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Temperature Dependence of the Mechanical Properties of Equiatomic Solid Solution Alloys with FCC Crystal Structures

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Abstract

Compared to decades-old theories of strengthening in dilute solid solutions, the mechanical behavior of concentrated solid solutions is relatively poorly understood. A special subset of these materials includes alloys in which the constituent elements are present in equal atomic proportions, including the high-entropy alloys of recent interest. A unique characteristic of equiatomic alloys is the absence of "solvent" and "solute" atoms, resulting in a breakdown of the textbook picture of dislocations moving through a solvent lattice and encountering discrete solute obstacles. To clarify the mechanical behavior of this interesting new class of materials, we investigate here a family of equiatomic binary, ternary, and quaternary alloys based on the elements Fe, Ni, Co, Cr, and Mn that were previously shown to be single-phase face-centered cubic solid solutions. The alloys were arc-melted, drop-cast, homogenized, cold-rolled, and recrystallized to produce equiaxed microstructures with comparable grain sizes. Tensile tests were performed at an engineering strain rate of 10^{-3} s^{-1} at temperatures in the range 77-673 K.

Unalloyed FCC Ni was processed similarly and tested for comparison. The flow stresses depend to varying degrees on temperature, with some (e.g., NiCoCr, NiCoCrMn and FeNiCoCr) exhibiting yield and ultimate strengths that increase strongly with decreasing temperature, while others (e.g., NiCo and Ni) exhibit very weak temperature dependencies. To better understand this behavior, the temperature dependencies of the yield strength and strain hardening were analyzed separately. Lattice friction appears to be the predominant component of the temperature-dependent yield stress, possibly because the Peierls barrier height decreases with increasing temperature due to a thermally induced increase of dislocation width. In the early stages of plastic flow (5~13% strain, depending on material), the temperature dependence of strain hardening is due mainly to the temperature dependence of the shear modulus. In all the equiatomic alloys, ductility and strength increase with decreasing temperature down to 77 K.

Keywords: High entropy alloy; Face-centered cubic crystals; Solid solution strengthening; Mechanical properties; Temperature;

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1. Introduction

Dissolved solute atoms, to varying degrees, affect the mechanical properties of metals. Conventional treatments of solid solution strengthening assume that dislocations move through a solvent lattice of like atoms and encounter discrete unlike atoms (solutes) that can affect their mobility. The simplest case to consider is the energetics of, and the force resulting from, the elastic interaction of a dislocation with the strain field of a single solute atom [e.g., 1-7]. Both atomic size misfit and modulus mismatch between the solute and solvent atoms can contribute to this interaction. In reality, however, a dislocation interacts with multiple solute atoms simultaneously, and the net force exerted by all the solute atoms needs to be considered. For dilute solutions, early theories assumed that the interaction force between the dislocation and the solute atoms is either the maximum value possible (strong obstacles lying exactly in the slip plane), or zero (obstacles lying above or below the slip plane) [8, 9]. Taking into account the Friedel [10] separation between strong obstacles encountered by a dislocation, Fleischer developed a description in which the critical shear stress to overcome obstacles varied as the square root of the solute concentration, a result that was confirmed by early computer simulations [11, 12]. For more concentrated solutions, Labusch [13-15] developed a statistical treatment of a dislocation moving through an array of obstacles with a distribution of interaction strengths, rather than the binary interaction assumed in Fleischer's treatment, and obtained a critical shear stress that varied as the two-thirds power of solute concentration. Since the development of these early theories, there have been many refinements over the years [e.g., 16-21].

The picture of a dislocation moving through a solvent lattice and encountering discrete solute obstacles breaks down as the solute concentration and compositional complexity increase.

Relatively little is known about the fundamental mechanisms of solid solution strengthening in compositionally complex alloys, i.e., alloys comprised of multiple elements in high concentrations. An interesting subset of compositionally complex alloys is one in which the constituent elements are present in equal atomic concentrations. In such *equiatomic* alloys, there is no "solvent" or "solute" in the conventional sense. Therefore, rather than considering a dislocation moving through a solvent lattice and interacting with discrete solute atoms, it may be more appropriate to envisage the dislocation as moving through a mythical "average solvent" or "effective medium." In other words, the equiatomic alloy is not a simple extension or extrapolation from the dilute solution limits but rather a distinct new state akin to a stoichiometric compound with fixed atomic ratios, albeit disordered.

In order to develop accurate effective medium theories of solid solution strengthening, it is desirable to experimentally characterize the mechanical behavior of a range of equiatomic solid solution alloys. To this end, we investigate here several equiatomic binary, ternary and quaternary alloys that were previously shown to be single-phase face centered cubic (FCC) [22]. In addition, the alloys are all subsets of an equiatomic, quinary high-entropy alloy, FeNiCoCrMn, that is known to be a FCC-structured single-phase solid solution alloy [23-28]. Tensile tests showed that the yield and ultimate strengths of this high-entropy alloy increase as the temperature is decreased [24, 26].

