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Deformation microstructures and strength of face-centered cubic high/medium entropy alloys

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Abstract. In this study we report the deformation microstructures and strength of medium entropy alloys (MEAs) and high entropy alloys (HEAs), which are defined as alloys composed of four or less, and five or more principal elements, respectively, with (near-) equi-atomic concentrations. The friction stress (fundamental resistance to dislocation motion in the crystal lattice) and Hall-Petch relationship of various MEAs (CoCrFeNi, CoCrNi, etc.), taken as subsystems of the equi-atomic CoCrFeMnNi HEA, were precisely measured at room temperature. Experimental values of the friction stresses were found to fit with a theoretical model proposed by Toda-Caraballo *et al*. very well, which indicates that the strength of the alloys is closely related to a heterogeneously distorted crystal lattice. At the same time, values of the average lattice distortion in the alloys were found to be comparable to those in some dilute alloys, contradicting the belief that "severe" lattice distortion is a reason for the higher strength than in dilute systems. Finally, a strengthening mechanism due to element-element interactions was proposed as an additional mechanism in FCC HEAs and MEAs.

1. Introduction
Conventionally, metallic materials have been designed simply based on one kind of solvent element, such as Fe, Al, etc., where a small amount of alloying elements, such as C, Cr, Cu, etc., are added to achieve superior properties. In contrast, in 2004, Yeh *et al*. [1] and Cantor *et al*. [2] independently proposed the concept of high entropy alloys (HEAs), which are defined as alloys composed of five or more alloying elements with (near-) equimolar composition, focusing on the center part of a phase diagrams. Since then, discoveries of various kinds of new HEAs and of their exceptional physical properties have been reported extensively [3]. Furthermore, as derivatives of HEAs, a concept of medium entropy alloys (MEAs), composed of four or fewer alloying elements with (near-) equimolar concentration was also proposed. Some of these MEAs have been found to possess similar, or even superior, physical properties compared with HEAs. For example, Gludovatz *et al*. investigated mechanical properties and fracture toughness of equiatomic CoCrFeMnNi HEA [4] and CoCrNi MEA [5] with FCC single-phase and found that these materials showed excellent resistance to fracture.

Although many experimental evidences have shown their outstanding mechanical properties, the underlying physics of strengthening effect is still unclear.

In this study, we have investigated the effect of alloying elements on the strength of HEAs and MEAs, focusing particularly on their dislocation microstructures. The friction stress, i.e., the fundamental resistance to dislocation motion, of various kinds of HEAs and MEAs were obtained from intercepts of Hall-Petch relationships of their yield strength in tensile tests. Two kinds of theoretical model were adapted to understand the strengthening effect in the HEAs and MEAs. In addition, their deformation microstructures upon yielding were observed by scanning transmission electron microscopy (STEM) under diffraction contrast conditions. Finally, we discuss the strengthening mechanism that dominates the mechanical behavior of HEAs and MEAs.

2. Experimental methods

Ingots of Ni-60Co (= $Co_{60}Ni_{40}$), CoCrFeNi, CoFeMnNi, CoFeNi, CoMnNi, FeMnNi, $(CoNi)_{80}Cr_{20}$, and $Co_{20}(CrNi)_{80}$ were produced by vacuum arc-melting of constituent pure-metal elements with purities of more than 99.9 at.% and casting in a water-cooled copper mold under a protective Ar atmosphere. To remove macro-segregation of constituent elements, the ingots were subsequently cold-rolled by about 90% reduction in thickness and homogenized at 1200 °C for 12 h under a vacuum environment using a tube furnace. Afterwards, disc-shaped specimens with a diameter of 10 mm and a thickness of 0.8 mm were cut from the homogenized materials for high-pressure torsion (HPT).

The HPT was performed at room temperature under a pressure of 6 GPa at a speed of 0.2 rpm (rotation per minute). The total rotation angle applied was 1800° (5 rotations). After the heavy deformation by HPT, the materials were annealed at various temperatures ranging from 600 °C to 1000 °C for 20 s to 7.2 ks to obtain specimens with a wide range of mean grain sizes. Tensile tests using small-sized specimens cut from the HPT processed specimens (gauge length: 2 mm, gauge cross section: 1 mm × 0.5 mm) were performed at room temperature at a quasi-static strain rate of 8.3×10^{-4} s^{-1} to characterize mechanical properties of the materials. Tensile deformation of Ni-60Co and $Co_{20}(CrNi)_{80}$ with a mean grain size of 2 μm was interrupted at a nominal strain of $e \sim 2\%$ to investigate deformation microstructures after yielding. The displacement of the gauge section was precisely measured by a CCD video camera extensometer, and the strain was calculated by a digital image correlation (DIC) technique.

