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The equimolar alloy FeCoCrNi, a high-entropy alloy, forms in the face-centered-cubic crystal structure and has a ferromagnetic Curie temperature of 130 K. In this study, we explore the effects of Cr concentration, cold-rolling, and subsequent heat treatments on the magnetic properties of FeCoCr$_x$Ni alloys. Cr reductions result in an increase of the Curie temperature, and may be used to tune the T$_C$ over a very large temperature range. The magnetic entropy change for a change in applied field of 2T is $\Delta S_m = -0.35$ J/(kg K) for cold-rolled FeCoCrNi. Cold-rolling results in a broadening of ΔS_m, where subsequent heat treatment at 1073 K sharpens the magnetic entropy curve. In all of the alloys, we find that upon heating (after cold-rolling) there is a re-entrant magnetic moment near 730 K. This feature is much less pronounced in the as-cast samples (without cold-rolling) and in the Cr-rich samples, and is no longer observed after annealing at 1073 K. Possible origins of this behavior are discussed. © *2013 American Institute of Physics.*
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High-entropy alloys (HEAs) are systems containing four or more elemental constituents with nearly equimolar compositions.[1] The magnetic properties of FeCoCrNi based HEAs have been reported by several groups. Wang *et al.* presented *M(H)* curves at room temperature for as-cast FeCoCrNiCu and FeCoCrNiCuAl.[2] Zhang *et al.* presented *M(H)* curves at room temperature and *M(T)* curves from 100 to 350 K for as-cast and annealed FeCoCrNiCuAl alloys.[3] Lucas *et al.* performed high temperature *M(T)* measurements and showed that the addition of Pd increases the T$_C$ of FeCoCrNi from below room temperature to 440 K for FeCoCrNiPd and to 503 K for FeCoCrNiPd$_2$.[4] The purpose of this work was to determine the effects of Cr composition and annealing on the thermomagnetic properties of FeCoCr$_x$Ni alloys.

Alloys with the stoichiometry Fe$_1$Co$_1$Cr$_x$Ni$_1$ (referred to as FeCoCr$_x$Ni) were prepared from elemental Fe, Co, Cr, and Ni of purities 99.97%, 99.9%, 99.2%, and 99.95%, respectively, by arc-melting under an argon atmosphere. Each sample of approximately 5 g was melted and flipped three times to ensure homogeneity. All samples were cold rolled to a thickness of 350 μm. The samples were quite ductile and were easily cold rolled to a thickness of 15 μm without tearing of the resulting foil. One sample of FeCoCr$_{0.50}$Ni was sectioned after casting using a diamond saw to dimensions of 1.3 mm × 2.1 mm × 2.1 mm for

comparison to the rolled sample. Individual sections of the rolled FeCoCr$_{0.50}$Ni were sealed in quartz tubes with a partial pressure of Ar and heat treated at 673 K, 773 K, 873 K, 973 K, and 1073 K for 1 h followed by a quench in iced brine. Other samples of FeCoCr$_x$Ni were heat treated *in-situ* during high temperature magnetization measurements for further measurements in the low temperature apparatus. Samples were characterized using x-ray diffraction (XRD) with a Cu-Kα source and vibrating sample magnetometers at low temperature (5 K–350 K) in a Quantum Design PPMS and at high temperature (293 K–1073 K) in a Lakeshore VSM. X-ray diffraction on the as-rolled samples revealed all samples to be fcc. The lattice parameter was linear with Cr composition in the range $x = 0.5$ to $x = 1.15$ (in accordance with Vegard's law) following the relationship $a = 3.5665$ Å + $x \times 0.0102$ Å.

The change in magnetic entropy upon a change in applied field was determined by measuring M(H) loops from -2 T to 2 T applied fields at temperature increments of 10 K and making use of the relation[5,6]

$$\Delta S(\mathrm{T}, \Delta H) = \int_{H_0}^{H_1} \left(\frac{\partial M(T,H)}{\partial T} \right)_H \mathrm{d}H. \quad (1)$$