The term high-entropy alloy (HE alloy) was coined by Yeh et al. [29] to denote alloys containing five or more elements in approximately equiatomic concentrations. These authors reasoned that the high configurational entropies of such alloys would stabilize the formation of a solid solution by counteracting the enthalpies of phase separation and compound formation. However, most of the so-called HE alloys discussed in the literature are multi-phase alloys [e.g.,

30-32] whose configurational entropies, as pointed out by Otto et al. [27], should in fact be low rather than high. There are only a few multi-element alloys that are true single-phase solid solutions with FCC [23-28] or BCC crystal structures [33-35]. The configurational entropy of these single-phase alloys is likely to be high, approaching the value of the ideal mixture assumed in the analysis of Yeh et al. [29]. The present study of equiatomic binaries, ternaries, and quaternaries aims to provide an experimental basis to understand the mechanical behavior of all equiatomic alloys, including the more complex HE alloys containing five or more elements.

2. Experimental Methods

2.1. Alloy Preparation and Characterization

The equiatomic alloys listed in Table I were produced by arc melting the elements Fe, Ni, Co, Cr, and Mn (>99.9% pure) in a water-cooled copper hearth under Ar atmosphere. All these alloys are single-phase, FCC solid solution alloys, as shown in an earlier paper [22], and all are subsets of the quinary, single-phase, FCC-structured, high-entropy alloy, FeNiCoCrMn [23-27]. For comparison, pure Ni was produced using the same process. When Mn was added as an alloying element, special care was taken in the processing because of its high vapor pressure and tendency to oxidize rapidly, as discussed elsewhere [22, 24, 26, 27]. The arc-melted buttons were flipped and re-melted at least five times to promote thorough mixing and then drop-cast into copper molds to produce rectangular ingots measuring 12.7 mm × 25.4 mm × 127 mm. The drop-cast ingots were homogenized for 24 hours at either 1373 or 1473 K (see Table I), followed by water quenching. They were then cold rolled along the longitudinal ingot direction to a total thickness reduction of 90-92% (Table I) without cross-rolling or intermediate annealing. Annealing studies

were conducted on the rolled sheets to determine the temperatures and times that would yield fully recrystallized microstructures and comparable grain sizes (see Table I). In addition, the grain size of one of the alloys (FeNiCoCr) was systematically varied to investigate its influence on mechanical behavior. The annealed samples were ground (through 800-grit SiC paper), polished (through 20-nm colloidal silica suspension) and their microstructures examined in a JEOL 6500 SEM operated in the back-scattered electron (BSE) mode.

2.2. Tensile Tests

Flat dog-bone-type specimens with a gage length of 10 mm were cut from the cold-rolled sheets by electrical discharge machining (EDM) with their longitudinal axes perpendicular to the rolling direction. The specimens were annealed at the temperatures and times listed in Table 1, and all faces of their gage sections ground through 600-grit SiC paper. Nine Vickers microhardness indents spaced 1 mm apart were made along the specimen gage lengths using a LECO LM 100_{AT} Vickers Hardness tester with a force of 200 g. Uniform elongations to fracture were calculated by averaging the change in the distance between adjacent indents, excluding the two indents on either side of the fracture plane.

Tensile tests were performed with a screw-driven tensile testing machine (Instron) at an engineering strain rate of 10^{-3} s^{-1} and temperatures of 77, 203, 293, 473, and 673 K. For the tests below room temperature, the specimens and grips were first fully immersed in a bath of liquid nitrogen (77 K tests) or a dry ice plus ethanol mixture (203 K tests) for about 15 minutes before starting the test. During the tests, the baths were topped off as needed to keep the specimen and grips fully immersed at all times. Room-temperature tests were performed in ordinary ambient

air and those above room temperature in vacuum. X-ray diffraction was performed on the gage sections of specimens tested at 77 and 673 K to determine whether any phase transformation or second phase precipitation had occurred. No significant changes indicative of any phase transformations were observed on the XRD patterns. Fracture surfaces were examined in a JEOL JCM-5000 microscope operated at 10 kV.

2.3. Melting Temperature, Shear Modulus and Poisson's Ratio Measurements

The melting temperatures of the materials were measured using a NETZSCH 404 C differential scanning calorimeter (DSC). The melting point was determined during heating from room temperature as the start temperature of the endothermic melting peak observed on the DSC trace.

To determine the room-temperature elastic constants, densities were first measured with an AccuPyc 1330 pycnometer. Right cylindrical samples (7 mm length × 6 mm diameter) were cut from the homogenized ingots and ground through 600-grit SiC paper followed by compression to ~3 mm before being used for the density measurements. The purpose of this ~60% compression was to close up any casting pores that may have been present. After density measurements, the samples were annealed at 900 °C for 3 h to produce fully recrystallized microstructures. The annealed samples were carefully ground, their thicknesses measured, and time of flight measurements made with appropriate acoustic transducers to obtain longitudinal and shear wave velocities. Assuming the recrystallized (polycrystalline) materials are isotropic, their two independent elastic constants were calculated from the longitudinal and shear wave velocities using techniques described elsewhere [36].

