Slip nucleation in single crystal FeNiCoCrMn high entropy alloy

L. Patriarca a, A. Ojha a, H. Sehitoglu a,b, Y.I. Chumlyakov b

a Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, 1206 W. Green St., Urbana, IL 61801, USA
b Siberian Physical-Technical Institute at Tomsk State University, Tomsk 634050, Russia

1. Introduction

Engineering structures and components can experience extreme loading conditions, therefore the development of new materials with exceptional mechanical properties is of significant importance. The recently proposed high entropy alloys with equal atomic mass of multi-component elements hold considerable promise and provide a potential breakthrough where high strength and high toughness may coexist [1,2]. The key to engineer these alloys is to exploit the solid solution hardening that derives from the choice of the elements for strengthening and, alongside, to obtain a single phase alloy which promotes high toughness. In this direction, as already suggested in recent works [3,4], the FeNiCoCrMn alloy represents one of the most promising high entropy alloys. As discussed in the aforementioned works, in the early stages of FeNiCoCrMn deformation slip represents the main deformation mechanism. It is thus of fundamental importance to (i) precisely determine the stress required to nucleate slip, and (ii) accurately predict this critical resolved shear stress (CRSS) with theory and simulation without using empirical constants. Previous treatments focused on experiments on polycrystalline alloys. In this work, we focus on single crystals because they allow precise determination of CRSS for slip based on the applied stress through the Schmid factor. We successfully grew single crystals of this alloy for the first time which is an important undertaking in pursuit of better understanding of the mechanical response. In particular, we deform [531] oriented crystals, a predominantly single slip orientation, and determine the CRSS experimentally.

Recent experiments have been conducted to study the temperature dependence on the yield strength of FeNiCoCrMn [3–6]. It is found that the ultimate tensile strength and the uniform elongation to fracture in these alloys increase with decreasing temperature. Slip is considered the main deformation mechanism even at low temperatures. However, since most of the previous experiments are conducted on polycrystalline samples, it is difficult to determine CRSS, a fundamental quantity, because the stress state at the grain level is not known [7]. In the current work, we use single crystals of FeNiCoCrMn where the stress state is completely defined as stated above, and the CRSS can be established. We are utilizing high resolution digital image correlation (DIC) methodology developed in our early work [8,9] to accurately establish local strain development due to onset of slip. Similar to the fcc metals, slip occurs on {111}<110> system in FeNiCoCrMn with Burgers vector of magnitude \(|b| = a_0/\sqrt{2}\), where \(a_0\) is the lattice constant. We choose the [531] crystal orientation such that the [111]<110> slip system with the highest Schmid factor nucleates providing a way to precisely pinpoint the CRSS. With the choice of single crystal, the role of other defects such as grain boundaries is removed, and an intrinsic measure of CRSS for slip is obtained. The CRSS is an important parameter in crystal plasticity, dislocation dynamics or other continuum mechanics treatments of stress–strain response. This represents a fundamental step in multiscaling.

Concurrently, we undertake atomistic calculations to obtain the lattice constant \(a_0\) and the important energy terms, \(\gamma_{ss}\) (the unstable stacking fault energy) and \(\gamma_{sf}\) (the intrinsic stacking fault energy) associated with the generalized stacking fault energy (GSFE) curve. The GSFE curve represents the free energy differences between a crystal fault and the bulk lattice with various degrees of shear displacements.
Single crystals of the equiatomic FeNiCoCrMn high entropy alloy were grown using the Bridgman technique in a He atmosphere utilizing high purity single element pieces. Single crystal ingots were homogenized at 1200 °C for 24 h in vacuum and subsequently quenched. Compression specimens were sectioned into 3.8 mm × 3.8 mm × 8 mm using electro-discharged machining with the loading axis along the [110] crystallographic direction. The single crystal compression specimens were successively solution-treated at 1100 °C for 1 h in air and quenched in oil. The crystal orientations of the specimens in three directions and the lattice parameters were determined by a Philips Xpert 2 X-ray diffractometer. The chemical composition was checked on one solution-treated sample by means of an ICP-MS PerkinElmer instrument providing the atomistic percentages Fe = 21.64%, Ni = 19.09%, Co = 21.47%, Cr = 18.35%, and Mn = 19.45%.

The experiments in compression were conducted on a MTS servo hydraulic load frame in displacement control at an average strain rate of 10^-4 s^-1. A fine speckle pattern adapted for DIC correlation was deposited on one surface of the specimens. The images suited for DIC strain measurements were captured by means of an IMI model IMB-202 FT CCD camera (1600 × 1200 pixels) with a Navitar optical lens. Two different image acquisition techniques were adopted for the experiments in compression. For the entire specimen side after unloading. High strain localizations were performed on one solution-treated sample by means of an ICP-MS PerkinElmer instrument providing the atomistic percentages Fe = 21.64%, Ni = 19.09%, Co = 21.47%, Cr = 18.35%, and Mn = 19.45%.

