Elastic and plastic deformations in a high entropy alloy investigated using a nanoindentation method

D. Wu^{a*}, J.S.C. Jang^b, T.G. Nieh^a

^a Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

^b Institute of Materials Science and Engineering; Department of Mechanical Engineering, National Central University, Chung-Li 32001, Taiwan, ROC

* Please send all correspondence to Dr. D. Wu (Email: dwu10@vols.utk.edu)

Abstract

We employed instrumented indentation technique to study the elastic and plastic deformations in a face-centered cubic (fcc) high-entropy alloy NiFeCoCrMn. Single-crystal Ni was also examined for direct comparison. Tests were carried out using indenters with different tip radii to investigate the effect of indented volume on deformation processes. It was found that when the tip radius increased, the shear stress required for the occurrence of indentation pop-in decreased, which was attributable to a higher probability to find dislocations under a larger tip radius. We proposed a statistical model to describe the results quantitatively. In the plastic region, NiFeCoCrMn was much stronger than Ni, presumably resulted from a large lattice distortion in the multicomponent NiFeCoCrMn alloy. We found that the response of both materials at large indentation depth could be described by the classical Nix-Gao model, but when the indentation depth was shallow, the indenter tip must be treated as a sphere and Swadener's model offered a better description. In any event, it was necessary to introduce a scaling factor f to describe the effective stressed volume underneath the indenter tip to compensate for the overestimated hardness values. A map of indentation pressure against dislocation density was also summarized in this study.

Keywords: A. high-entropy alloys; B. incipient plasticity; B. indentation size effect; B. dislocation dynamics; F. nanoindentation

1. Introduction

High entropy alloys (HEAs) have received large attention from the materials science community due to their extraordinary properties [1] since they were introduced about a decade ago [2]. HEAs are multicomponent alloys containing several components (often 5) in equal atomic proportions. This new class of alloys is, in principle, expected to exhibit a large degree of mutual solubility in a single-phase structure, instead of complex ordered intermetallics, as a result of having high configurational entropy. However, the majority of HEAs is actually multiphase [3–12], suggesting a high entropy, sometimes, is not a guarantee for the formation of simple solid-solution phase, and the competition between entropy and enthalpy eventually determines the final phase formation.

There are, in fact, only a few HEAs with a true single-phase face-centered cubic (fcc) [13,14], body-centered cubic (bcc) [15–18] or hexagonal close-packed (hcp) [19] structure, in which the high-entropy effect dominates. Among them, the equiatomic fcc-NiFeCoCrMn alloy [13] is a prominent example that exhibits high phase stability, and its mechanical properties and microstructure have been studied [20–26]. For instance, Otto et al [23] reported that both yield strength, σ_y , and tensile strength, σ_{UTS} , of this HEA increased with decreasing temperature, and the temperature dependence of σ_{UTS} was determined by deformation twins at low temperature, but the temperature dependence of σ_y was from a solid-solution effect. Wu et al [27,28] further investigated the effect of temperature on the mechanical strength of this fcc-NiFeCoCrMn

system, and found that each constituent elements produced different strengthening effects on the alloys, and the effect of temperature depends on the number and the types of constituents.

Recently, studies on the elastic-plastic deformation behavior of HEAs using micromechanical tests, e.g., micropillar compression [15] and nanoindentation [26], also began to emerge. These micro-mechanical tests have major advantage of revealing the intrinsic properties of a material with a minimum possible influence from 2-dimensional microstructural defects (e.g., grain boundary, twin boundary). Zou et al [15] conducted compression on high-entropy alloy NbMoTaW micropillars and observed a higher compression strength in the alloy pillar as compared to pure Nb, Mo, Ta, and W pillars, indicating homogeneous intermixing of constituent elements can produce strong lattice friction in the multicomponent HEA. They also observed the strength of bcc HEA micro-pillar is about 3 times higher than that of their bulk counterparts, suggesting some kind of sample size effect.

The elastic-plastic deformation behavior of HEAs has also been characterized by nanoindentation technique. For example, Zhu et al [26] studied indentation pop-ins and determined the critical shear stress for the incipient plasticity in the fcc-NiFeCoCrMn alloy. Their results indicated that plastic yielding of the NiFeCoCrMn alloy is different from that of the pure metals. Other papers [29,30] also reported that yield strength of pure metals (e.g., Mo, Ni, Cr) depends on the tip radius of the indenter, and specifically the smaller is the tip radius, the higher is the yield strength.