The temperature dependence of the shear modulus of the FeNiCoCr alloy was measured using resonant ultrasound spectroscopy (RUS) using a commercial RUS system (RUSpec®, Quasar International Inc., Albuquerque, NM, USA) with a tripod transducer configuration. To make the measurements, a cylindrical ingot of this alloy, 25.4 mm in diameter, was cast and homogenized at 1473 K for 24 hours. A7-mm-thick slice of this ingot was then compressed to 3 mm and annealed at 1073 K for 3 hours. From this slice, a cylindrical specimen 25.4 mm in diameter and 3mm thick was cut using EDM and used for the RUS measurements. Additional details of the measurement procedures are described elsewhere [37].

3. Results and Discussion

Figure 1 shows the recrystallized microstructures of the equiatomic alloys and pure Ni after the annealing treatments listed in Table I. The BSE images in this figure were taken on cross-sections perpendicular to the rolling direction. All of the alloys have equiaxed microstructures and similar grain sizes (24-48 μm), as summarized in Table I, but with different densities of annealing twins. Unfortunately, a pure Ni specimen with a grain size in this range could not be produced. As discussed in a previous paper [22], Ni undergoes abnormal grain growth at temperatures below 1073 K when processed by the methods employed here. Normal grain growth occurs only at 1073 K and above. The smallest grain size we could produce at 1073 K was 85 μm, so the test results presented for pure Ni here are for this larger grain size.

Figure 2 shows the engineering stress vs. engineering plastic strain curves of the equiatomic alloys and pure Ni as a function of temperature. The curves were obtained from the tensile load-displacement data with the crosshead displacement calibrated using the elongation of the gage

length determined from the microhardness indents described earlier. To compute the plastic components of the strain, a line was fit to the linear elastic portion of the stress-strain curves and the amount of the elastic strain at a given point on the curve was subtracted from the total strain to obtain the plastic strain. In general, the flow stress (σ_{flow}) decreases with increasing temperature, and the stress-strain curves systematically shift up with decreasing temperature. Some of the alloys, namely, NiCoCr, FeNiMn, NiCoMn, FeNiCoMn and NiCoCrMn, exhibit pronounced serrations on their 673-K stress-strain curves that extend essentially from the yield point all the way to the start of necking. In two of the alloys, FeNiMn and NiCoMn, the serrations were also observed at 473 K. Such serrations are often associated with dynamic strain aging [38].

Figure 3 summarizes the 0.2% offset yield strengths (σ_y), ultimate tensile strengths (UTS), and uniform elongations to fracture, all of which increase with decreasing temperature, with maximum values attained at liquid nitrogen temperature (77 K). Since there are variations in the melting points of the different alloys (Table II), we also plotted yield strengths versus homologous temperatures (not shown here). Basically the same trends and order of the different alloys as seen in Fig. 3 were observed also in the homologous temperature plots. At any given temperature, the alloys have large ranges of strength and ductility, with the ternary alloy, NiCoCr, having the highest values overall.

Broadly speaking, there are two types of effects evident in the mechanical properties shown in Figs. 2 and 3 – those due to the different alloying elements and those due to temperature. Considering first the former effect, it has been speculated [29] that equiatomic HE alloys will have higher strengths than conventional alloys containing just one principal element due to the higher degree of solid solution hardening from the increased number of elements. However, the

current results show that yield strength is not a simple function of the number of elements in the equiatomic alloys. In fact, the yield strength does not increase monotonically as the number of elements increases: one of the ternary alloys (NiCoCr) has the highest strength, two of the quaternaries (FeNiCoCr and NiCoCrMn) are next, and all three have higher yield strengths (Fig. 3) than the five-element equiatomic alloy, FeNiCoCrMn [26]. Therefore, strength is not solely determined by the number of elements but also depends on the type of added elements. In the present family of alloys, Cr appears to be the most potent strengthener. A similar behavior was observed previously in the microhardness data of these alloys [22].

While traditional notions of solid solution hardening may shed some light on possible mechanisms by which composition affects strength, as noted before, because of their equiatomic compositions, there are no "solvents" or "solutes" in these alloys. Therefore, new "averaging" schemes may be needed to properly account for the complex atomic arrangements that are present both in the dislocation cores and in the surrounding lattice. Nevertheless, among the factors that can produce solid solution hardening, such as size misfit, modulus mismatch, stacking fault energy changes, and short-range ordering, the first two may be important based on trends observed in relatively dilute alloys [39]. For the elements in our alloys (Fe, Ni, Co, Cr and Mn), the largest (pair-wise) differences in atomic sizes and Young's moduli are 3.7% between Ni and Mn [40] and 40.9% between Cr and Mn [41], respectively, suggesting that the observed differences in strength may be due to modulus mismatch rather than size misfit. However, further studies are needed to develop a deeper understanding of compositional effects in equiatomic alloys.

The second broad trend that can be seen in the data in Figs. 2 and 3 is that the flow stress, σ_{flow}, depends to varying degrees on the test temperature. It is convenient to think of the flow stress as

consisting of two parts:(1) the yield stress (σ_y), which depends on the initial dislocation density (ρ_i), and (2) an incremental hardening ($\Delta\sigma_\rho$) due to the evolution of dislocation density (ρ) with strain, such that:

$$\sigma_{flow}(T) = \sigma_y(T) + \Delta\sigma_r(T) \qquad (1)$$

Consequently, the temperature dependence of flow stress seen in Figs. 2 and 3 may be due to the temperature dependencies of either, or both, of the terms on the right hand side. In the following sections we address the potential mechanisms by which temperature can affect the yield strength and strain hardening behavior of the equiatomic alloys.

