¹ with peak entropy change temperatures of 333, 363, and 443 K for 10, 30, and 50 h of ball milling, respectively. From the Fe–Ni phase diagram⁷ and the composition dependence of the Curie temperatures of each powder, the Fe content in the nanoparticles is estimated. The Fe content was 71 at. % Fe after 10 h of milling and systematically decreases to 69 and 67 at. % Fe for 30 and 50 h of milling.

The maximum entropy change is 0.19 J kg⁻¹ K⁻¹ with a peak entropy change around 333 K for 50 h milled γ -Fe₇₂Ni₂₈ powder. Since the Curie temperatures of the 10 and 30 h milled γ -Fe₇₂Ni₂₈ powders were slightly below the room temperature, their peak entropy and other magnetocaloric properties could not be assessed. The ΔS_m and RC_{FWHM} can be expressed as a power law for materials with a second order phase transition¹²

$$\Delta S_m = AH^n, \quad (2)$$

where A is a prefactor. With this equation, ΔS_m and RC_{FWHM} can be extrapolated to higher fields, which is necessary for comparing the magnetocaloric response with some of the benchmark refrigerants. The magnetic entropy was calculated using the experimental results obtained for a range of fields from 100 Oe to 5500 Oe in 200 Oe field increments and fitted to Eq. (2). The fitting parameters obtained from the experimental data were used to extrapolate the ΔS_m and RC_{FWHM} . In calculating the RC_{FWHM} , the aforementioned relationship, $RC_{FWHM} = |\Delta S_M^{pk}| \Delta T$, was used. The extrapolated RC_{FWHM} at 5 T for γ -Fe₇₀Ni₃₀ are 342, 470, and 324 J K⁻¹ for 10, 30, and 50 h milled powders, respectively. The fitting parameters from Eq. (2) are $A = 0.0320, 0.0283, 0.0134$ and $n = 0.858, 0.898, \text{ and } 0.933$ for 10, 30, and 50 h milled powders, respectively. The decrease in RC after 50 h of milling is due mainly to the increased oxide formation as it lowers the magnetic moment. The extrapolated RC_{FWHM} value for 50 h milled Fe₇₂Ni₂₈ is

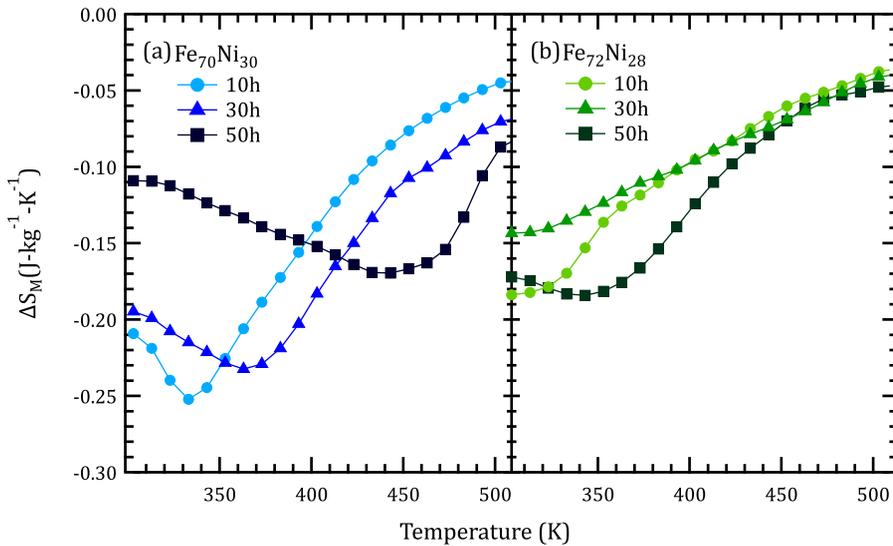


FIG. 2. Temperature dependence of the magnetic entropy change, ΔS_M , corresponding to a magnetic field change $\Delta H_M = 0.55$ T for (a) γ -Fe₇₀Ni₃₀ and (b) γ -Fe₇₂Ni₂₈ at different milling times followed by an additional solution annealing treatment to obtain the γ phase.

TABLE I. Peak temperature, peak entropy change, RC_{FWHM} , RC_{AREA} , and RC_{WP} values of promising magnetocaloric refrigerants are presented.

Nominal composition	T_{pk} (K)	$ \Delta S_M^{pk} (1.5\text{ T})$ J kg ⁻¹ K ⁻¹	$RC_{FWHM}(1.5\text{ T})$ J kg ⁻¹	$RC_{FWHM}(2\text{ T})$ J kg ⁻¹	$RC_{FWHM}(5\text{ T})$ J kg ⁻¹	$RC_{AREA}(5\text{ T})$ J kg ⁻¹	$RC_{WP}(5\text{ T})$ J kg ⁻¹	Ref.
Fe ₇₅ Nb ₁₀ B ₁₅	250	0.6	115		445		283	13
Mn _{1.1} Fe _{0.9} Pe _{0.78} Ge _{0.22}	280	10			400			14
La(Fe _{0.89} Si _{0.11}) ₁₃ H _{1.3}	291			165.6				15
Pr ₂ Fe ₁₇	300				573			16
Gd ₅ Fe _{1.9} Si ₂ Fe _{0.1}	300				630	355	240	17
Fe ₈₈ Zr ₇ B ₄ Cu ₁	300	1.3	166		654	496		18
Fe ₇₂ Ni ₂₈	333	0.5	84	110	250			This study
(Fe ₇₀ Ni ₃₀) ₈₉ Zr ₇ B ₄	342	0.7			330			19
Fe ₇₉ Gd ₁ Cr ₈ B ₁₂	355	1.42	153		627	459		20
Fe ₇₀ Ni ₃₀	363	0.65	158	204	470			This study

250 J K⁻¹ with $A = 0.0141$ and $n = 0.905$. The peak magnetic entropy change and RC values of the studied alloys with their extrapolations to 5 T are shown in Table I. Other magnetocaloric materials are listed for comparison.

From Table I, Gd₅Fe_{1.9}Si₂Fe_{0.1} and Fe₈₈Zr₇B₄Cu₁ have slightly higher refrigeration capacities than γ -Fe₇₀Ni₃₀ and γ -Fe₇₂Ni₂₈ alloys. However, as previous study on Fe based alloys showed, Fe-Ni system is economically more advantageous which would facilitate its industrial scale-up.²¹ Fe based alloys suffer from relatively low magnetic entropy change, which would result in low adiabatic temperature changes but may be attractive in cycles designed to span large temperature ranges, i.e., between the freezing and boiling points of typical fluid carriers.

Microstructure and magnetocaloric response of mechanically alloyed Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ compositions have been studied with the following observations:

- (1) With milling time, we found that the bcc phase was destabilized with respect to fcc phase. This also agrees well with previous studies, which state that the composition ranges of the fcc and bcc single phase regions are greatly extended with respect to their equilibrium ranges by mechanical alloying.^{8,22}
- (2) Extended milling times induce oxidation of particles due to high temperatures achieved during operation. This can be utilized to tune the T_C of γ -FeNi alloy since preferential oxidation of Fe atoms changes the composition of the particles.

- (3) Fe₇₀Ni₃₀ and Fe₇₂Ni₂₈ are introduced as an alternative to other rare-earth containing magnetocaloric refrigerants operating near room temperature.

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