Magnetic and vibrational properties of high-entropy alloys

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I. INTRODUCTION

High-entropy alloys (HEAs) are multicomponent alloys where the atomic fraction of each of the elements is nearly equal. These materials have been studied for their high hardness, resistance to wear, and corrosion resistance. A recent report by Chou et al. indicated that FeCoCrNi$_5$ alloys exhibit minima in the thermal expansion between 500 and 600 °C. The authors attributed this to the Curie temperature, which would make these alloys useful for applications requiring magnetic materials at elevated temperatures. Direct measurements of the magnetization by Zhang et al. have shown the HEA FeCoCrNi$_5$Al$_5$ to have a Curie temperature of ~70 °C after a 2 h heat treatment. The research presented in this article was performed to verify these results and to assess the usefulness of such materials for magnetic applications at elevated temperatures.

At moderate temperatures, the vibrational entropy $S_{\text{ph}}$ dominates the Gibbs free energy, $G = H - T S$, where $H$ is the enthalpy and $S$ is the entropy. As a function of temperature and composition, the alloy phase or combination of phases with the lowest Gibbs free energy is the equilibrium state. Therefore, even though the vibrational entropy may be large in magnitude, what matters is the difference in vibrational entropy between phases. Differences in $S_{\text{ph}}$ between phases can be small, as is the case for the ordering transition in FeCo alloys, or quite large, as is the case for the ordering transition in NiAl.

II. EXPERIMENTS

Alloys of stoichiometric $^{57}\text{FeNi}$, $^{57}\text{FeCoCrNi}$, $^{57}\text{FeCoCrNiPd}$, $^{57}\text{FeCoCrNiAl}_2$, and $^{57}\text{FeCoCrNiAlCu}$ were prepared by arc melting under an argon atmosphere using 96.06% enriched $^{57}\text{Fe}$ and elemental Co, Cr, Ni, Pd, Al, and Cu of purity 99.99% or greater. The as-cast buttons were cold rolled to thicknesses of 100–250 μm, with the exception of the Al-containing alloys, which were too brittle to roll. X-ray diffraction (XRD) patterns were acquired at room temperature for all samples. Electron microprobe measurements confirmed the compositions to be accurate to 0.5 at. %.

Nuclear resonant inelastic x-ray scattering (NRIXS) was performed at beamline 16ID-D at the Advanced Photon Source (APS) of the Argonne National Laboratory. The experimental procedures were the same as those reported for a recent experiment on FeCo alloys. All measurements were performed at room temperature. The monochromator resolution function was measured in situ using a single APD in the forward direction. The FWHM was ~2.2 meV. The NRIXS data reduction was performed with the software PHOENIX.

III. RESULTS AND DISCUSSION

The x-ray diffraction patterns showed $^{57}\text{FeNi}$, $^{57}\text{FeCoCrNi}$, $^{57}\text{FeCoCrNiPd}$, and $^{57}\text{FeCoCrNiAlCu}$ to all be single phase.
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1. REPORT DATE
   OCT 2010

2. REPORT TYPE

3. DATES COVERED
   00-00-2010 to 00-00-2010

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
   Air Force Research Laboratory, Wright-Patterson AFB, OH, 45433

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR’S ACRONYM(S)

11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
   Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:
   a. REPORT
      unclassified
   b. ABSTRACT
      unclassified
   c. THIS PAGE
      unclassified