3.1. Effects of Temperature on Yield Strength

Because of their negligible Peierls-Nabarro barriers, the yield strengths of pure FCC metals are relatively insensitive to changes in temperature (at least at low homologous temperatures), as has been confirmed by previous studies [42-45], as well as our present results on pure Ni (Fig. 3a). Nevertheless, temperature-dependent yield strengths have been reported for binary FCC alloys, including Cu-Mn [46, 47], Cu-Al [48-50], Cu-Ge [51-53], Cu-Zn [54, 55], Cu-Ni [56], Au-Ag [56], and Al-Mg [57], with the yield strength typically increasing at lower temperatures. Both the thermal and athermal portions of the yield strength vs. temperature curves of these binaries often shift to higher values as the solute concentration increases [58, 59], suggesting an increase in the number of both short-range dislocation obstacles that can be overcome by thermal activation and longer range obstacles that cannot. Consistent with previous observations in binary alloys (most of which were relatively dilute solid solutions), the compositionally complex

equiatomic alloys examined here also exhibit varying degrees of strengthening at lower temperatures, with at least some, for example NiCoCr, NiCoCrMn, and FeNiCoCr, exhibiting significant strengthening as the temperature is decreased into the cryogenic range.

Yield stress is a combination of the frictional stress (σ_{fr}), or the intrinsic lattice resistance to dislocation motion, plus the various incremental strengthening contributions, such as those due to the initial dislocation density ($\Delta\sigma_{\rho i}$), solid solution hardening ($\Delta\sigma_{ss}$), precipitate hardening ($\Delta\sigma_{ppt}$), and grain boundary (Hall-Petch) strengthening ($\Delta\sigma_{gb}$). A general expression for the yield strength can therefore be written as:

$$\sigma_y = \sigma_{fr} + \Delta\sigma_{\rho i} + \Delta\sigma_{ss} + \Delta\sigma_{ppt} + \Delta\sigma_{gb}\,. \qquad (2)$$

In the present analysis, two of the terms on the right hand side ($\Delta\sigma_{ppt}$ and $\Delta\sigma_{\rho i}$) can be eliminated immediately. First, no precipitates are present in our alloys, at least based on their x-ray diffraction spectra and BSE images [22], both of which indicate that the alloys are single-phase solid solutions, so $\Delta\sigma_{ppt}$ can be ignored. Higher magnification transmission electron microscopy (TEM) also failed to reveal any precipitates in the related FCC quinary FeNiCoCrMn [26]. Since all the alloys investigated here are equiatomic FCC subsets of this “parent” alloy, it seems reasonable to assume that the lower order alloys are also free of second phases. Second, TEM of the equiatomic quinary alloy, FeNiCoCrMn, found that representative images from foils of the recrystallized alloy contained practically no dislocations [26]. Since the current alloys were processed similarly and fully recrystallized to produce comparable grain sizes, it is reasonable to assume that their initial dislocation densities are also very low. Assuming that is the case, we ignore the limited contribution of initial dislocation density to yield stress in our analysis.

Next, we address the third term on the right, $\Delta\sigma_{ss}$. Mechanistically, as mentioned before, solid solution strengthening has traditionally been considered in relatively dilute solutions where there is a solvent lattice through which the dislocations move and interact with discrete solute atoms. In such cases, the dislocation core is comprised almost exclusively of like (solvent) atoms that encounters unlike (solute) atoms as it moves through the lattice. At low solute concentrations, the flexibility of the dislocation line allows it to bend around obstacles and take on low-energy configurations. This becomes progressively more difficult as the spacing between obstacles decreases. In the limit of the equiatomic alloys, there is no "solvent" lattice through which the dislocations move and no "solute" atoms that they occasionally encounter, assuming the constituent atoms are truly randomly arranged on the FCC lattice. In this sense, the equiatomic alloys represent a new state of material more akin to a stoichiometric compound with fixed atomic ratios, albeit disordered, than a traditional dilute solid solution. When viewed in this light, it is logical to fold the solid solution hardening term ($\Delta\sigma_{ss}$) in Eq. (2) into the lattice friction term (σ_{fr}), where the latter now represents some "average" resistance offered by all the constituent atoms rather than a single type of solvent atom. This allows us to simplify the expression for the yield strength to:

$$\sigma_y(T) = \sigma_{fr}(T) + \Delta\sigma_{gb}(T), \qquad (3)$$

where the temperature dependence of yield strength can be the result of either, or both, of the two terms on the right. In what follows, we first address the second term on the right, $\Delta\sigma_{gb}$, which is the contribution of grain boundaries to strength, and then focus mostly on the lattice friction σ_{fr}.

In the classical Hall-Petch treatment of grain boundary strengthening, a plot of yield strength versus the inverse square root of grain size is linear. Figure 4 is such a plot for one of the quaternary equiatomic alloys, FeNiCoCr, at five different temperatures. If the grain boundary strengthening term in Eq. (3) were temperature-dependent, then the Hall-Petch slopes would vary with temperature. However, it is apparent that the slopes in Fig. 4 are all essentially the same. This, coupled with the fact that the alloys in Fig. 3a all had roughly the same grain size (Table I), leads us to conclude that grain boundary strengthening does not contribute significantly to the observed temperature dependence of yield strength in the present study.