In this study, the elastic/plastic deformation of a high entropy alloy NiFeCoCrMn is studied using instrumented indentation technique and directly compared with that of a nickel

single crystal. The indented volume was regulated by the applied load and the radius of the indenter tip, and its effect on the deformation behavior of the HEA was evaluated.

2. Materials and methods

Samples with the nominal composition of NiFeCoCrMn (in atomic proportion) were prepared by arc-melting a mixture of the constituent elements (purity > 99 wt%) in a Ti-gettered high-purity argon atmosphere. The alloy ingots were remelted four times in high-purity argon atmosphere to ensure their homogeneity. In the last melting, the liquid melt was suction-cast into a water-cooled rectangular Cu mold with a dimension of 30 mm W x 60 mm L x 3 mm T. The as-cast ingots were homogenized at 1200 °C for 4h, and then cold rolled to 50% reduction in thickness. Rectangular samples were sliced from the rolled plates, ground, and polished to a mirror finish. The polished samples were additionally annealed at 1000 °C in vacuum for 2h to induce recrystallization and grain growth, and to remove residual surface stresses from the mechanical polishing. The microstructure of the annealed alloy was examined using optical microscopy and SEM, and the grain size was found in the range of 60 ~ 120 μm . XRD pattern has shown a single phase fcc-NiFeCoCrMn alloy with the lattice parameter of about 3.594 Å. For comparison, a nickel single crystal was also tested. The single-crystal Ni(100) sample was prepared using a directional floating zone melting technique [31], and the test sample was ground and electropolished in an electrolyte containing 40% sulfuric acid before the indentation tests.

Instrumented indentation tests were performed on samples at room temperature using a Hysitron Triboindenter (Hysitron Inc., Minneapolis, MN). Three diamond indenters (two Berkovich tips and a cube corner tip) were used to evaluate the elastic-plastic response, and the tip radii of these three tips were calibrated on single-crystal tungsten to be 80 nm (cube corner),

255 nm (Berkovich) and 759 nm (Berkovich). To avoid the overlap of the plastic zone underneath the indenter, indentation tests were conducted with a 6 μm interval with a maximum load of 200 μN for tips $R = 80, 255$ nm and 1000 μN for the tip $R = 759$ nm. At least 70 indents were made for each tip radius. During each indentation test, a constant loading rate of 400 $\mu\text{N/s}$ was imposed to eliminate loading rate effect, and the maximum load was held for 1s before unloading. Indented sites are within the same grain and at least 6 μm away from the grain boundary to avoid possible effects of orientation and grain boundary. To investigate the plastic behavior, indentation tests were also performed in a neighboring grain with a maximum load of 10 mN and a 20 μm interval. A Berkovich indenter ($R = 255$ nm) was used, and its area function was calibrated with fused silica.

An atomic force microscope MFP-3D^{TM} (Asylum Research Inc, Santa Barbara, CA) was utilized under the air image mode to evaluate the sample surface before and after indentation tests. The probe (AC160TS-R3) used for imaging has a tip radius of about 9 ± 2 nm. Both the annealed NiFeCoCrMn and single-crystal Ni have an rms roughness value of about 2 nm.

3 Results

3.1 Elastic response of NiFeCoCrMn

In an indentation test, the transition from elasticity to plasticity is marked by the first pop-in on the load-displacement curves, as shown in Figure 1a and 1b, for NiFeCoCrMn and single-crystal Ni, respectively. In the figures, three different tip radii are used and it is evident that the larger is the tip radius, the higher is the load to reach a given penetration depth for the occurrence of pop-in. The residual indented marks from the indenters ($R = 80$ and 759 nm) were examined

by AFM, as shown in Figure 2. It is noted that the pyramidal indenter actually exhibits a spherical bottom with a curvature that is consistent with the calibrated tip radii.

Figure 1 Typical load-displacement curves from the nanoindentation tests on the annealed NiFeCoCrMn (a) and single-crystal Ni (b) using indenters with three tip radii ($R = 80, 255, 759$ nm), respectively. The elastic part of the loading curves can be well described by the Hertzian relation. The reduced elastic moduli of 190.21 ± 1.22 and 187.18 ± 1.59 GPa were calculated from the slopes of $P-h^{1.5}$ plot at pop-in for NiFeCoCrMn (c) and single-crystal Ni (d), respectively.

