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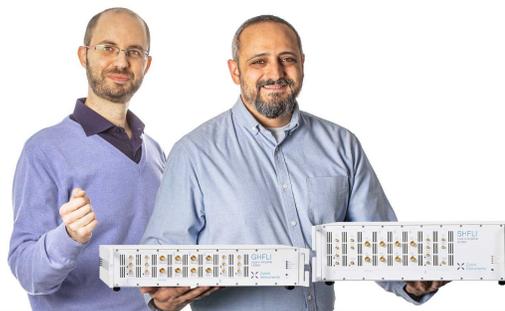
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# Mechanisms of Plastic Deformation of CoCrFeNi High-Entropy Alloy Single Crystals during Solid Solution Hardening by Mo Atoms

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**Abstract.** The effect of alloying with Mo atoms 4 at % on the temperature dependence of critical resolved shear stresses (CRSS)  $\tau_{cr}(T)$ , strain hardening coefficient, plasticity and deformation mechanism was studied on  $[\bar{1}11]$ -oriented crystals of the fcc CoCrFeNi (at %) high-entropy alloy (HEA) within the temperature range  $T = 77\text{--}973$  K under tension. It was shown that during solid solution hardening by Mo atoms, the CRSS  $\tau_{cr}$  increased by 45 and 23 MPa, respectively, at 77 and 296 K compared to crystals of this orientation of the equiatomic CoCrFeNiMn HEA. The onset of plastic deformation is associated with slip, and a planar structure with dislocation pile-ups was found at  $T = 77\text{--}296$  K. At 77 K, with the development of twinning in one system simultaneously with slip, high values of  $\Theta = d\sigma/d\varepsilon = 1750$  MPa and maximum stresses before failure  $\sigma_{max} = 1650$  MPa were found, and the plasticity was 57%. With an increase in the test temperature, deformation developed only by slip;  $\Theta = d\sigma/d\varepsilon$ , and  $\sigma_{max}$  decreased, but the plasticity remained at the level of 50–57%.

## INTRODUCTION

HEAs are a new class of materials that do not have a “base element” and consist of five or more principal elements in equal or nearly equal atomic compositions [1]. Due to the high mixing entropy, these alloys form a single-phase structure with a set of unique properties. In particular, HEAs with a face-centered cubic lattice (fcc), an example of which is the well-studied equiatomic CoCrFeNiMn HEA, have high strain hardening, good plasticity and ductile fracture, especially at cryogenic temperatures [1, 2]. However, their practical application is locked by low stresses at the yield point ( $\sigma_{0.1} \ll G/200$ ) of test temperatures above room temperature due to the strong temperature dependence of  $\sigma_{0.1}(T)$  [2, 3]. The stress level at the yield point in fcc HEAs is increased due to alloying with elements with a large atomic radius in comparison with the atoms that make up the basis, for instance, Al, Ti and Mo atoms [4, 5]. These atoms lead not only to solid solution but also to dispersion hardening due to the ability to form intermetallic phases with the elements Co, Cr, Fe and Mo [4, 5]. Solid solution and dispersion hardening affect the type of developing dislocation structure (cellular and planar) and the deformation mechanism (slip and twinning), which, in turn, determine the strain hardening and plasticity of these alloys. Solid solution hardening by Al, Ti and Mo atoms of different atomic concentrations was studied mainly on HEA polycrystals [4, 5]. On the fcc CoCrFeNi HEA single crystals, only solid solution and dispersion hardening by alloying with Al and Ti atoms was performed with respect to mechanical behaviour, dislocation structure and deformation mechanism [3].

In this study, using single crystals of the fcc equiatomic CoCrFeNi (at %) HEA, oriented along the  $[\bar{1}11]$  direction, the task was to investigate the effect of alloying by Mo atoms (with a concentration of 4 at %) on the temperature dependence of CRSS,  $\tau_{cr}$ , dislocation structure and deformation mechanism (slip and twinning) under tensile strain in the temperature range from 77 to 973 K. The  $\text{Co}_{24}\text{Cr}_{24}\text{Fe}_{24}\text{Ni}_{24}\text{Mo}_4$  (at %) alloy, when up to 4 at % Mo