Figure 1 shows the change in magnetic entropy for a change in applied field of 2 T as a function of temperature, composition, and heat treatment. The results are summarized as a function of Cr composition in Fig. 2. There is a decrease in the peak temperature of the entropy change with increasing Cr
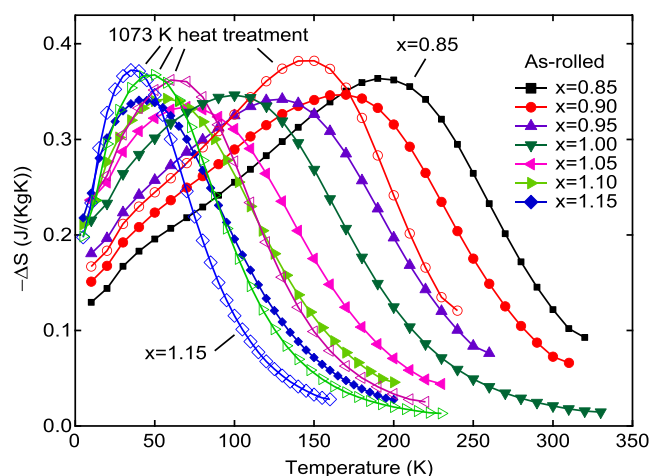
FIG. 1. Change in the magnetic entropy for a change in applied field of 2 T for the as-rolled samples (solid markers) and samples after heat treatment at 1073 K (open markers).

composition. This is expected as Cr addition leads to a reduction in the average exchange interaction. A linear extrapolation gives a peak temperature of $T_{peak} = 632.6$ K $- x \times 524.9$ K/ (at. frac. Cr), which is 300 K at $x = 0.63$. The peak height is less dependent on Cr concentration than the peak temperature, though the same general trend of decreasing $|\Delta S_{max}|$ with increasing Cr concentration is observed. Annealing the samples at 1073 K results in an increase in the peak height with a concomitant decrease in both the peak temperature and width of the peak. A linear extrapolation for the annealed samples gives a peak temperature of $T_{peak} = 568.4$ K $- x \times 471.1$ K/ (at. frac. Cr), which is 300 K at $x = 0.57$.

The magnitude of the change in magnetic entropy of FeCoCr$_x$Ni alloys is very low relative to rare-earth containing materials, though at a much lower cost. Recent work by Ucar *et al.* has shown that γ-FeNi alloys have refrigeration capacities in J/\$ that are orders of magnitude higher than rare-earth containing materials.[7] It was reported that the alloy Fe$_{0.70}$Ni$_{0.30}$ for a change in field of 1.5 T has a peak temperature of 363 K, a peak change in magnetic entropy of 0.6 J/(kg K), and a refrigeration capacity (RC$_{FWHM}$) of

158 J/kg. The value RC$_{FWHM} = |\Delta S_{max}| \times \Delta T$, where ΔT is the full width at half-maximum (FWHM) of the peak. For the rolled FeCoCrNi alloy for a change in field of 1.5 T, the peak is at 100 K with a maximum entropy change of 0.27 J/ (kg K), a ΔT of 160 K, and an RC$_{FWHM}$ of 43 J/kg. This is approximately one quarter the value for the γ-Fe$_{0.70}$Ni$_{0.30}$ alloy. The cost of Cr and Co is much higher than Fe and Ni, leading to an increase in cost of the FeCoCrNi alloy of 320% as compared to the FeNi alloy. The refrigeration capacities in J/\$ of FeCoCrNi is only 8% the value of γ-Fe$_{0.70}$Ni$_{0.30}$.

The results shown in Figs. 1 and 2 indicate that the magnetocaloric properties are dependent both on concentration and sample preparation. The effect of heat treatment was further investigated by x-ray diffraction and high temperature magnetization measurements. Diffraction patterns for the rolled FeCoCr$_{0.5}$Ni sample for different annealing temperatures are given in Fig. 3. The as-rolled sample has a large amount of peak broadening that significantly drops between the 773 K and 973 K annealing temperatures from a FWHM of 0.31° to 0.11° in 2θ, respectively. This is consistent with strain induced by cold-rolling that is alleviated at elevated temperatures. There is also a change in the relative intensities of the (200), (311), and (400) reflections with annealing. As temperature increases, especially above 773 K, the "cube on face" texture (a tendency for $\langle 100 \rangle$ directions to be normal to the plane of rolling) becomes more obvious. A 1273 K heat treatment (not shown) results in an order of magnitude increase in the relative intensities of the (200) and (400) peaks.