Figure 2 The blunt bottom of the indent profiles (a) and (c), which are extracted from the AFM topographic images of residual impressions on NiFeCoCrMn (b) and (d), agree well with the tip radii $R = 80$ and 759 nm, respectively.

The elastic part of the loading curve prior to a pop-in event is described by the Hertzian relation,

$$P = \frac{4}{3} E_r \sqrt{Rh^3} \quad (1)$$

where R is the tip radius of the indenter, h is the indentation depth, $E_r = [(1-\nu_{in}^2)/E_{in} + (1-\nu_s^2)/E_s]^{-1}$ is the reduced elastic modulus of the tested sample, (ν_{in}, E_{in}) and (ν_s, E_s) are the Poisson's ratio and elastic modulus of the indenter and sample, respectively. Data of $P-h^{1.5}$ pairs at pop-ins obtained from NiFeCoCrMn and Ni single crystal under the indenter ($R = 255$ nm) are plotted in Figure 1c and 1d. The reduced elastic moduli for NiFeCoCrMn and Ni are calculated to be 190.21 ± 1.22 and 187.18 ± 1.59 GPa, respectively. Using these E_r values, the elastic loading curves for other tip radii $R = 80$ and 759 nm are found to agree with the Hertzian relation. Using the mechanical parameters for the diamond indenter ($\nu_{in} = 0.07$, $E_{in} = 1141$ GPa) [32] and samples ($\nu_{HEA} = 0.26$, $\nu_{Ni} = 0.31$) [28], the elastic moduli of NiFeCoCrMn and Ni are deduced as 212.62 and 202.2 GPa, respectively. The fact that the NiFeCoCrMn alloy has a higher elastic modulus but a larger lattice parameter than Ni (0.359 nm for NiFeCoCrMn and 0.352 nm for Ni) suggests a stronger bond in the alloy.

3.2 Plastic response of NiFeCoCrMn

Figure 3 Typical load-displacement curves (a) produced from the Berkovich indenter ($R = 255$ nm) on single-crystal Ni and NiFeCoCrMn. A hardening effect ΔH in NiFeCoCrMn with respect to Ni was observed from the plotting of hardness H against indentation depth h (b). This term was incorporated in the Nix-Gao model (Eq. (S2)) to provide a good prediction (red solid line) of the load-displacement curves. A major breakdown of the linear relation H^2 vs $1/h$ (c) when $h < 30$ nm probably results from the spherical tip geometry of indenter

Figure 4 AFM topographic images of typical indents on NiFeCoCrMn (a) and single-crystal Ni (b) using the Berkovich tip ($R = 255$ nm) at a maximum load of 10 mN, and the general shape (c) and blunt tip geometry (d),(e) of the Berkovich indenter shown by the extracted 2-D profiles. A modified area function of the Berkovich indenter $A_c = 24.5(h + 0.06R)^2$ is then proposed (f).

Load-displacement curves from indentation tests of NiFeCoCrMn and single crystal Ni at a high load of 10 mN are shown in Figure 3a. A shallower indentation depth indicates the HEA is harder than Ni. In Figure 3b, hardness values of these two materials are plotted against the indentation depth, h . Both curves exhibit similar trend and the HEA is harder than pure Ni, i.e.,

$$H_{\text{HEA}} = H_{\text{Ni}} + \Delta H \quad (2)$$

Hardness is also noted to decrease with increasing h , revealing an indentation size effect (ISE) in both materials. Similar observation has been made in several crystalline materials [33,34], and Nix and Gao [35] proposed the dependence of the hardness H on depth h as:

$$H^2 = H_o^2(1 + h^*/h) \quad (3)$$

where H_o corresponds to the hardness at infinite depth, and h^* is the characteristic length that depends on the indenter shape. The linear relation between H^2 and $1/h$ appears to apply well in the micro-indentation scale, whilst significant deviation from the theory occurs when the indentation depth is below 100 nm [36,37]. The breakdown of self-similar indenter geometry and incorrect size of plastic zone have been suggested to be the main causes of such deviation [38]. In fact, AFM tomographic images (Figure 4) of the residual impressions clearly demonstrate the current Berkovich indenter has a blunt tip. The 3-sided pyramid (Figure 4c) exhibits a spherical tip (Figure 4d and 4e) and the tip curvature agrees with the calibrated tip radius $R = 255$ nm. Consequently, the area function of a blunt Berkovich indenter is modified as $A_c = 24.5(h + 0.06R)^2$, as indicated in Figure 4f. It is apparent that, in Figure 3c, the predicted H^2 value begins to deviate from experimental data when h is less than 50 ~ 75 nm, and becomes appreciable when the depth is about 30 nm. It is particularly noted that whereas self-similar indenter geometry is obeyed at large indentation depth, a blunt spherical shape profile should experimentally be found at the bottom of the indent. As shown in Figure 3c, data fit well at $h > 100$ nm according to the Nix-Gao model (Eq. (3)), and the depth-independent hardness H_o is extrapolated from the intercept of the fitting, as listed in Table 1. Evidently, the classic Nix-Gao model is useful even in the micrometer range. However, it is necessary to modify the model in order to describe very shallow depth, and it is presented in the following discussion sections.

Table 1 Parameters in the Nix-Gao model for the indentation size effect in Ni single crystal and high-entropy alloy NiFeCoCrMn

Materials	E_r (GPa)	H_0 (GPa)	$3\sigma_f$ (GPa)	f
NiFeCoCrMn	190.21 ± 1.22	1.88 ± 0.08	1.56[23]	2.45
Ni	187.18 ± 1.59	0.90 ± 0.04	1.02[28]	2.35

According to the Nix-Gao model, H_0 is the resistance to plastic flow in a material independent of the indenter geometry. Since the lattice frictions in pure fcc metals are usually negligible [39], H_0 or resistance to plastic flow arises from the statistically stored dislocations (SSDs). According to Taylor's relation, the density of SSDs in the single crystal Ni can be estimated by the equation:

$$H_{o,Ni} = C\sigma_f = CM\alpha Gb\sqrt{\rho_{SSD}} \quad (4)$$

where $C = 3$ is the Tabor's factor, M is the Taylor factor, 3.06 for fcc metals, $\alpha = 0.5$ is applied for the complex stress field underneath the indenter, G is the elastic shear modulus, 76 GPa for Ni, b is the Burgers vector, 0.249 nm for Ni. The value of ρ_{SSD} is, thus, estimated to be about $1.065 \times 10^{14} \text{ m}^{-2}$, which is one order higher than $\rho_{SSD} = 1 \times 10^{13} \text{ m}^{-2}$ reported in a fully annealed aluminum [40].

Under indentation, $\chi = \tan\theta/a$ is defined as a measure of the strain gradient underneath the indenter [35]. When $a \rightarrow \infty$, corresponding to infinite indentation depth, the strain gradient goes to zero at a fixed indenter angle θ . Under this circumstance, the strain ϵ is fixed and only depends on the indenter geometry. Since Ni and NiFeCoCrMn alloy have the same fcc structure and similar Burgers vector (0.249 nm vs 0.254 nm), the same strain ϵ at the infinite indentation depth essentially would give the same ρ_{SSD} value in these two materials. However, NiFeCoCrMn has a much higher H_0 value than Ni ($H_{o,HEA} = 1.88$ GPa, $H_{o,Ni} = 0.9$ GPa) and the hardening term is

$\Delta H = H_{o,HEA} - H_{o,Ni} = 0.98$ GPa. The hardness values of the two materials are consistent with the classical Tabor relation, namely, $H=3\sigma_f$, where σ_f is the flow strength [23,28].

This strengthening difference has been ascribed to be solid solution hardening before [2], but, in principle, the solid solution hardening refers to the strengthening locally distorted solvent lattice by the individual solute atoms. In HEAs, each element contributes equally to the composition, and the lattice is universally distorted, therefore, no element can be treated as solvent or solute. In such a case, the higher strength of NiFeCoCrMn compared to Ni is probably resulted from a higher lattice friction stress for dislocation motion in the distorted lattice of NiFeCoCrMn [41].