The experiments in compression were conducted on a MTS servo hydraulic load frame in displacement control at an average strain rate of 10^-4 s^-1. A fine speckle pattern adapted for DIC correlation was deposited on one surface of the specimens. The images suited for DIC strain measurements were captured by means of an IMI model IMB-202 FT CCD camera (1600 × 1200 pixels) with a Navitar optical lens. Two different image acquisition techniques were adopted for the experiments in compression. For the entire specimen side after unloading. High strain localizations were performed on one solution-treated sample by means of an ICP-MS PerkinElmer instrument providing the atomistic percentages Fe = 21.64%, Ni = 19.09%, Co = 21.47%, Cr = 18.35%, and Mn = 19.45%.

The stress-strain curve obtained at 293 K is reported in Fig. 1. In the top-right of Fig. 1 we provide the inverse pole figure calculated from X-ray data representing the [110] crystal orientation of the specimens along the load direction. Contour plots of the real time in-situ DIC strain fields are reported in the insets from 1 to 4. Inset marked 1 shows the strain field of the analyzed region captured before slip onset. Inset marked 2 shows the appearance of strain localizations at σ = 140 MPa which indicate slip onset. With increasing the applied deformation, the regions displaying early slip show one primary (011)[111] slip system (Schmid factor 0.50) and one secondary (011)[111] slip system (Schmid factor 0.44). Inset marked 5 shows the strain field captured for the entire specimen side after unloading. High strain localizations (>10%) were measured along the primary slip system, while large areas of the specimen remain undeformed.

Fig. 2 illustrates the results following the experimental procedure aimed to capture slip onset at 77 K. Only the main strain measurements...
are reported for the sake of brevity. Two strain plots are shown representing the strain field after loading/unloading the specimen at a maximum compressive stress of 340 MPa and 360 MPa at 77 K. The first strain field (340 MPa) indicates that no slip was active following the first stress cycle at 340 MPa; we then conclude that at 77 K, a compressive stress of 360 MPa is not sufficient to activate slip. The second strain field displays strain localization along the dashed line which indicates that following the load step at 360 MPa some irrecoverable process occurred. According to the stress levels tested we then established the axial stress required to slip initiation as \( \sigma = (350 \pm 10) \) MPa. Slip has been determined to be the dominant deformation mechanism even at 77 K. Twinning is not expected for this orientation.

In Fig. 3 we summarized and compared the stress–strain curves for the compressive experiments carried out at 293 K and at 77 K for the present [511] orientation. Using the Schmid law, we calculated the CRSS and obtained \( \tau_{77K} = 175 \) MPa and \( \tau_{293K} = 70 \) MPa at 77 K and 293 K respectively. The elastic moduli are \( E_{77K} = 206 \) GPa and \( E_{293K} = 127 \) GPa. In Fig. 3 we also report the X-ray diffraction data obtained on the single crystal specimen. The peak shown comes from the reflection of the (111) plane. We calculated the lattice parameter to be 3.585 Å.

### 4. Modeling of Critical Resolved Shear Stress for Slip

Using the first principles density functional theory (DFT) calculations, we obtained the equilibrium lattice constant of FeNiCoCrMn as \( a_0 = 3.59 \) Å which is in close agreement with experiments, and this is the starting point for the simulations. The DFT calculations were performed utilizing the Vienna ab initio Simulation Package (VASP) [17,18] with the Projector Augmented Wave (PAW) method and the Generalized Gradient Approximation (GGA) [19,20]. To determine the slip nucleation stress, the unstable stacking fault energy (\( \gamma_{us} \)) and the intrinsic stacking fault energy (\( \gamma_{if} \)) values associated with the GSFE curve for \( [111] \) slip system were theoretically determined for the first time, as shown in Table 1. In order to address potential solute segregation effects [21–23] near the fault, it is important to check systematically the role of solute positions on the intrinsic stacking fault energy. In the present case, after many simulations, we noted that the presence of Co atoms are favored near the fault reducing the intrinsic stacking fault energy by almost 55% (lowered from 38 mJm\(^{-2}\)) when compared to the presence of Co positions away from the fault. Therefore, the stacking fault energies reported in Table 1 correctly represent the lowest energy values possible for the \( [111] \) slip system. A relaxation scheme utilized in our previous work [24] ensured correct energy values as well. We note that without accounting for the solute segregation effects and implementing the relaxation scheme, the results would be in error. The GSFE landscape also allows us to derive the \( [110] \) shear modulus using the equation \( G = 2\pi a_0 \gamma_{max} \), where \( \gamma_{max} \) is the maximum slope of the GSFE curve. Using this well-established formulation, the \( [110] \) shear modulus \( (G) \) is obtained to be 84 GPa. We then utilized the ‘modified’ Peierls–Nabarro equation for cubic metals from our early studies [16,25–27] noting the appearance of the lattice parameter \( a_0 \), \( \gamma_{us} \) and \( \gamma_{if} \) terms in the equation. Subsequently, the slip stress for FeNiCoCrMn was obtained as 178 MPa using modified PN stress equation \( \tau = \frac{1}{2} \max (\frac{\gamma_{us}}{\gamma_{max}}, \frac{\gamma_{if}}{\gamma_{max}}) \) as reported in Table 2. It is important to note that the misfit energy term in PN equation is dependent on \( a_0 \), \( \gamma_{us} \) and \( \gamma_{if} \) and we obtained these terms theoretically in the present analysis. For complete description of the energy terms, and the PN formalism, please see Ref [11–13,15,16].