Therefore, the only remaining factor that could produce the observed temperature dependence of yield stress is a temperature-dependent lattice friction stress (σ_{fr}). To analyze this, we note that the Peierls-Nabarro stress (henceforth referred to as the Peierls stress, σ_p), which is commonly used to explain lattice friction, is given by [39]:

$$\sigma_p = \frac{2G}{1-\nu}\exp\left(-\frac{2\pi\omega}{b}\right), \qquad (4)$$

where G is the shear modulus, ν is Poisson's ratio, ω is the dislocation width, and b is the magnitude of the Burgers vector. The temperature dependencies of G and b in this expression can obviously lead to a small temperature dependence of the Peierls stress. However, it has been pointed out that the dislocation width ω can also be temperature dependent, and, since it appears in the expression inside the exponential, it may be the dominant factor. The dependence of dislocation width on temperature has been approximated by Dietze [60] as:

$$\frac{\omega}{b} = \left(\frac{\pi\omega_0}{b}\right)\exp\left(\frac{T}{3T_m}\right), \qquad (5)$$

Where $\left(\frac{w}{b}\right)_0$ indicates values at 0 K, T is the test temperature, and T_m is the melting temperature. Ignoring the change of b with temperature, and using a simple Taylor expansion, we can rewrite equation (5) as:

$$w \approx w_0\left(1+\frac{T}{3T_m}\right), \qquad (6)$$

where ω_0 is the dislocation width at 0 K. This indicates a linear relationship between dislocation width and absolute temperature provided the temperature is low compared to the melting temperature, a relationship used previously by Petch [61]. Therefore, to a first approximation:

$$w = w_0\left(1+aT\right), \qquad (7)$$

Where α is a small positive constant. Combining equations (7) and (4), the temperature dependence of the Peierls stress becomes:

$$s_p = \frac{2G}{1-n}\exp\left(-\frac{2pw_0}{b}\right) * \exp\left(-\frac{2pw_0}{b}aT\right) \qquad (8).$$

From the above expression, the Peierls stress at 0 K can be obtained as:

$$s_p\left(0\right) = \frac{2G}{1-n}\exp\left(-\frac{2pw_0}{b}\right) \qquad (9).$$

This suggests that if the temperature-dependence of yield stress is the same as that of the Peierls stress, the yield stress will decay with temperature in an exponential way.

To check the validity of these concepts, the yield stress data are re-plotted in Fig. 5, along with data obtained previously for the equiatomic quinary alloy FeNiCoCrMn of comparable

grain size [26]. It was found that the data are well described by curve fits (dashed lines) shown in Fig. 5 of the form:

$$\sigma_y(T) = \sigma_a \exp\left(\frac{T}{C}\right) + \sigma_b, \qquad (10)$$

Where σ_a, C, and σ_b are fitting constants. When written this way, the first term on the right represents the thermal or temperature-dependent part of the yield strength and the second term is the temperature-independent or athermal part. Equating the temperature-dependent part of Eq. (10) with the temperature-dependent Peierls stress in Eq. (8) yields:

$$\sigma_a = \sigma_p(0) = \frac{2G}{1-\nu}\exp\left(\frac{2\pi w_0}{b}\right) \qquad (11)$$

and

$$C = \frac{b}{2\pi w_0 a} \qquad (12).$$

Values of the parameters σ_a, C, and σ_b determined from least squares fits of the experimental data are listed in Table III. Since it has been shown [62, 63] that Eq. 4 is a reasonable approximation of the Peierls stress over the range ~0.4<ω/b< ~2.1 (i.e., 0.5b<ω < 2b), the table also includes values of the Peierls stress at 0 K, $\sigma_p(0)$, calculated from Eq. 9 assuming $\omega_0 = 0.5b$, b, 1.5b and 2b,which can be compared with the values of σ_a found from the curve fits. The shear moduli and Poisson's ratios used in the calculations were measured by ultrasonic techniques and are given in Table II. For the equiatomic alloys, the calculated Peierls stress at 0 K ($\sigma_p(0)$) has the best match with the fitted σ_a values when $\omega_0 = b$. For pure Ni, on the other hand, the match is better when $\omega_0 = 1.5b$. We are not aware of any published data for the dislocation widths in pure

Ni, but a value of 1.5b has been reported for pure Cu [53, 66], and this agrees well with the value derived here for Ni. The reasonable match between the calculated and fitted values lends credence to the analysis and suggests that the dislocations in the equiatomic alloys are narrower than in pure FCC metals. Additionally, the analysis suggests that the temperature dependence of the yield strength of the equiatomic alloys may be due to thermally-induced changes in dislocation width that, in turn, produce a temperature dependence of the Peierls stress.