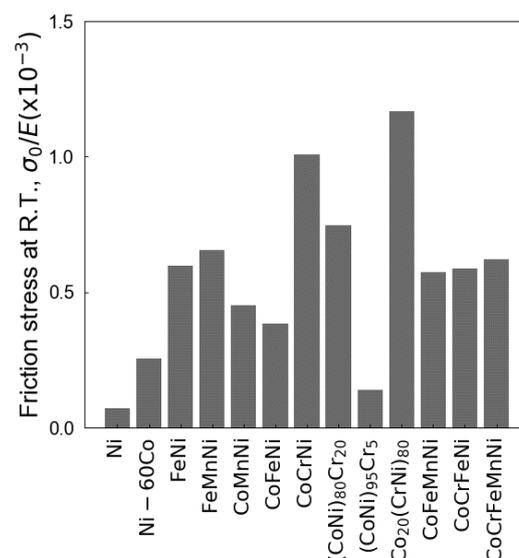**Figure 1**: Friction stresses (σ_0) of various alloys at room temperature (R.T.). The values of friction stress were extracted from the Hall-Petch relationship and normalized by their Young's modulus (E) to eliminate the effect of elastic modulus.

Grain sizes of the tensile specimens were measured by an intercept method based on microstructural images obtained by a JEOL, JSM-7800F field emission (FE) scanning electron microscope (SEM), equipped with a backscattered electron (BSE) detector. Deformation microstructures were observed by using STEM (JEOL, JEM-2100) equipped with bright field (BF) and annular dark field (ADF) detectors. The STEM observations were conducted under diffraction contrast conditions (so-called diffraction contrast imaging (DCI)-STEM). Experimental details of the technique are explained in Ref. [6]. In each material, more than 20 grains from two thin-foils were observed to confirm the reproducibility of the results.

3. Results and discussion

Figure 1 shows experimentally obtained friction stresses, σ_0, of the alloys at room temperature, together with the data for pure Ni [7], CoCrNi MEA [8], and CoCrFeMnNi HEA [9], all normalized by Young's modulus, E, to eliminate the effect of elasticity. The σ_0 values were obtained by fitting the yield strength (0.2% proof stress), σ_Y, and mean grain sizes, d, of the materials according to the Hall-Petch relationship [10,11]:

$$\sigma_Y = \sigma_0 + kd^{-\frac{1}{2}}, \tag{1}$$

where k is a constant (the Hall-Petch slope). Note that more than 10 data points with a wide range of grain sizes were used for the fitting of each material. It was found that a simple increase in the number of alloying elements did not always result in an increase in the friction stress.

Toda-Caraballo *et al.* [12,13] modified a well-known solid solution strengthening model originally proposed by Labusch [14]. In their model, the material strength is expressed as

$$\frac{\tau(0 \text{ K})}{G} \propto \varepsilon_{\text{ave}}^{\frac{4}{3}}. \tag{2}$$

where $\tau(0\text{ K})$ is the critical resolved shear stress (CRSS) for dislocation slip at 0 K, and G is the shear modulus. In the model ε_{ave} is an average atomic size misfit parameter evaluated by simple equations, of
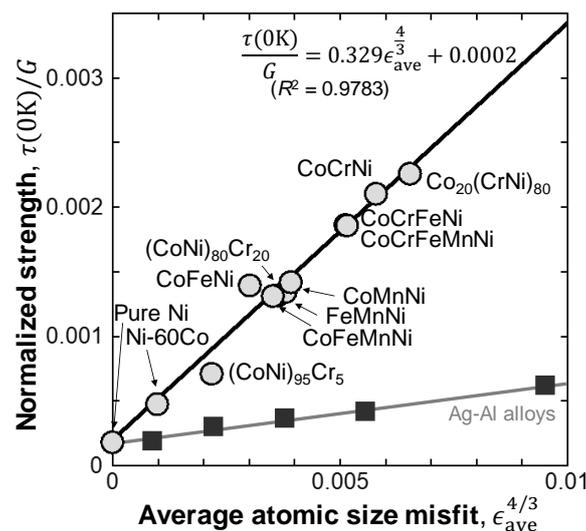