In addition, we also obtained the twinning stress for this alloy as 208 MPa using the methodology proposed in our early work (Wang-Sehitoglu [15]).

According to the experimental results shown in Fig. 3, the dependence of the CRSS on the temperature is striking. The CRSS at room
temperature is 70 MPa while that at 77 K is 175 MPa, an increase in the stress by more than two-fold with decrease in temperature. Further simulations and derivation of the CRSS using PN formalism showed that the CRSS at low temperature is 178 MPa (see Table 2). It is suggested that the temperature dependence on the yield strength in these alloys is dictated by the Peierls stress similar to the bcc metals, albeit weaker [28]. Nonetheless, the Peierls barriers in these alloys appear to be stronger than those in other fcc metals. Our framework holds considerable promise in constitutive modeling in the future providing considerable insights to high entropy alloys design. In summary, our approach using multiscale resources ranging from atomistic to mesoscale, devoid of empirical constants, can help guide the work of others trying to predict stress–strain response via crystal plasticity and molecular dynamics approaches.

5. Conclusions

The work supports the following conclusions:

- The CRSS to initiate slip for the new FeNiCoCrMn high entropy alloy was determined using DIC strain measurements along a selected single crystal orientation to be $\tau_{77K} = 175$ MPa and $\tau_{293K} = 70$ MPa at 77 K and 273 K, respectively.
- Using the first principles density functional theory calculations we calculated the equilibrium lattice constant of FeNiCoCrMn as $a_0 = 3.59$ Å, showing close agreement with the lattice constant $a_0 = 3.585$ Å determined using X-ray diffraction.
- Using the calculated lattice parameter $a_0$, the fault energy parameters $\gamma_{\text{usf}}, \gamma_{\text{ifs}}$, the shear moduli, $G$, the modified Peierls–Nabarro formalism proposed in our early work, we established the CRSS for slip to be 178 MPa which is in very close agreement with experiment ($\tau_{77K} = 175$ MPa). The remarkably close agreement between experiment and theory confirms the efficacy of our modeling framework and its potential to be applied to other high entropy alloys of significant interest.

Acknowledgments

The work was supported by Nyquist Chair Funds which is gratefully acknowledged. The authors also acknowledge the Frederick Seitz Materials Research Laboratory and Dr. Mauro Sardela for assistance with X-ray diffraction.

References


Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>$a_0$ (Å) (this study)</th>
<th>Shear modulus $G_{111}$</th>
<th>$\gamma_{\text{usf}}$ (mJ m$^{-2}$)</th>
<th>$\gamma_{\text{ifs}}$ (mJ m$^{-2}$)</th>
<th>Simulation (this study)</th>
<th>Experiment [28]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNiCoCrMn</td>
<td>3.59</td>
<td>84</td>
<td>192</td>
<td>17</td>
<td>20–25</td>
<td></td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (K)</th>
<th>Critical resolved shear stress for slip $\gamma$ (MPa)</th>
<th>Experiment (this study)</th>
<th>Theory$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNiCoCrMn</td>
<td>77</td>
<td>$175 \pm 5$</td>
<td>178</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Based on Peierls–Nabarro equation, $\gamma = \frac{1}{2}\max_{\mathbf{g}}\left[\frac{\mathbf{g} \cdot \mathbf{a}}{d}\right]$. 

Please cite this article as: L. Patriarca, et al., Slip nucleation in single crystal FeNiCoCrMn high entropy alloy, Scripta Materialia (2015), http://dx.doi.org/10.1016/j.scriptamat.2015.09.009