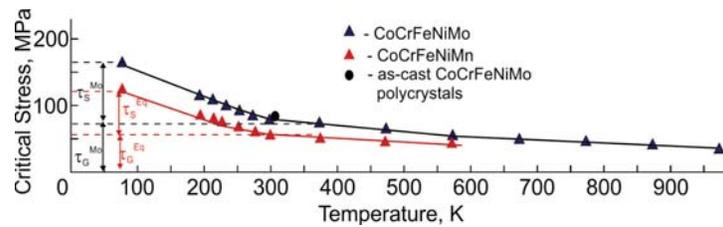
atoms were added to the CoCrFeNi system, was high-entropy, since the mixing entropy  $\Delta S_{\text{mix}}$  was 12.46 J/mol K [1] and was characterized by stacking fault energy  $\gamma_0$  equal to 0.030 J/m<sup>2</sup> [5]. In  $[\bar{1}11]$ -oriented crystals, the Schmid factor for twinning  $m_{\text{tw}}=0.31$  is greater than the Schmid factor for slip  $m_{\text{sl}}=0.27$ , and this orientation is favorable for twinning deformation if conditions are achieved for its development, namely a high level of deforming stresses combined with low stacking fault energy.

## MATERIALS AND RESEARCH METHODS

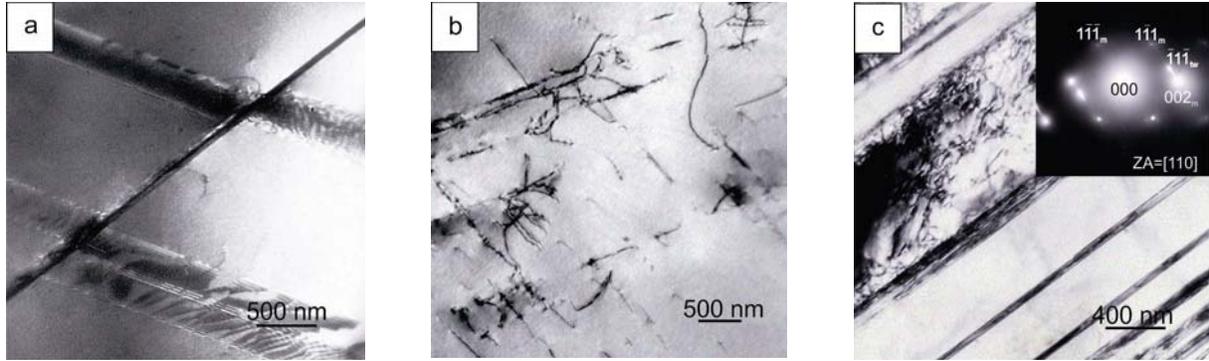
Single crystals of fcc Co<sub>24</sub>Cr<sub>24</sub>Fe<sub>24</sub>Ni<sub>24</sub>Mo<sub>4</sub> (at %) (CoCrFeNiMo) HEA were grown by the Bridgman method in a helium atmosphere using ingots cast in a resistance furnace. The crystals were homogenized in a helium atmosphere at 1473 K for 48 hours and then water quenched. Dog-bone-shaped tension samples had a gauge length of 12 mm and a cross section of  $2 \times 1.5$  mm<sup>2</sup>. Samples were cut using wire electrical-discharge machining. The crystal orientation was determined using a DRON-3M X-ray diffractometer. Transmission electron microscopy (TEM) was performed using a JEOL-2010 electron microscope at an accelerating voltage of 200 kV. The mechanical properties within a temperature range of 77 to 973 K were determined using an Instron 5969 universal testing machine at a strain rate of  $4 \times 10^{-4}$  s<sup>-1</sup>. The CRSS for slip were calculated using the equation  $\tau_{\text{cr}}^{\text{sl}} = \sigma_{0.1} \times m_{\text{sl}}$  (where  $\sigma_{0.1}$  is the uniaxial stress at the 0.1% offset strain yield point). X-ray analysis and TEM showed that single crystals of the CoCrFeNiMo HEA had the fcc structure.

## EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the CRSS,  $\tau_{\text{cr}}$ , for  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals under tensile strain within a wide temperature range  $T=77\text{--}973$  K, and for comparison,  $\tau_{\text{cr}}$  are also given for single crystals of the same orientation of the equiatomic CoCrFeNiMn HEA and as-cast CoCrFeNiMo polycrystals with a close concentration of Mo atoms [5]. The  $\tau_{\text{cr}}$  for polycrystals were determined using the equation  $\tau_{\text{cr}} = \sigma_{0.1}/M$  ( $M=3.06$  is the Taylor factor [2]). The temperature dependence of  $\tau_{\text{cr}}(T)$  of the  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals, as well as for single crystals of the equiatomic CoCrFeNiMn HEA, consisted of two sections characteristic of the slip deformation of fcc solid substitutional solutions [6]. At  $T < 373$  K, there was a strong temperature dependence  $\tau_{\text{cr}}(T)$ , (the thermally activated  $\tau_{\text{S}}$  component of  $\tau_{\text{cr}}$ ), which exceeded the temperature dependence of the shear modulus  $G(T)$  [3]. At  $T > 373$  K,  $\tau_{\text{cr}}(T)$  was weakly dependent on temperature as  $G(T)$ , and the athermal  $\tau_{\text{G}}$  component of  $\tau_{\text{cr}}$  was observed. Figure 1 shows  $\tau_{\text{S}}$  and  $\tau_{\text{G}}$  for two HEAs. Our analysis of the data presented in Fig. 1 showed, firstly, that alloying by Mo atoms up to 4 at% led to solid solution hardening of the  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals. At 77 K, the  $\Delta\tau_{\text{cr}} = \tau_{\text{cr}}^{\text{Mo}} - \tau_{\text{cr}}^{\text{Eq}} = 45$  MPa ( $\tau_{\text{cr}}^{\text{Mo}}$  and  $\tau_{\text{cr}}^{\text{Eq}}$  are the CRSS, respectively, for CoCrFeNiMo and CoCrFeNiMn HEAs); at 296 K, the  $\Delta\tau_{\text{cr}} = 23$  MPa; at 573 K,  $\Delta\tau_{\text{cr}} = 15$  MPa. The effect of solid solution hardening in single- and as-cast polycrystals of the CoCrFeNiMo HEA at a close concentration of Mo atoms turned out to be close at 296 K [5]. Secondly, upon solid solution hardening with Mo atoms with a concentration of 4 at%, an increase in the temperature dependence of  $\tau_{\text{cr}}(T)$  was observed. In  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals, the thermally activated component  $\tau_{\text{S}}^{\text{Mo}} = \tau_{\text{cr}}^{\text{Mo}} - \tau_{\text{G}}^{\text{Mo}} = 90$  MPa became larger than  $\tau_{\text{S}}^{\text{Eq}} = \tau_{\text{cr}}^{\text{Eq}} - \tau_{\text{G}}^{\text{Eq}} = 70$  MPa of the equiatomic CoCrFeNiMn HEA (Fig. 1). With solid solution hardening by Mo atoms, an increase in both the thermally activated  $\tau_{\text{S}}^{\text{Mo}}$  and athermal  $\tau_{\text{G}}^{\text{Mo}}$  components was observed, but  $\tau_{\text{S}}^{\text{Mo}}$  increased more than  $\tau_{\text{G}}^{\text{Mo}}$  ( $\Delta\tau_{\text{S}} = \tau_{\text{S}}^{\text{Mo}} - \tau_{\text{S}}^{\text{Eq}} = 20$  MPa, and  $\Delta\tau_{\text{G}} = \tau_{\text{G}}^{\text{Mo}} - \tau_{\text{G}}^{\text{Eq}} = 15$  MPa).



**FIGURE 1.** Temperature dependence of the CRSS,  $\tau_{\text{cr}}$ , in the  $[\bar{1}11]$ -oriented CoCrFeNiMo and CoCrFeNiMn high-entropy alloys single crystals and as-cast CoCrFeNiMo polycrystals under tensile strain [5].  $\tau_{\text{S}}^{\text{Mo}}$ ,  $\tau_{\text{S}}^{\text{Eq}}$ ,  $\tau_{\text{G}}^{\text{Mo}}$ ,  $\tau_{\text{G}}^{\text{Eq}}$  are the thermally activated and athermal components of  $\tau_{\text{cr}}$  for the CoCrFeNiMo and CoCrFeNiMn single crystals, respectively.