Use the value of ρ_{SSD} and ΔH for each material, the load-displacement responses can be well modeled by $P = (\Delta H + CM\alpha Gb\sqrt{\rho_{SSD} + \rho_{GND}})A_c$ (Eq. (S2) in the supplementary material) and are shown as solid lines in Figure 3a. A scaling factor f is introduced in the term for the density of geometrical necessary dislocation $\rho_{GND} = \frac{3 \tan^2 \theta}{2 f^3 b h}$ [42,43] to describe the effective size of plastic zone with respect to the contact radius. In the modeling, this factor is about 2.4 for both the HEA and Ni. It should be noted that this analytical model only describes the load-displacement curves at large indentation depth ($h > 25$ nm) as a result of inadequate area function. A more accurate description for shallow indentation will be discussed in the sections below.

4. Discussion

4.1. Statistical analysis of the incipient plasticity of NiFeCoCrMn

In general, a pop-in event is triggered when the maximum shear stress τ_{max} underneath the indenter exceeds a critical value. The event usually consists of the nucleation and subsequent

propagation of dislocations. According to contact mechanics, $\tau_{\max}$ occurs at about half of the contact radius a underneath the indenter and is given by [44]

$$\tau_{\max} = 0.47 p_m = 0.47 \frac{P}{\pi R h} \quad (5)$$

where p_m is the mean pressure beneath the indenter, P is the applied load. For a spherical tip, the contact area is πa^2 , where $a = \sqrt{Rh}$ is the contact radius.

Figure 5 The cumulative pop-in probability F underneath the indenters on NiFeCoCrMn (a) and single-crystal Ni (b). Solid lines are predictions based on a model combining dislocation nucleation process and the activation process of pre-existing dislocation (Eq. (10)). The activation volume for dislocation nucleation is deduced from the slope of the plot of $\ln[-\ln(1-F)]$ against $\tau_{\max}$ underneath indenters with the tip radius $R = 80$ nm for NiFeCoCrMn (c) and single-crystal Ni (d).

To study effect of the indenter tip size, we carried out pop-in experiments using indenters with different tip radii. The maximum shear stresses for the occurrence of pop-in in NiFeCoCrMn and Ni single crystal are calculated under different indenter tips, and the cumulative probability of pop-in F for each tip radius is plotted against $\tau_{\max}$ in Figure 5a and 5b.

It is noted that, in both NiFeCoCrMn and pure Ni, the maximum shear stress ranges from 4 GPa to 10 GPa, which is in the proximity of the theoretical strength for each material [31] ($G/30 \sim G/5$, where G is the elastic shear modulus of the material, 80 GPa for NiFeCoCrMn [28] and 76 GPa for Ni). As the tip radius increases, the $\tau_{\max}$ value decreases and a tail begins to develop in the low-stress end on the cumulative probability function F (encircled in green). This tailing phenomenon has also been previously observed in Cr [29] and Mo [30,45], and is attributable to a transition of mechanism from dislocation nucleation in a dislocation-free material to dislocation activation in a material containing dislocations when the tip radius increases.

When applying a small indenter tip, there is a high probability to probe a region within which dislocation is absent and the shear stress for the pop-in is close to the theoretical strength for the nucleation of new dislocations in the material. The dislocation nucleation process has been proposed as a shear-biased event and the nucleation rate in a unit volume of material under a shear stress τ [46] can be written as

$$\dot{N} = N_0 \exp\left(-\frac{\varepsilon - \tau \nu}{kT}\right) \quad (6)$$

where N_0 is the pre-exponential attempt frequency, ε is the energy barrier for dislocation nucleation, and ν is the activation volume. Assume F is the cumulative probability for pop-ins, then, $(1-F)$ is the population of indentations in which the pop-in event has not yet occurred, and the rate of change in F can be described by the following equation:

$$\dot{F} = (1 - F)\dot{N} \quad (7)$$

Insert Eq. (6) into Eq. (7), and take an integration over the highly stressed volume underneath the indenter (scales with the contact radius, $\Omega \sim \pi a^3$), the cumulative probability for nucleation

events within the sampling volume can be written as a function of the maximum shear stress $\tau_{\max}$ for pop-in [46]:

$$F_{\text{nucleation}}(\tau_{\max}) = 1 - \exp\left[-\frac{9\pi R\eta}{4E_r\dot{P}\alpha^6}\gamma(\tau_{\max})\right] \quad (8)$$