The results of high temperature magnetization measurements are presented in Fig. 4. Figure 4(a) shows a re-entrant magnetic moment upon heating of the rolled FeCoCr$_{0.85}$Ni sample that begins near 600 K, reaches a maximum at 733 K, and disappears at 825 K. Measurements upon cooling and subsequent re-heating do not show this behavior, and the M(T) curve is shifted to lower temperature by ~30 K. Figure 4(b) shows that the re-entrant magnetization is the result of a second magnetic phase. After a heat treatment at 828 K, the rolled FeCoCr$_{0.5}$Ni sample has a second phase with a magnetic signature that is less than 2% that of the primary fcc phase. This re-entrant magnetization is the result of rolling
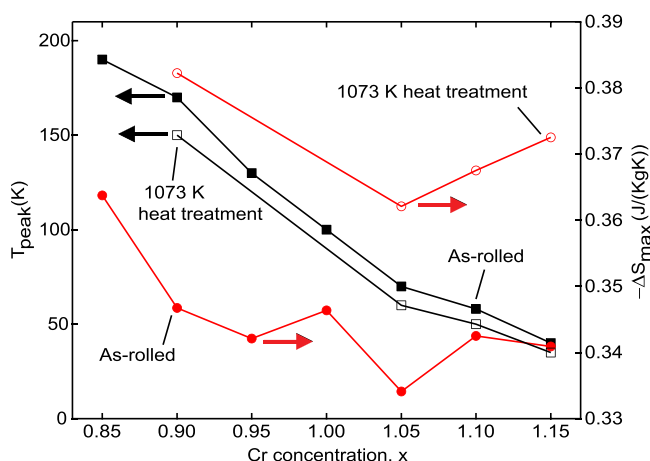

FIG. 2. Peak temperature comparison (left axis) and maximum entropy change (right axis) for a change in applied field of 2 T for the as-rolled samples (solid markers) and samples annealed at 1073 K (open markers).
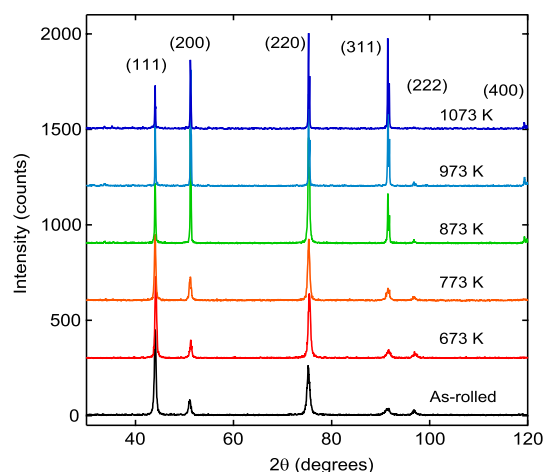

FIG. 3. X-ray diffraction of rolled FeCoCr$_{0.5}$Ni sample as a function of annealing temperature.
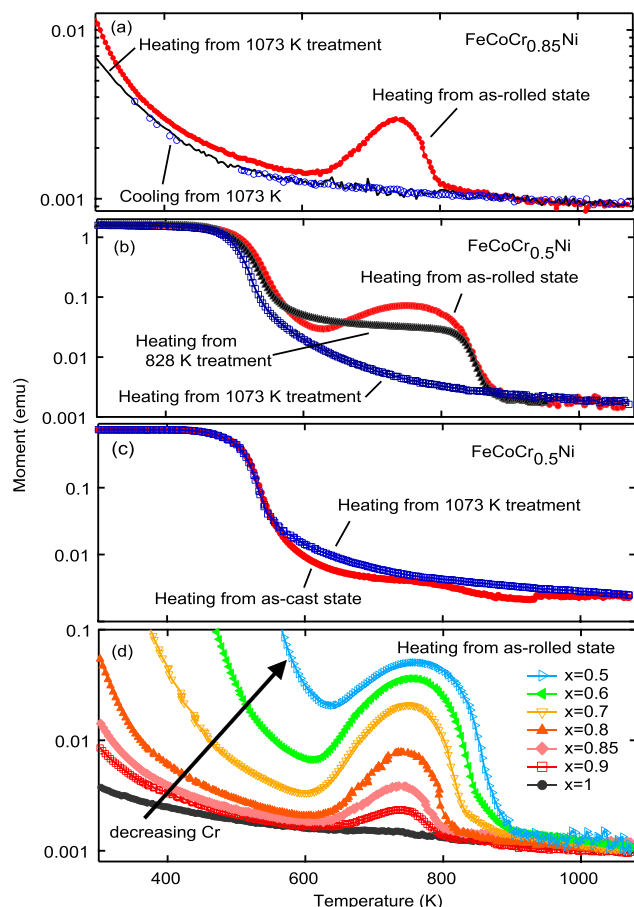
FIG. 4. Magnetization on a logarithmic scale as a function of temperature from vibrating sample magnetometry for FeCoCr$_x$Ni alloys from different sample preparations and heat treatments.