To further check the validity of this analysis, values for α in Eq. (8) were calculated from the fitted C values by means of Eq. 12 where it was assumed that $\omega_0 = b$ for the equiatomic alloys and 1.5b for pure Ni. These are listed in Table III, along with values for the product of α and T_m. For most of the equiatomic alloys and pure Ni, the product of α and T_m lies in the neighborhood of 1 (~0.8-1.5), implying that $\alpha \approx \frac{1}{T_m}$. Inserting this into equation (8) gives:

$$\sigma_p \approx \frac{2G}{1-\nu} \exp\left(\frac{2\pi\omega_0}{b}\right) * \exp\left(\frac{2\pi\omega_0}{bT_m} T\right) = \sigma_p(0) * \exp\left(\frac{2\pi\omega_0}{bT_m} T\right) \qquad (13).$$

This expression is very similar to an equation derived by Dietze [60] to take into account the increase of dislocation width with temperature and consequent decrease in the Peierls stress:

$$\sigma_p \approx \sigma_p(0) * \exp\left(\frac{2\pi\omega_0}{3bT_m} T\right) \qquad (14).$$

The only difference between equations (13) and (14) is the factor 3, which, as noted by Nabarro [65], is unlikely to be significant in light of the various assumptions made in the derivations.

It is generally believed that Peierls barriers are high in BCC metals and relatively low in FCC metals and that a major factor contributing to this difference is the relative widths of the

dislocations. The present analysis suggests that the dislocations in equiatomic FCC alloys may be narrower than those in pure FCC metals, which could lead to a stronger Peierls barrier and temperature dependence of strength. However, the temperature dependence of the equiatomic alloys, while stronger than that of pure FCC metals, is not as strong as that of BCC metals. Specifically, from room temperature to liquid nitrogen temperature the yield stress of the equiatomic FCC alloys increases by a factor of ~1.3-2.0 in comparison to a factor of ~3.5 for BCC metals such as iron [66] and tantalum [67]. Thus, the Peierls barrier height of the FCC equiatomic alloys is likely intermediate to that of pure FCC and BCC metals.

It should be noted that all of these arguments are premised on the notion that the primary source of the temperature dependence of the yield strength is the temperature-dependent height of the Peierls barrier. Other temperature dependences could accrue from the thermally activated processes that control dislocation mobility during glide, but these have not been explicitly addressed here. Detailed knowledge of the specific mechanisms responsible for these thermally activated processes would be needed to model them accurately in future investigations.

3.2. Effects of Temperature on Strain Hardening

Since flow stress depends on the yield stress and work hardening [Eq. (1)], either one or both could cause the observed temperature dependence of flow stress in the equiatomic alloys. As discussed above, yield stress does indeed depend on temperature, and its origin can be ascribed to a temperature-induced change in the dislocation width and friction stress. To investigate the temperature dependence of strain hardening, we first note that the engineering stress-strain curves of some of the equiatomic alloys in Fig. 2 appear to be parallel to each

other at different temperatures. If this is generally true, it implies that the strain-hardening component of the flow stress ($\Delta\sigma_\rho$) is essentially temperature independent, leaving the temperature dependence of the yield stress (σ_y) as the primary contributor. To determine whether this is in fact the case, the engineering stress-strain curves in Fig. 2 were converted to true stress-strain curves and the 0.2% yield stress was subtracted from each value of stress to give the portion of the flow stress associated with strain hardening, $\Delta\sigma_\rho = \sigma_{flow} - \Delta\sigma_y$. The results are shown in Fig. 6. Clearly, the curves do not fully converge, indicating that the strain hardening ($\Delta\sigma_\rho$) does indeed depend on temperature to some extent.

The classical Taylor model [39] for strain hardening due to forest dislocations is usually described by

$$\Delta s_p = \beta G b \rho^{\frac{1}{2}}, \qquad (15)$$

Where β is a constant that depends on the strength of the dislocation-dislocation interaction, G is the shear modulus, b is the magnitude of the Burgers vector, and ρ is the dislocation density. Among the terms on the right hand side of Eq. 15, the shear modulus G is certainly temperature dependent. To investigate if this is the primary origin of the temperature dependence of the strain hardening, the isotropic shear modulus of FeNiCoCr was measured at 293, 473 and 673 K using resonant ultrasound spectroscopy. The shear moduli of pure Ni at these temperatures were obtained from [68], and the modulus of FeNi was calculated from known single crystal elastic constants C_{11}, C_{12} and C_{44} [68] using the formula given by Hashin and Shtrikman [69]. Table V lists the measured and calculated shear moduli.

The strain hardening curves for FeNiCoCr, FeNi, and Ni in Fig. 6 were normalized using their respective temperature-dependent shear moduli in Table V, and the resulting values ($\Delta\sigma_\rho/G$) are plotted in Fig. 7 as a function of plastic strain. These normalized curves generally converge up to certain strains, namely, ~13% for the two alloys and ~5% for pure Ni. This suggests that, at low strains, the temperature dependence of strain hardening in equation (14) is indeed mainly due to the temperature dependence of shear modulus and that dislocation multiplication, interaction and accumulation occur in a temperature-independent manner during the early stages of plastic deformation.

