Polycrystalline elastic moduli of a high-entropy alloy at cryogenic temperatures

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Abstract

CrMnCoFeNi is a FCC high-entropy alloy (HEA) that exhibits strong temperature dependence of strength at low homologous temperatures in sharp contrast to pure FCC metals like Ni that show weak temperature dependence. To understand this behavior, elastic constants were determined as a function of temperature. From 300 K down to 55 K, the shear modulus (G) of the HEA changes by only 8%, increasing from 80 to 86 GPa. This temperature dependence is weaker than that of FCC Ni, whose G increases by 12% (81 to 91 GPa). Therefore, the uncharacteristic temperature-dependence of the strength of the HEA is not due to the temperature dependence of its shear modulus.

KEYWORDS: A. High-entropy alloys; B. Elastic Properties

1. Introduction

Traditional alloys usually consist of one major element to which various alloying elements are added to optimize one or more of their properties. Recently, a new class of alloys in which there is no principal element but rather multiple elements in equal atomic proportions has been receiving extensive attention in the scientific literature¹⁻⁴. Most of these alloys contain multiple phases, but a subset has been shown to form single-phase solid solutions with the FCC^{5,6} or BCC⁷ crystal structure. Yeh et al.⁸ hypothesized that the high configurational entropies of equiatomic alloys containing five or more elements promotes solid solution formation at the expense of phase separation or precipitation.

Since then, the whole class of multi-element, equiatomic (and near-equiatomic) alloys has been referred to as high-entropy alloys even though, in reality, the multiphase alloys likely have low configurational entropies⁶. Since phase stability depends on the total free energy of an alloy, which includes both enthalpy and entropy contributions, in many multi-component alloys it appears that configurational entropy is not able to overcome the enthalpies of compound formation, thus leading to multi-phase microstructures. Some of these second phases might go undetected unless high-resolution techniques are used for microstructural analysis [9]. Consequently, the reported mechanical properties (e.g., strength) of certain HEAs that appear to be single-phase might well be "composite" responses of multi-phase microstructures

Relatively little is known about the mechanical properties of *single-phase* high-entropy alloys and the few reports available include results of compression and hardness tests for Al_xCoCrFeNi, FeNiCrCuCo, FeNiCrCuMo, CuCoNiCrAl_{0.5}Fe, Nb₂₅Mo₂₅Ta₂₅W₂₅,

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4 $V_{20}Nb_{20}Mo_{20}Ta_{20}W_{20}$, and $FeCrNiCoMn$ ^{7,10-13}. Tensile properties have been reported
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7 only very recently and are almost exclusively focused on the FCC-structured equiatomic
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9 $CrMnCoFeNi$ high-entropy alloy^{14,15} or its related non-equiatomic FCC derivative¹⁶.
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11 Unlike pure FCC metals, this alloy exhibits a strong temperature dependence of yield
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13 strength, which increases with decreasing temperature at relatively low homologous
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15 temperatures¹⁴. Normally, such behavior implies the overcoming of obstacles to
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17 dislocation motion by some kind of thermally activated process¹⁴. While the height of the
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19 activation barrier depends on the precise nature of the obstacle (intrinsic frictional or
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21 Peierls resistance, solute pinning, etc.), in general it scales with the shear modulus of the
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23 material. For example, the Peierls stress depends linearly on the shear modulus and
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25 exponentially on the dislocation width¹⁷ while the strength of solute pinning depends
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27 linearly on the shear modulus¹⁸. An obvious question, therefore, is whether the elastic
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29 constants of the $CrMnCoFeNi$ high-entropy alloy are strongly temperature dependent, as
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31 that might contribute to the observed temperature dependence of strength^{14,15}. In
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33 addition, elastic moduli are needed also for the determination of other mechanical
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35 properties such as the fracture toughness¹⁹ and work hardening rate²⁰. Therefore, our goal
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37 here is to measure the elastic moduli of the $CrMnCoFeNi$ high-entropy alloy over the
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39 temperature range 50-300 K using resonant ultrasound spectroscopy (RUS). For
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41 comparison, we also measure the moduli of pure Ni over the same temperature range.
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53 **2. Experimental Details**

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55 Resonant ultrasound spectroscopy (RUS) is a nondestructive technique that allows for the
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57 determination of the elastic constants of a solid sample by measuring its free body
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4 mechanical resonances²¹. Given the mass and dimensions of the sample, an initial
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6 estimate of the stiffness tensor is used to begin an iterative procedure that “matches” the
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8 calculated resonances to the measured resonances. This allows determination of all the
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10 elastic constants of the solid from a single frequency scan, which constitutes a main
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12 advantage of RUS: there is no need for separate measurements to probe different moduli,
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14 and multiple sample remounts and temperature sweeps are avoided.
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18 Polycrystalline sheets of the CrMnCoFeNi HEA were produced as described in reference
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20 19. The alloy was arc-melted, drop-cast, homogenized, forged and rolled at room
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22 temperature by approximately 60% reduction in thickness followed by annealing at
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24 800 °C for 1 h in air and air-cooling to obtain recrystallized equiaxed grains with a grain
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26 size of ~6 µm. A previous study had shown that this alloy exhibits weak texture after a
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28 thermomechanical processing treatment consisting of 90% cold work by rolling followed
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30 by recrystallization at 800°C to yield equiaxed grains ~4 µm in size¹⁵. Therefore, we
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32 assume that the polycrystalline specimens tested in the present study are elastically
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34 isotropic. Previous studies^{6, 14, 15, 19} also showed that this alloys is single-phase and has
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36 the FCC crystal structure. A polycrystalline sheet of pure (unalloyed) FCC Ni was
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38 processed similarly to the HEA and its elastic constants were measured for comparison.
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48 Rectangular parallelepiped samples were cut from both processed ingots and polished to
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50 produce specimens with dimensions of approximately 1 mm x 1 mm x 1.5 mm. It is
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52 imperative that the samples to be used for RUS measurements are well prepared, i.e. cut
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54 in rectangular parallelepipeds with smooth surfaces and sharp corners, however, a mirror-
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polish is unnecessary, and errors in parallelism and perpendicularity of a few parts in 1000 can be tolerated.