where $\dot{P}$ is the indentation loading rate, the parameter $\eta = N_0 \exp(-\varepsilon/kT)$ indicates the rate at which defects nucleate in an unstressed crystal due to thermal activation alone, $\gamma(\tau_{\max})$ is a complex function of $\tau_{\max}$, and the parameter α is a collection of time-independent terms given by $\alpha = \frac{0.47}{\pi} \left(\frac{4E_r}{3R}\right)^{\frac{2}{3}} \frac{\nu}{kT}$. Eq. (8) is noted for a crystal that does not contain a dislocation and the shear stress for the pop-in is near the theoretical strength of the crystal.

However, when a large indenter tip radius is applied, there is a higher probability to find pre-existing defects in the plastic zone underneath the indenter, and pop-in can be triggered from one of these defects (e.g. Frank-Read sources) at a relatively low shear stress $\tau_{\text{pop-in}}$. Assuming the defect distribution follows Poisson's statistics, Morris et al [30] have shown that the probability for the absence of pop-in in the highly stressed zone is $\exp[-\rho_{\text{defect}}V(\tau > \tau_{\text{pop-in}})]$, where ρ_{defect} is the density of pre-existing defects, V is the high-stressed volume where the local stress $\tau > \tau_{\text{pop-in}}$, and $\tau_{\text{pop-in}}$ is the critical shear stress to activate the source at the pre-existing defects. The cumulative probability for pop-in arising from the activation of pre-existing defects is, then,

$$F_{\text{activation}} = 1 - \exp[-\rho_{\text{defect}}V(\tau > \tau_{\text{pop-in}})] \quad (9)$$

In general, while indenting a material, both of the above two situations should be considered. In

such a case, the probability for the absence of pop-in is $\exp(-\rho_{\text{defect}} V) \exp[-\frac{9\pi R\eta}{4E_r \dot{P}\alpha^6} \gamma(\tau_{\text{max}})]$, and the

resultant cumulative probability for pop-in is

$$F_{\text{total}} = 1 - \exp[-\rho_{\text{defect}} V - \frac{9\pi R\eta}{4E_r \dot{P}\alpha^6} \gamma(\tau_{\text{max}})] \quad (10)$$

Table 2 Parameters used for modeling the cumulative probability of pop-in F in NiFeCoCrMn and Ni single crystal

Materials	v (b^3)	η ($\times 10^{13} \text{s}^{-1} \text{m}^{-3}$)	ρ_{defect} (m^{-3})
NiFeCoCrMn	0.65	9.92 ~ 93.2	4×10^{16}
Ni	0.69	2.15 ~ 84.9	2.3×10^{17}

Mathematically, we can rewrite Eq. (8) into a double logarithmic form as $\ln[-\ln(1-F)] = v\tau_{\text{max}}/kT + \beta(\tau_{\text{max}})$, where $\beta(\tau_{\text{max}})$ in the equation is a weak function of τ_{max} as compared with the first term, one can deduce the activation volume v from the slope of the linear fitting of $\ln[-\ln(1-F)]$ against τ_{max} . In Figure 5c and 5d, the pop-in data for NiFeCoCrMn and Ni are plotted in such form and the activation volume is determined to be around $0.7b^3$, as listed in Table 2. To minimize data variation caused by pre-existing defects, data obtained from the sharpest indenter ($R = 80$ nm) are particularly used to evaluate the activation volume.

The cumulative probability of pop-in F for NiFeCoCrMn and Ni under different tips is fitted using Eq. (10) and the results are shown in Figure 5. In the fitting, $\tau_{\text{pop-in}}$ was taken to be 38 MPa ($\sim G/2000$), which is close to the resolved shear stress in Ni (~ 28 MPa) [47,48], and the activation of slip systems in Ni micropillars (40-60 MPa) [49]. The parameters for modeling are summarized in Table. 2. It is noted in the modeling that the density of pre-existing defects is set

in the range of $10^{16} \sim 10^{17} \text{ m}^{-3}$. Assuming dislocation lines are spaced in a cubic array, this defect density is equivalent to a dislocation density of about 10^{11} m^{-2} , which is the typical value in a fully recrystallized crystal [30,50].