Figure 2: Relationship between the average atomic size misfit parameter (the average lattice distortion) calculated by the Toda-Caraballo model and the strength (the friction stress at 0 K divided by the Taylor factor of random texture, $M = 3.06$) normalized by shear modulus (G) of the alloys studied in the present study. The solid black line is a fitting line determined based on the model proposed by Toda-Caraballo (equation (2)). Similar plots for the data of Ag-Al binary alloys extracted from previous literature is also shown in the figure.

which details can be found in Ref. [12,13]. Wu *et al*. [15] already reported the shear modulus, *G*, and temperature dependence of the yield strength in various HEAs and MEAs.

In this study, the experimental values of σ_0 were extrapolated to 0 K by using the results reported by Wu *et al*. [15], assuming that the Hall-Petch slope was independent of temperature in low-temperature region. Next, τ (0 K) was determined by dividing σ_0 at 0 K by the Taylor factor for FCC materials having random texture (M = 3.06). Figure 2 shows the relationship between the average atomic size misfit and τ (0 K) normalized by the shear modulus of the HEAs and MEAs, together with that of Ag-Al binary alloys for comparison [16]. It was found that equation (2) fitted very well with the experimental data points of various HEAs and MEAs. This indicates that crystal lattices of equi-atomic multicomponent alloys are heterogeneously distorted due to the difference in atomic sizes of the constituent alloying elements. Accordingly, dislocations in such crystal lattices are considered to be always affected by the elastic fields originating from the lattice distortions. It is also very interesting that values of the average atomic size misfits for the dilute alloys are distributed over a wide range up to 0.01, which is comparable to the distribution of the misfit values for the MEAs and HEA, despite the fact that it has been believed that the reason for the high strength of HEAs is due to the "severe" lattice distortion effect caused by many kinds of elements. It should be noted, on the other hand, that the strength of the MEAs and HEAs were found to be much higher than that of the dilute alloys even at an equivalent average lattice distortion (average atomic size misfit). This suggests that the high strength of HEAs and MEAs cannot be simply explained only by the effect of lattice distortion.
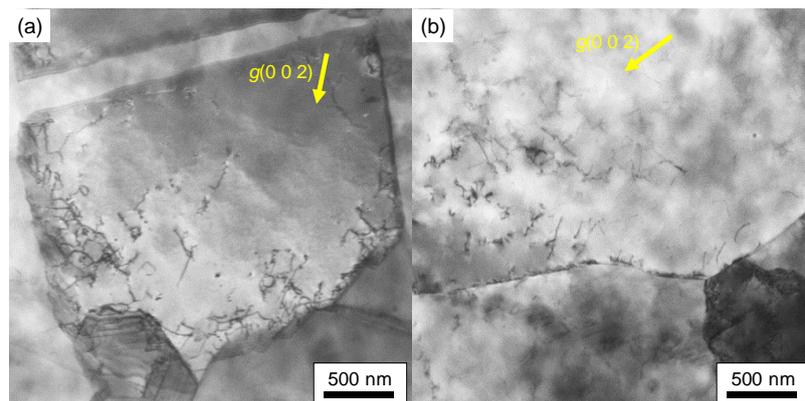

Figure 3: (a) Representative DCI-STEM image showing the dislocation microstructure in Ni-60Co alloy tensile-deformed to *e* ~ 2%. (b) DCI-STEM micrographs taken at different position in the same sample.
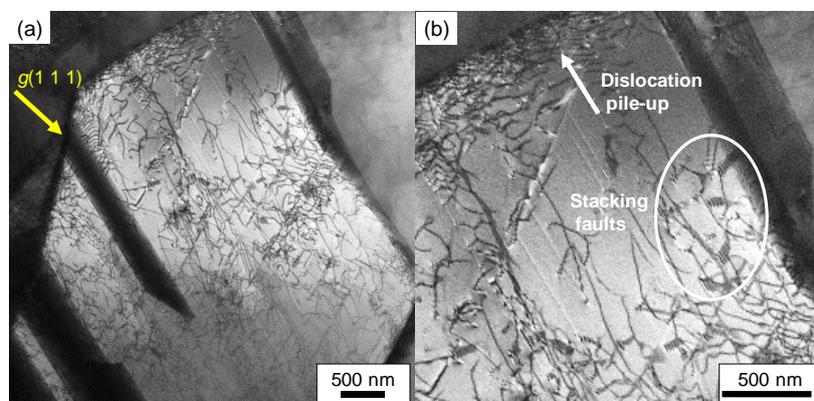

Figure 4: (a) Representative DCI-STEM image showing the dislocation microstructure in the $Co_{20}(CrNi)_{80}$ alloy tensile-deformed to *e* ~ 2%. (b) Enlarged image of (a).