The samples were corner mounted between the transducers of the RUS probe to produce the strongest signal. Frequency measurements were recorded as a function of temperature from 50 to 300 K using an RUS probe specifically designed to fit in a Quantum Design VersaLab. The elastic moduli were determined using 23 resonances for CrMnCoFeNi, and 20 resonances for the Ni specimen, with an overall root-mean-square error of ~ 0.3% for CrMnCoFeNi, and ~ 0.5% for Ni. Because most of the low-frequency modes are shear, the shear moduli are always found more accurately than the other moduli. For both Ni and CrMnCoFeNi, the shear modulus was defined with a precision of 0.2%. The longitudinal modulus was defined with a precision of 2%.

3. Results and Discussion

Both the pure nickel and the high-entropy alloy studied here were polycrystalline and therefore assumed to be elastically isotropic. Isotropic materials have only two independent elastic constants, and acoustic measurements yield the longitudinal modulus L and the shear modulus G , which are connected to the bulk modulus (B), Young's modulus (E) and Poisson's ratio (ν) through the following relations²²:

$$B = (L + 2G)/3$$

$$E = G(3L + 2G)/(L + G)$$

$$\nu = (L - 2G)/(2(L + G))$$

Table 1 lists selected values for the elastic moduli of the HEA (CrMnCoFeNi) and Ni obtained at 300 K (room temperature), 201 K (approximate temperature of a dry ice and

ethanol mixture), 77 K (liquid nitrogen temperature) and 55 K (close to the lower limit of temperatures at which experiments were conducted in this study) using RUS. These values were extracted from the full data set over the entire temperature range from 300 to 50 K, because of their relevance to other mechanical testing studies^{14, 15, 19}.

Table 1 - Elastic moduli for the HEA (CrMnCoFeNi) and Ni, at various temperatures between 300 K and 55 K. For comparison, the table also includes results from DFT calculations for CrMnCoFeNi reported by Zaddach *et al.*²³ and experimental results for Ni reported by Ledbetter *et al.*²⁴.

		CrMnCoFeNi (this study)	Ni (this study)	CrMnCoFeNi (ref.23)	Ni (ref. 24) ^a
L (GPa)	300K	250	288		294
	201 K	257	304		298
	77K	260	316		305
	55 K	260	320		306
	DFT calc.			172	
G (GPa)	300K	80	81		80
	201 K	83	86		85
	77K	85	90		86
	55 K	86	91		87
	DFT calc.			86	
B (GPa)	300K	143	180		187
	201 K	146	189		185
	77K	147	196		190
	55 K	145	199		190
	DFT calc.			117	
E (GPa)	300K	202	211	137	210
	201 K	209	224		221
	77K	214	234		224
	55 K	215	237		226
	DFT calc.			207	
ν	300K	0.265	0.304		0.313
	201 K	0.261	0.303		0.300
	77K	0.257	0.301		0.303
	55 K	0.253	0.301		0.302
	DFT calc.			0.204	

^(a) Moduli reported by Ledbetter are for single crystals; values reported here are estimated for polycrystals, using the Reuss-Voigt-Hill averaging scheme²².

Figure 1: Temperature-dependence of Young's modulus E and the shear modulus G for the HEA, CrMnCoFeNi. The dashed line is the estimated Varshni background (with parameters $s = 7$ GPa and $t = 225$ K for the shear modulus G ; $s = 10$ GPa and $t = 175$ K for Young's modulus E). Inset: shear modulus vs. temperature for the HEA and nickel

The temperature dependence of the elastic moduli of the HEA CrCoFeMnNi, plotted in Figure 1, shows a gradual stiffening with decreasing temperature between 300 and 50 K. The high entropy alloy behaves similarly to fcc Ni (inset of figure 1), albeit with a slightly lower temperature dependence of G with temperature. These temperature dependencies are consistent with the “Varshni behavior”, after Varshni²⁵ who modeled the temperature dependence of the elastic constants $[c_{ij}(T)]$ of over 20 compounds with the empirical formula $c_{ij}(T) = c_{ij}^0 - s/(e^{t/T} - 1)$, where T is the temperature, c_{ij}^0 the elastic

constants at 0 K and s and t are fitting parameters. This function was shown by Varshni to describe the temperature-dependence of the elastic constants of many simple substances and characterizes to some extent ‘normal’ elastic behavior. The normal, Varshni-like behavior of the shear modulus of CrCoFeMnNi is important in light of the relatively strong temperature dependence of strength observed in this material. The experimental data presented in this paper eliminate the possibility that a strong temperature dependence of the shear modulus is a significant contributor to this behavior.

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