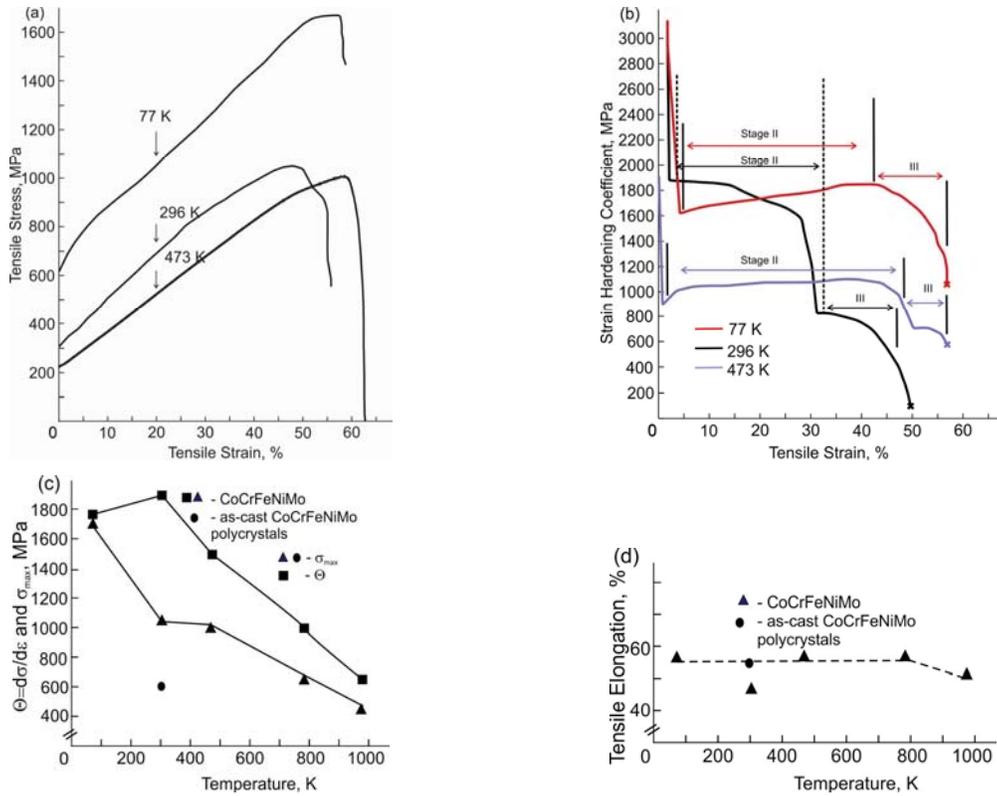


**FIGURE 2.** Dislocation structure in the  $[\bar{1}11]$ -oriented CoCrFeNiMo high-entropy alloy crystals under tensile strain: (a) 5% strain at 77 K; (b) 5%, 296 K; (c) 10%, 77 K.

A similar increase in  $\tau_s$  and  $\tau_G$  was observed in poly- and single crystals of HEAs upon solid solution hardening with Al and Ti atoms [3]. In single and polycrystals of fcc HEAs with Ti and Al atoms, the growth of  $\tau_s$  relative to the equiatomic CoCrFeNiMn HEA was determined by the local interaction of slip dislocations with atoms of a larger atomic radius. Since single crystals showed the same increase in  $\tau_s$  upon alloying with Al, Ti and Mo atoms, an increase in  $\tau_s$  upon solid solution hardening with Mo atoms was also due to the local interaction between slip dislocations and Mo atoms.

The onset of plastic deformation of the  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals was found to be associated with slip. The dislocation pile-ups and stacking faults (SFs) were observed within the temperature range from 77 to 296 K (Figs. 2a, 2b). Formation of dislocation pile-ups was associated with the difficulty of cross-slip of dislocations due to the low SF energy  $\gamma_0$  and the high resistance to dislocation motion from the side of substitutional atoms. In  $[\bar{1}11]$ -oriented crystals of the equiatomic CoCrFeNiMn HEA, in contrast to crystals of this orientation of the CoCrFeNiMo HEA, dislocation pile-ups in the dislocation structure after strain of 3–5% at 296 K were not observed and the dislocation structure was a uniform distribution of dislocations [7]. Such a difference in the dislocation structure at 296 K and close values of  $\tau_{cr}$  and  $\gamma_0$  ( $\gamma_0$  was equal to 0.030 and 0.022 J/m<sup>2</sup>, respectively, for CoCrFeNiMo and CoCrFeNiMn HEA [2, 5]) was associated with the effect of short-range order in the arrangement of Mo atoms in the CoCrFeNiMo HEA single crystals and its absence in the CoCrFeNiMo HEA single crystals [7–9]. Twinning in the  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals was detected after 10% strain at 77 K (Fig. 2c).