To investigate the yielding mechanism of the alloys having different friction stresses, we observed dislocation microstructures of Ni-60Co (Low σ_0) and Co$_{20}$(CrNi)$_{80}$ (High σ_0), alloys showing the lowest and highest friction stress among the HEAs and MEAs studied, by the DCI-STEM technique. Figure 3 (a) and (b) are representative microstructures of Ni-60Co tensile-deformed to $e \sim 2\%$. The images show dislocations randomly-tangled near grain boundaries. On the other hand, figure 4 (a) shows representative microstructures of Co$_{20}$(CrNi)$_{80}$ deformed to $e \sim 2\%$. It can be seen that the dislocation density in Co$_{20}$(CrNi)$_{80}$ is higher than that in Ni-60Co, and Co$_{20}$(CrNi)$_{80}$ showed some dislocations forming planar structures. In addition, the enlarged image (figure 4 (b)) shows some stacking faults and dislocations piled up at grain boundaries. Investigation of the effect of grain orientation is our on-going work and will be presented in a future publication. Although the yielding mechanism of both alloys seemed to be dislocation slip, the difference in dislocation microstructures was confirmed to depend on the friction stress. The planarity of dislocation microstructures in FCC metals is often attributed to (1) low stacking fault energy or (2) short-range ordering (SRO) and short-range clustering (SRC) [17].

Based on the above experimental facts, we propose a new strengthening mechanism by element-element interaction originating from weak elemental inhomogeneity (deviation from "random" distribution) in equi-atomic or near-equi-atomic alloys, i.e., SRO and SRC, for understanding the additional strengthening mechanism. In general, the SRO and SRC states are responsible for the strength of solid solutions, which is not simply because of the increased value of ε_{ave}. When a dislocation passes through an ordered or clustered region, the stable arrangement of elements (SRO or SRC state) is destroyed by shifting one atomic plane along the Burger's vector, which causes extra resistance to the dislocation motion. In dilute alloy systems, the change in the atomic arrangement around solute atoms before and after a dislocation passes through rarely happens because the majority of atoms are the solvent element, and such an effect on the strength is limited. In this case, it is enough to consider only the effect of lattice distortion, as Labusch did [14]. On the other hand, in high-alloy systems, even weak element-element interactions* (SRO or SRC) can have a significant impact on the strength since the concentration of alloying elements is high [18]. (*Note that we name the interaction among alloying elements as element-element interaction, different from "solute-solute interaction", because it is difficult to distinguish between solutes and solvent in HEAs and MEAs.) The destruction of the stable arrangement of elements can happen everywhere and will lead to larger fluctuations of local potential energy for dislocation segments, resulting in an additional strengthening effect in high-alloy systems. The importance of element-element interactions was also demonstrated by Zhang *et al.* [19] very recently, based on their theoretical modeling of SRO in HEAs. This effect of weak elemental inhomogeneity has been omitted in conventional dislocation theory, but the present results suggest that the strengthening effect of element-element interactions cannot be neglected in high-alloy systems such as HEAs and MEAs because of their particularly high concentration of alloying elements.

4. Conclusion
In the present study, we precisely obtained the friction stress and Hall-Petch relationship of various MEAs and HEAs at room temperature. Experimental values of the friction stresses were found to fit with a theoretical model proposed by Toda-Caraballo *et al*. very well. This indicates that the strength of the alloys is closely related to the crystal lattice distortion. At the same time, values of the average lattice distortion in the alloys were found to be comparable to those in some dilute alloys, although "severe" lattice distortion had been believed as a reason for the higher strength than dilute systems. The results of DCI-STEM observations showed a planar morphology of the dislocation microstructure in Co$_{20}$(CrNi)$_{80}$ with higher σ_0 while randomly tangled dislocations were observed in the Ni-60Co alloy with lower σ_0. From those results, a strengthening mechanism based on element-element interactions was proposed as an additional mechanism in FCC HEAs and MEAs.

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