In addition to displaying higher strengths, many of the equiatomic alloys are significantly more ductile than pure Ni, and their ductilities generally increase with decreasing temperature, as shown in Fig. 3. Similar trends were reported in earlier papers on high and medium entropy alloys [24, 26], where the high ductilities were ascribed to their high work hardening capability, which postpones the onset of necking instability according to Considere's criterion. To evaluate whether its role in the present study, the extent of work hardening, defined here as the difference between the ultimate tensile strength (UTS) and the yield strength, is plotted as a function of temperature in Fig. 8 for the equiatomic alloys and pure Ni. To varying degrees, the work hardening capability of all the materials increases with decreasing temperature, similar to what was observed before in the equiatomic quinary alloy FeNiCoCrMn [24, 26], as well as in other FCC alloys [70-75]. It appears therefore that this may be the reason for the increasing ductility with decreasing temperature.

One of the mechanisms for the much higher work hardening capability at cryogenic temperatures in the FeNiCoCrMn alloy is deformation-induced twinning [26], which can provide strengthening because of the additional internal twin boundaries generated, the so-called

“dynamic Hall-Petch” effect. Deformation twinning occurs in FCC metals and alloys with low stacking fault energy (γ_{SFE}) such as 70:30 brass, [76], but not in FCC metals with medium or high stacking fault energy such as Al [77]. The critical stacking fault energy below which twinning occurs in FCC materials has been reported to be ~45mJ/m2. At higher stacking fault energies (>45 mJ/m2), deformation is controlled by dislocation glide whereas at very low stacking fault energies (<18 mJ/m^2), martensitic transformation is favored over deformation twinning [78, 79]. At low temperatures, even materials with γ_{SFE}> 45 mJ/m^{2}are found to be mechanically twinned, for example, Cu [80], whose γ_{SFE} is ~80 mJ/m^2 [39]. Even in pure Ni (γ_{SFE} ~ 150 mJ/m^2) [39], deformation twinning occurs under shock loading conditions [81]. Previous studies have shown that the addition of Fe, Co, Cr and Mn to pure Ni all reduce the stacking fault energy, with Cr having the largest effect and Fe the smallest [82, 83]. Additional work is needed to confirm whether, and to what extent, twinning contributes to work hardening in the present alloys. Martensitic transformation appears not to be a contributing factor since post-fracture x-ray diffraction performed on specimens tested at 77 K revealed no new phases.

The representative fracture surfaces in Fig. 9 show that there is significantly less macroscopic necking in the equiatomic alloy, FeNi, than in pure Ni, consistent with its higher tensile ductility and work hardening capability that postpones the onset of necking instability according to Considere’s criterion. Microscopically, however, both exhibit ductile dimples on their fracture surfaces. A similar lack of necking was observed in the other equiatomic alloys that exhibited high ductilities. Microscopically, all the FCC alloys examined here exhibited ductile dimples on their fracture surfaces.

5. Summary and Conclusions

Several binary, ternary and quaternary alloys with equiatomic compositions were arc-melted, cast, cold rolled and recrystallized to produce equiaxed grains of comparable size. All the alloys are subsets of a quinary FCC high-entropy alloy that was previously investigated (FeNiCoCrMn) and consisted of single-phase solid solutions with the FCC structure. For comparison, unalloyed FCC Ni was also investigated. The effects of temperature on tensile properties were quantified over the temperature range of 77-673 K yielding the following observations:

(1) The flow stress of the equiatomic alloys is temperature dependent to varying degrees depending on the alloy. The yield and ultimate strengths of NiCoCr, NiCoCrMn, and FeNiCoCr increase strongly with decreasing temperature whereas those of NiCo and Ni exhibit very weak temperature dependencies.

(2) Alloying affects both the thermal and athermal portions of the yield stress vs. temperature curves.

(3) The stronger alloys are not necessarily the ones with the most elements. The nature of the constituent elements is also important, with the Cr-containing alloys in general being the strongest.

(4) The Hall-Petch slopes of the FeNiCoCr alloy are essentially independent of test temperature. This implies that grain-boundary strengthening is unlikely to be a major contributor to the observed temperature dependence of the yield strength.

(5) An analysis suggests that the temperature dependence of the yield strength in the alloys may be determined by Peierls-barrier-dominated lattice friction, with the height of the Peierl's barrier controlled by thermal influences on the width of the dislocation. By fitting the experimental yield stress vs. temperature curves to the Peierls-Nabarro equation, the

barriers in the equiatomic FCC alloys appear to be stronger than those in pure FCC metals but weaker than those in pure BCC metals.

(6) The ultimate tensile strength and uniform elongation to fracture of all the equiatomic alloys increase with decreasing temperature, with the largest increase occurring between 77 and 293 K. It is possible that deformation twinning similar to that observed in the FeNiCoCrMn high-entropy alloy [26] contributes to the enhanced ductility at cryogenic temperatures in some of the alloys. Additional work is needed to verify this.

(7) During the initial stages of plastic deformation (5-13% strain, depending on material), the temperature dependence of strain hardening is due almost entirely to the temperature dependence of the shear modulus. This indicates the athermal nature of dislocation multiplication, accumulation and interaction during the early stages of deformation.