4.2. Plastic deformation of NiFeCoCrMn under spherical tip of indenters

It has been pointed out that, when a blunt pyramidal indenter is used, it actually produces a spherical impression at an extremely shallow indentation depth ($h < R/10$). Swadener et al [51] has extended Nix and Gao's framework [35], and developed a model that describes the ISE under spherical indenters. In the model, the density of geometrically necessary dislocation beneath a spherical indenter is derived as $\rho_{\text{GND}} = 1/bR$, where R is the radius of the spherical tip. Swadener's model generally agrees with the experimental results under larger spherical indenter ($R > 10 \text{ }\mu\text{m}$), but overestimates the hardness when the depth is shallow under a smaller indenter. On the other hand, the traveling distance of the leading dislocation just after pop-in [52] was measured, and it could be regarded as the size of the plastic zone ($\sim 1 \text{ }\mu\text{m}$). This zone size was about twice the diameter of the residual indent impression, i.e., $2\sqrt{2Rh-h^2} \sim 475 \text{ nm}$. A scaling factor f was subsequently introduced to correct the radius of plastic zone a_{pz} , namely, $a_{\text{pz}} = fa_c$, where a_c is the contact radius [42,53]. In such a case, ρ_{GND} becomes $\rho_{\text{GND}} = 1/f^3bR$ (refer to the supplementary material), and $P = kh$ (Eq. S3), where $k = 2\pi R(\Delta H + CM\alpha Gb\sqrt{\rho_{\text{SSD}} + 1/f^3bR})$ is constant for a given indenter with a tip radius of R . Insert the parameters (R , b , ΔH , G , α , and ρ_{SSD}) into Eq. S3 we find that the load-displacement responses (Figure 6) agree well with this linear correlation [54]. The scaling factor f used in the modeling ranges from 2.4 to 2.65, as listed in Table 3. These results are close to 2.4 used previously in Figure 3 and also consistent with

values reported in the literature [42,53]. It is noted that within data scatter, f values for NiFeCoCrMn and Ni appear to be similar.

Figure 6 Load-displacement curves for the indentation tests on NiFeCoCrMn alloy and single-crystal Ni using indenters $R = 80$ (a), 255 (b), 759 nm (c), respectively. The red curves show the elastic response given by Hertzian theory, and the dotted blue curves show the plastic response predicted by Eq. (S3) under a spherical indenter tip.

Table 3 Plastic zone size factor f used in the modeling of the plastic responses in nanoindentation

Materials	$f(R = 80 \text{ nm})$	$f(R = 255 \text{ nm})$	$f(R = 759 \text{ nm})$
NiFeCoCrMn	2.55	2.45	2.65
Ni	2.5	2.4	2.5

4. 3 Effect of tip radius on the mean pressure underneath the indenter

In previous sections, the elastic and plastic deformations of NiFeCoCrMn alloy and Ni single crystal have been discussed and the pop-in event divides/connects these two deformation regions. In this section, we address the variation of mean pressure underneath the indenter

before and after the pop-in event, and further evaluate the effects of alloying and tip radius on the strength of NiFeCoCrMn.

Figure 7 Mean pressure underneath the indenter before and after pop-in in NiFeCoCrMn at $R = 80$ nm (a), 255 nm (b), 759 nm (c)

During indentation tests, the deformation resistance of the material can be evaluated from the mean pressure p_m underneath the indenter, namely, the applied load over the projected contact area. Apply the contact radius $\sqrt{Rh}$ and $\sqrt{2Rh - h^2}$ for the elastic loading prior to pop-in and plastic contact after pop-in (Figure S3b), respectively, evolutions of mean pressure p_m throughout a pop-in event at different tip radii in NiFeCoCrMn are calculated and shown in Figure 7. It is noted that, in both samples and regardless of the tip radii, the mean pressure p_m reaches a high value (11 ~ 25 GPa) in the elastic loading stage, but sharply drops to a low value (3 ~ 5 GPa) once the pop-in takes place. The high p_m value prior to the pop-in corresponds to a high shear stress required to nucleate (or activate) dislocation in the materials, while the low p_m

value after the pop-in is the stress required to overcome the lattice friction and dislocation interactions for plastic flow.