Figure 3 displays the  $\sigma(\epsilon)$  curves and the change in the strain hardening coefficient  $\Theta = d\sigma/d\epsilon$  for three test temperatures and also the temperature dependence of the strain hardening coefficient  $\Theta$ , the maximum stress level  $\sigma_{max}$  achieved before failure and plasticity in a wider temperature range of the  $[\bar{1}11]$ -oriented CoCrFeNiMo HEA crystals under tensile strain. It can be seen that in the  $[\bar{1}11]$ -oriented crystals, the plastic flow developed predominantly in one linear stage (Figs. 3a, 3b). At 77 and 296 K,  $\Theta$  at the linear stage reached its maximum value, which decreased with increasing test temperature. An analysis of  $\Theta$  of the  $[\bar{1}11]$ -oriented crystals at 77 K revealed its dependence on the strain level; i.e. up to 7% strain,  $\Theta = 3500$  MPa, and then at  $\epsilon > 7\%$ , it decreased to 1630 MPa and again increased with an increase in strain (Fig. 3b). The dependence of  $\Theta$  on the strain level is not a characteristic feature of the plastic flow of fcc crystals at the linear stage during slip deformation, and such  $\Theta$  behavior with an increasing strain level is usually observed during twinning. An increase in  $\Theta$  at the linear hardening stage is a unique property and is called the TWIP effect. This has previously been observed in other poly- and single crystals of HEAs [2, 3]. At high test temperatures ( $T \geq 296$  K), there was found to be no change in  $\Theta$  from the strain level as at 77 K. At 77 K and maximum  $\Theta$  in the  $[\bar{1}11]$ -oriented crystals during tensile strain, the maximum stress level  $\sigma_{max} = 1650$  MPa before failure was reached, which decreased by a factor of four at 973 K. However, plasticity in the investigated temperature range of 77 to 973 K remained close (Fig. 3c). In the  $[\bar{1}11]$ -oriented crystals, plasticity was close in magnitude to that of as-cast polycrystals at 296 K. With close plasticity at 296 K in as-cast polycrystals,  $\sigma_{max} = 600$  MPa [5], and in the  $[\bar{1}11]$ -oriented crystals,  $\sigma_{max} = 1040$  MPa.



**FIGURE 3.** Stress-strain response (a), strain hardening coefficient (b), temperature dependence of strain hardening and ultimate stresses (c) and temperature dependence of plasticity (d) of the  $[\bar{1}11]$ -oriented CoCrFeNiMo high-entropy alloy crystals under tensile strain.

Studies of the dislocation structure showed that at 77 K, in the  $[\bar{1}11]$ -oriented crystals, the maximum values of  $\Theta$  and  $\sigma_{max}$  reached before failure were associated with the development of slip and twinning, which developed in one system at  $\varepsilon \geq 10\%$  (Fig. 2c). In the  $[\bar{1}11]$ -oriented crystals, with the development of twinning in one system, the condition for necking  $\sigma > d\sigma/d\varepsilon$  at 77 K was achieved at stresses  $\sigma \geq 1650$  MPa, which were much higher than the stresses at  $T \geq 296$  K, when there was no twinning. In addition, at 77 K, these crystals satisfied the consider condition, at which  $\sigma_{max} \approx \Theta$ . With an increase in temperature, this condition was not achieved, since the crystals were destroyed earlier, and the difference between  $\sigma_{max}$  and  $\Theta$  was significant in the temperature range from 296 to 700 K (Fig. 3).

## CONCLUSION

Alloying of  $[\bar{1}11]$ -oriented CoCrFeNi HEA crystals, with Mo atoms up to 4 at%, was found to lead to an increase in the CRSS,  $\tau_{cr}$ , by 45 and 23 MPa, respectively, at 77 and 296 K in comparison with crystals of this orientation of the equiatomic CoCrFeNiMn HEA. In the  $[\bar{1}11]$ -oriented crystals upon solid solution hardening by Mo atoms, a planar structure with dislocation pile-ups was found in the temperature range of 77 to 296 K. At 77 K, the development of twinning in one system simultaneously with slip provided a high strain hardening coefficient  $\Theta = 1750$  MPa and shifted the condition for neck formation  $\sigma > d\sigma/d\varepsilon$  to high stresses  $\sigma \geq 1650$  MPa. With the development of deformation only by slip, with an increase in the test temperature  $\Theta = d\sigma/d\varepsilon$  and the stresses for necking decreased.

## ACKNOWLEDGMENTS

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