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Figure Captions

Fig. 1. Back-scattered electron images of: (a) FeNiCoCr, (b) FeNiCo, (c) NiCoCr, (d) FeNi, (e) NiCo, (f) FeNiMn, (g) NiCoMn, (h) FeNiCoMn, (i) NiCoCrMn,and (j) pure Ni after cold-rolling and annealing (annealing temperatures and times are shown in Table I).

Fig. 2. Engineering stress vs. engineering plastic strain as a function of temperature for the equiatomic alloys.

Fig. 3. Temperature dependence of: (a) the 0.2% offset yield stress (σ_y); (b) the ultimate tensile strength (UTS); and (c) the uniform elongation to fracture for the equiatomic alloys.

Fig. 4. Hall-Petch plots showing the effects of grain size, *d*, on the yield strength of the FeNiCoCr equiatomic alloy at different temperatures.

Fig. 5. The temperature dependence of the 0.2% offset yield stress of the equiatomic alloys and pure Ni. The dashed lines are curve fits to the form of Eq. 10. Data for the quinary alloy FeNiCoCrMn are from [26].

Fig. 6. Strain hardening portion of the flow stress ($\Delta\sigma_\rho = \sigma_{flow} - \sigma_y$) vs. true plastic strain as a function of temperature for the equiatomic alloys.

Fig. 7. Shear modulus corrected strain hardening versus true plastic strain curves for: (a) the FeNiCoCr equiatomic alloy; (b) the FeNi equiatomic alloy; and (c) pure Ni.

Fig. 8. Temperature dependence of the extent of work hardening (UTS – σ_y) for the equiatomic alloys.

Fig. 9. High and low magnification fractographs of tensile samples tested to failure at 77 K: (a, b) FeNi and (c, d) Ni.

List of Tables

Table I. Processing conditions and grain sizes of the equiatomic alloys.

Alloy	Homogenization temperature (K)	Reduction in thickness (%)	Annealing temperature (K), time (h)	Grain size (μm)
FeNiCoCr	1473	92	1173, 1	24
FeNiCoMn	1373	90	1273, 1	48
NiCoCrMn	1373	90	1273, 1	36
FeNiCo	1473	92	1173, 1	28
NiCoCr	1473	92	1273, 1	41
FeNiMn	1373	90	1173, 1	30
NiCoMn	1373	90	1173, 1	32
FeNi	1473	92	1173, 1	35
NiCo	1473	92	1073, 1	35
Ni	1473	92	1073, 0.5	85

Table II. Measured melting temperatures, room temperature shear moduli and Poisson's ratios of the equiatomic alloys.

Alloy	Melting temperature (K)	Shear modulus (GPa)	Poisson's ratio
FeNiCoCrMn	1553	80	0.26
FeNiCoCr	1695	84	0.28
FeNiCoMn	1533	77	0.22
NiCoCrMn	1489	78	0.25
FeNiCo	1724	60	0.35
NiCoCr	1690	87	0.30
FeNiMn	1473	73	0.24
NiCoMn	1462	77	0.23
FeNi	1703	62	0.34
NiCo	1735	84	0.29
Ni	1728	76	0.31

Table III. The fitting parameters σ_a, C, and σ_b obtained from curve fits of the data in Fig. 5 according to the form of Eq. 10. The table also lists: the 0 K Peierls stress, $\sigma_p(0)$, calculated by assuming ω_0 = 0.5b, b, 1.5b, and 2b; the constant α; the melting temperatures (T_m); and the product of α and T_m. Additional descriptions of the parameters and their symbols are given in the text.

alloy	σ_a (MPa)	C (K)	σ_b (MPa)	$\sigma_p(0)$ (MPa) (ω_0=0.5b)	$\sigma_p(0)$ (MPa) (ω_0=b)	$\sigma_p(0)$ (MPa) (ω_0=1.5b)	$\sigma_p(0)$ (MPa) (ω_0=2b)	α (K^{-1})	T_m(K)	T_m*α
FeNiCoCrMn	423	180	109	9358	405	17	0.76	0.00088	1553	1.37
FeNiCoCr	443	184	184	9858	426	18	0.80	0.00087	1695	1.46
FeNiCoMn	282	219	101	8545	369	16	0.69	0.00073	1533	1.11
NiCoCrMn	491	207	166	9002	389	16	0.73	0.00077	1489	1.14
FeNiCo	292	252	125	7990	345	14	0.65	0.00063	1724	1.08
NiCoCr	489	228	167	10758	465	20	0.87	0.00070	1690	1.18
FeNiMn	283	195	182	8314	359	15	0.67	0.00082	1473	1.20
NiCoMn	302	190	170	8656	374	16	0.70	0.00084	1462	1.22
FeNi	341	291	74	8000	346	14	0.65	0.00055	1703	0.93
NiCo	130	336	50	10241	443	19	0.83	0.00047	1735	0.82
Ni	46	308	70	9534	412	17	0.77	0.00052	1728	0.89

Table V. Temperature dependence of the shear modulus of FeNiCoCr (this study), FeNi (calculated from [68]), and pure Ni (extracted from [68]).

	Shear modulus (GPa)		
Temperature (K)	FeNiCoCr	FeNi	Ni
77	--	68	84
203	--	66	80
293	84	62	76
473	79	62	73
673	72	60	70