and is not found in the as-cast material sectioned by a diamond saw (Fig. 4(c)). As the Cr concentration is reduced, the re-entrant behavior becomes more pronounced (Fig. 4(d)). Although the onset temperature remains constant near 600 K, the anomaly persists to higher temperatures with Cr reduction.

Cold rolling results in a higher Curie temperature compared to the annealed and as-cast samples as well as the onset of a second phase at higher temperatures. One possible explanation is that both the annealed and as-cast samples have some degree of short-range chemical ordering, but the rolled samples are chemically disordered during the mechanical processing. Long-range chemical ordering would be expected to significantly reduce the Curie temperature, as each Fe, Co, and Ni atom would have 4 out of its 12 first-nearest-neighbors (1nn) as Cr atoms. The difference in the transition temperature of ∼30 K is small and in a recent study, long-range chemical ordering was not observed in FeCoCrNi.[8] However, a change in the short-range chemical order would increase the number of unlike Cr bonds and could alter the T$_C$ by ∼30 K. Cold work provides many vacancies in the structure. Vacancies promote diffusion which on a local scale allows short range diffusion "turning on" at a typical temperature near 600 K. This could alter the local Fe chemical environment in a way that increases the

number of Fe-Fe, and to a lesser extent Fe-Ni and Fe-Co ferromagnetic bonds at the expense of Fe-Cr antiferromagnetic bonds resulting in an increased T$_C$. As the excess vacancies are removed at higher temperatures near 750 K, this process stops. As the temperature is further increased, thermal vacancies are activated and longer range diffusion may allow the local configuration of Cr atoms to change in a manner that promotes the formation of unlike Cr bonds. For bcc FeCo alloys, there is a similar phenomenon that occurs and is often termed as the "550 °C anomaly"[9] and may be attributed to the changes in the local chemical ordering. There is a minima that occurs in the resistivity as a function of temperature[10] that has also been observed by Chou *et al.* in FeCoCrNi at ∼830 K.[11]

Alternatively, the observation of the re-entrant moment could be the result of vacancies coalescing to form stacking faults. This would change the local co-ordination in a way that resembles a body-centered-cubic (bcc) phase with a higher T$_C$. The bcc phase is thermodynamically unstable and would transform to fcc at higher temperatures. In the bcc phase, FeCoCrNi would be expected to have a T$_C$ below room temperature due to the high concentration of Cr. As Cr is reduced, the T$_C$ of the bcc phase would be expected to increase along with the moment. This is consistent with the observed behavior shown in Fig. 4(d). However, no second phase is observed in the XRD patterns. It is important to note that XRD only gives the behavior of the material at the surface. The information depth is only a few microns for FeCoCrNi. The magnetization measurements probe the bulk of the 350 μm thick samples. To understand the origins of the hump in the magnetization of the rolled samples, it would be beneficial to perform high temperature neutron diffraction and transmission electron microscopy measurements.

To summarize, FeCoCr$_x$Ni alloys have tunable peak magnetic entropy temperatures with composition and annealing, a modest magnetic entropy change, are easily prepared in the fcc phase from the bulk, and are ductile. They are relatively cheap compared to rare-earth containing materials, though more expensive than FeNi alloys. A re-entrant magnetic moment was observed upon heating from the as-rolled state and coincided with changes in the diffraction pattern and magnetocaloric properties. It is argued that this may be due to changes in short range order or the coalescence of vacancies forming stacking faults. Further experiments are required to fully understand this phenomenon.

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