17. LIMITATION OF ABSTRACT
   Same as Report (SAR)

18. NUMBER OF PAGES
   3

19a. NAME OF RESPONSIBLE PERSON
TABLE I. Measured lattice parameter $a$, Curie temperature $T_C$, saturation magnetization $M_s$, entropy for the Fe atoms $S^{Fe}_{ph}$, and average phonon energy $\langle E \rangle$ of high-entropy alloys. All values are reported at room temperature, with the exception of $T_C$. Values in parentheses are for the alloys after cooling from 1000 °C. The configurational entropy of mixing for a fully disordered random solid solution $S^{ph}_{con}$ is shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_{xrc}$ ± 0.005 (Å)</th>
<th>$a_{frc}$ ± 0.005 (Å)</th>
<th>$T_C$ ± 3 (°C)</th>
<th>$M_s$ ± 2 (emu/g)</th>
<th>$\langle E \rangle$ ± 0.1 (meV)</th>
<th>$S^{Fe}_{ph}$±0.01 (kg/Fe-atom)</th>
<th>$S^{ph}_{con}$ (kg/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCoCrNiAlCu</td>
<td>2.8693</td>
<td>3.6260</td>
<td>41 (16)</td>
<td>24.9</td>
<td>3.40</td>
<td>1.792</td>
<td></td>
</tr>
<tr>
<td>FeCoCrNiAl₂</td>
<td>2.8867</td>
<td>157 (268)</td>
<td>13 (18)</td>
<td>26.2</td>
<td>3.25</td>
<td>1.561</td>
<td></td>
</tr>
<tr>
<td>FeCoCrNiPd₂</td>
<td>3.7068</td>
<td>230</td>
<td>34</td>
<td>22.6</td>
<td>3.66</td>
<td>1.561</td>
<td></td>
</tr>
<tr>
<td>FeCoCrNiPd</td>
<td>3.6473</td>
<td>167</td>
<td>33</td>
<td>22.8</td>
<td>3.65</td>
<td>1.609</td>
<td></td>
</tr>
<tr>
<td>FeCoCrNi</td>
<td>3.5643</td>
<td>517</td>
<td>129</td>
<td>24.1</td>
<td>3.50</td>
<td>0.693</td>
<td></td>
</tr>
<tr>
<td>FeNi</td>
<td>3.5868</td>
<td>773</td>
<td>218</td>
<td>26.6</td>
<td>3.18</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>2.8665</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

with the face-centered cubic (fcc) crystal structure. Alloying FeCoCrNi with Pd resulted in an increase of the lattice parameter, as expected for the larger Pd atom. The alloy $^{57}$FeCoCrNiAl₂ was single-phase body-centered cubic (bcc). The $^{57}$FeCoCrNiAlCu sample was two phase (fcc and bcc), with a fcc phase fraction of ~80% from the relative x-ray intensities. In both of the Al-containing alloys, (100) superlattice peaks were observed for the bcc phase. These peaks are indicative of chemical ordering, particularly the formation of an Al-rich sublattice, and are consistent with the measurements of Tung." and Yeh for FeCoCrNiAlCu. The values of the fcc and bcc lattice parameters in Table I for FeCoCrNiAlCu are also consistent with these reports. For FeCoCrNi and FeCoCrNiAl₂, the x-ray diffraction patterns and lattice parameters are consistent with the report by Chou." and Yeh for FeCoCrNiAlCu. The values of the fcc and bcc lattice parameters in Table I for FeCoCrNiAlCu are also consistent with these reports. For FeCoCrNi and FeCoCrNiAl₂, the x-ray diffraction patterns and lattice parameters are consistent with the report by Chou.²

The results of the magnetization measurements are presented in Fig. 1 and Table I. The saturation magnetizations at room temperature are low compared to the value for pure Fe of 218 emu/g. The Curie temperatures of the HEAs are also low compared to pure Fe (773 °C) and pure Co (1115 °C). The low saturation magnetizations and Curie temperatures make these alloys poor candidates for soft magnetic applications at high temperature. This is largely to be expected, since the ferromagnetic elements Fe, Ni, and Co are alloyed with antiferromagnetic Cr in the HEAs. The alloy FeCoCrNi was paramagnetic at room temperature. Alloying with Pd increases the magnetic moment and Curie temperature in the fcc phase. Control of the Curie temperature with Pd additions may make these alloys useful for magnetic refrigeration applications near room temperature.

The measured Curie temperature for FeCoCrNiAl₂ is much lower than those inferred by Chou from thermal expansion minima for FeCoCrNiAl₁ alloys.² These minima are very similar to those reported by Yokoyama for equiatomic FeCo (Ref. 14) after slow cooling from 800 °C. This behavior, termed the “550 °C anomaly,” has also been observed in a number of other properties and attributed to chemical reordering, although a complete explanation has not been provided to date.