Figure 8 Mean pressure p_m underneath the indenters as a function of tip radius (a) and dislocation density (b) in NiFeCoCrMn and Ni single crystal. Solid lines in (a) are theoretical predictions of p_m for global plasticity based on Eq. (11).

Mean pressures for the first pop-in (open symbols) and after the pop-in (solid symbols) are noted to decrease with increasing tip radius R in Figure 8a. However, the decreasing trends for data before and after the pop-in are caused by different mechanisms. For the onset of yielding, i.e., the start of very first pop-in, the drop of critical stress results from the activation of pre-existing dislocations in the highly stressed zone and it is more likely to encounter pre-existing dislocations beneath an indenter with a larger tip radius. On the other hand, after finishing the pop-in and in the plastic region, the flow stress is determined by the dislocation density, which is given by $\rho_{SSD} + 1/f^3 bR$. A larger tip radius R would lower the density of geometrically necessary dislocation, thus reduces p_m (or the flow stress). The fact that higher plastic flow stress is obtained in NiFeCoCrMn suggests this HEA has a stronger lattice friction or dislocation

interaction. The decreasing trend of mean pressure p_m with the tip radius in the plastic region can be predicted by the equation

$$p_m = \Delta H + CM \alpha G b \sqrt{\rho_{SSD} + 1/f^3 b R} \quad (11)$$

Inserting proper parameters, predicted values of mean pressure in Eq. (11) are found to agree well with the experimental results, as shown in Figure 8. As the tip radius increases, the size effect weakens and p_m converges to H_o at very large indentation depth.

The data of p_m are replotted against dislocation density and form a “U-shape” curve, as shown in Figure 8b. Similar schematic diagrams illustrating indentation plasticity have been presented by Zhang *et al* [52] and Lilleodden *et al* [55]. In the figure, the statistically stored dislocation density $\rho_{SSD} = 1.065 \times 10^{14} \text{ m}^{-2}$ obtained from the ISE analysis is located at the bottom of the U-curve. It represents the minimum dislocation density required to sustain continuum plasticity in the fcc-structure materials. In the current fully annealed HEA and Ni materials, the dislocation density ρ (10^{11} m^{-2}) is much lower than the critical value (10^{14} m^{-2}), plasticity can only be triggered in the form of pop-in under high p_m . The pop-in causes an abrupt increase in ρ and, meanwhile, a sudden increase in contact area, thus a rapid decrease in p_m underneath the indenter. Both p_m and ρ are tip radius-dependent, and a power-law correlation between them is revealed in Figure 8b. The power index is about 0.5, which is apparently resulted from the Taylor hardening.

5. Conclusions

We have studied the elastic and plastic deformations of a high entropy alloy NiFeCoCrMn using instrumented indentation techniques and directly compared the results with those of a single-crystal Ni. The effect of indentation tip radius on the deformation processes has also been evaluated and discussed. Several conclusions are drawn as follows.

1. Incipient plasticity revealed as indentation pop-in is generally observed in both NiFeCoCrMn and the Ni single crystal. The critical shear stresses required for the occurrence of pop-in are within the range of the theoretical strength of each material. The activation volumes for dislocation nucleation in NiFeCoCrMn (0.65 b^3) and Ni (0.69 b^3) are quite similar.
2. The pop-in stress decreases with increasing tip radius in both NiFeCoCrMn and Ni. This is attributable to the fact that a larger indented volume is expected to have a higher probability to contain pre-existing dislocations. A model combining dislocation nucleation in a dislocation-free crystal and dislocation activation in a crystal consisting of pre-existing dislocations is proposed, and it describes well the cumulative pop-in probability in both materials.
3. Indentation results in the plastic region indicate that NiFeCoCrMn is stronger than Ni. A strengthening effect ($\Delta H = 0.98 \text{ GPa}$) in the HEA is universally observed in the full range of indentation, and it agrees with the results obtained in the conventional tensile tests.
4. Indentation size effect is observed in both NiFeCoCrMn and Ni. The load-displacement responses under higher load (or larger indentation depth) can be described by the Nix-Gao model, whereas a modified Swadener's model for spherical indenter offers a better description in the case of shallow depth. In either case, a scaling factor f is necessarily introduced to describe the effective size of plastic zone underneath the indenter, and it ranges from 2.4 to 2.65 for NiFeCoCrMn and Ni.

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Graphical Abstract