The FeCoCrNiAlCu alloy lost its magnetic signature at ~650 °C. This is attributed to a phase transformation, not a Curie temperature, and is consistent with the phase diagram presented by Tong" showing spinodal decomposition at this temperature. The room-temperature saturation magnetizations for FeCoCrNiAlCu are also consistent with those reported by Zhang," where a decrease of $M_s$ was observed after a 2 h 1000 °C heat treatment.

The results of the NRIXS measurements are presented in Fig. 2. These curves are the $^{57}$Fe phonon partial density of states (Fe-PDOS). The total DOS is the concentration weighted sum of the PDOS of each atom species in the alloy, and is required for calculating thermodynamic quantities such as the vibrational entropy or phonon contribution to the heat capacity. The first moment $\langle E \rangle$ and vibrational entropy$^{15,16}$ from the Fe-PDOS are presented in Table I.

The results show that the Fe-PDOS for FeCoCrNi is similar to that of equiatomic FeNi, indicating similar interatomic forces for the Fe atom in both alloys. This may be expected, since the alloys have the same fcc crystal structure and similar molecular weights. Alloying with Pd causes a softening (decrease in phonon energies) of the Fe modes, consistent with a larger average mass. The increased lattice parameter induced by the addition of Pd is also expected to decrease the average phonon energy according to the quasi-ahmonic model.17 This softening results in an increase in the vibrational entropy of 0.20 kg/Fe-atom from FeCoCrNi to FeCoCrNiPd at 300 K. This is likely to be a lower bound on the total vibrational entropy change, since the Co, Cr, and

FIG. 1. Temperature dependence of magnetic moment (applied field of 0.05 T) for high-entropy alloys upon heating (→) and cooling (←).
Ni atoms (having masses similar to Fe) are likely to have a similar change in vibrational entropy, while the Pd atoms (having much larger mass than Fe) should have a larger vibrational entropy. In comparison, the resulting change in configurational entropy from alloying (assuming a random solid solution) is $0.22 \text{ k}_B/\text{atom}$. In general, the change in configurational entropy upon alloying decreases upon increasing the number of elements in equimolar HEAs.

The $(E)$ of the alloy FeCoCrNiAl$_2$ is much larger than the fcc alloys, but similar to the values for bcc Fe and FeCo of 26.6 meV. High-energy optical modes are observed between 40 and 50 meV. These modes are indicative of the formation of an Al-rich sublattice, which is consistent with the observation of superlattice reflections in the x-ray diffraction patterns. The high-energy modes are not observed in the FeCoCrNiAlCu alloy. Wang et al. showed that NiAl intermetallics form in this alloy, accounting for the observed superlattice reflections in the XRD patterns. The chemical analysis presented by Tong et al. showed the interdenrite regions to be Cu, Al, and Ni rich, so that the Fe atoms may not be present in the ordered phase. This would explain the observation of superlattice peaks in the XRD patterns and the lack of optical modes in the Fe-PDOS.

**IV. CONCLUSIONS**

High-entropy alloys based on FeCoCrNi were found to be poor candidates for soft magnetic applications, especially at elevated temperatures. Palladium additions increased the saturation magnetization and Curie temperature. The change in configurational entropy upon alloying with Pd is similar in magnitude to the change in the vibrational entropy. Evidence of chemical ordering in FeCoCrNiAl$_2$ was found in both the x-ray diffraction patterns and the inelastic x-ray results indicating the formation of Fe-aluminides. However, ordering in FeCoCrNiAlCu was observed only in the x-ray diffraction patterns, indicating the formation of Ni-aluminides.

**ACKNOWLEDGMENTS**

Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT is supported by CIW, CDAC, UNLV, and LLNL through funding from DOE-NNSA, DOE-BES, and NSF. Use of the APS was supported by DOE-BES, under Contract No. DE-AC02-06CH11357.