Indentation Pop-in Behavior of CoCrFeNiAl$_x$ High-Entropy Alloy

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Indentation pop-in behavior of CoCrFeNiAl$_{0.1}$, CoCrFeNiAl$_{0.3}$, and CoCrFeNiAl$_{0.6}$ high-entropy alloys (HEAs) at different loading rates is investigated using instrumental nanoindentation. Experimental results show that the increase in either loading rate or the aluminum atomic content (Al$_x$) of the alloy all have a reducing effect on the pop-in behavior on the load–displacement curve. Meanwhile, both conditions exert a lagging effect on the triggered depth of the first pop-in event and significantly affect the bursting width. The first pop-in event is characterized using the previous phenomenological model and the effects of loading rate and Al$_x$ are quantitatively analyzed through combining the elastic deformation energy prior to the first pop-in and the energy dissipation during the indentation process. In addition, the activation volumes for pop-in event are evaluated to be about 4–13 $\Omega$ much higher than that in pure metal, revealing the multiatom-coordinated migration process in HEAs.

1. Introduction

With regard to compression and tension experiment, the typical characteristic of serration behavior is fluctuation in the corresponding stress–strain curve. Similar serration flow was observed in the nanoindentation test and appeared in the form of pop-ins, manifested as burst displacement in the load–displacement curve. Typical pop-in behavior has been observed in a wide range of materials, such as single-crystal/polycrystalline metals, Al/Cu alloys, bulk metallic glasses, high-entropy alloys (HEAs), etc. Because of its excellent mechanical properties, HEA has good application prospects in advanced fields such as aeroengine turbine blades, rocket nozzles, marine vessels and high-frequency communicators, and other field, although it was only put forward in 2004. Thus, the study of plastic deformation at micrometer scale of HEAs is conducive to its development and application in the field of engineering as emerging structural material. It is generally accepted that the standard explanation of serration flow can be applied to HEAs, that is, solute atoms diffuse and lock dislocations to render them immobile. In the process of dislocation pinning of solute atoms, both interstitial and substitutional solutes can be involved. Cottrell et al. first provided a theoretical explanation for the interstitial solute participation in dislocation pinning. Herman et al. found that substitutional solutes can also participate in this phenomenon through vacancy mechanism during plastic deformation.

Nevertheless, not any atom can act as solute atoms in HEAs, and in some situations only certain atoms in the matrix can participate in dislocation locking. Several studies have shown that only certain additives (e.g., Al) hinder dislocation movement during deformation of HEAs. Yasuda et al. compared the mechanical behavior of Al$_x$CoCrFeNi and CoCrFeNi HEAs during the dynamic strain aging process and stated that Al-containing HEA has serration, while the latter specimen does not have serration. The research hypothesizes that the generation of the Al-containing solute atmosphere near the core of the moving dislocations leads to an increase in dislocation frictional stress and the serration flow. Niu et al. found a similar trend in studying the indentation pop-in behavior of Al$_x$CoCrFeNi and CoCrFeNi HEAs. This result indicated that Al atoms play an important role in serration flow of HEAs. Further, the indentation pop-in behavior of CoCrFeNiAl$_x$ HEA with different Al-contenting ($x = 0.1, 0.3, 0.6$) was investigated using instrumental nanoindentation test.

2. Experimental Section

Ingots with nominal compositions of CoCrFeNiAl$_{0.1}$, CoCrFeNiAl$_{0.3}$, and CoCrFeNiAl$_{0.6}$ were synthesized via arc melting five high-purity metal elements (>99.9 wt%) in a Ti-gettered argon atmosphere. Each ingot alloy was flipped and remelted at least five times to ensure the homogeneity of chemical composition, and then the molten alloys were sucked into a copper mold cavity with dimensions of 50 mm (length) x 10 mm (width) x 2 mm (depth). The obtained HEA with CoCrFeNiAl$_{0.3}$ composition was cold rolled along the length...
direction reducing 50% of the specimen with a final thickness of 1 mm; after that, the cold-rolled alloy was annealed at 1100° for 1 h and compared with the untreated specimen. The four specimens were preset and vertically fixed via inlay powder. The specimen surface was subjected to wet mechanical ground with varied-size-grained silicon carbide sandpaper (#500, #1000, #1500, #2000, #2500, #3000) and then underwent polishing with 2.5, 1.5, 0.5 μm diamond suspensions for mirror and electrolytic polishing.

Agilent Nano-indenter G200 test system with the force and displacement resolution of 50 nN and 0.01 nm was used to perform the quasistatic nanoindentation test. The spherical diamond indenter with an effective radius of 5 μm was used to probe the serration behavior of the four CoCrFeNiAlₓ HEAs. The maximum indentation load was set to 30 mN, and the five loading rates were 60, 150, 375, 750, and 1500 μNs⁻¹, respectively. When the maximum indentation load was reached, the indenter remained at the corresponding peak load for 10 s, and finally unloaded to 10% of the maximum indentation load within 2.5 s, and the thermal drift decreased to 0.05 nm s⁻¹. The test under each condition was repeated five times, and the representative indentation data were adopted for the subsequent research.

Figure 1a shows the X-Ray diffraction (XRD) patterns of CoCrFeNiAlₓ (x = 0.1, 0.3, 0.6) HEA. It can be clearly seen that the alloy with x = 0.1 and x = 0.3 had typical face-centered cubic (FCC) crystal structures and the lattice parameters were determined to be 3.58 and 3.59 Å. The alloy (x = 0.3) subjected to annealing treatment or the alloy with Al content of x = 0.6 both had the body-centered cubic (BCC) phase and FCC phase diffraction peak. Among them, CoCrFeNiAl₀.₆ HEA was composed of FCC + BCC biphasic solid solution with phase content of 38.2% and 61.8%, respectively, and lattice parameter of 3.60 Å. The as-cast CoCrFeNiAl₀.₃ HEA existed in the form of supersaturated solid solution of the simple FCC phase. However, when the alloy was annealed at 1100 °C for 1 h, the supersaturated Al and Ni atoms precipitated and nucleated and grew into B2 phase due to the large negative mixing content and the large difference in atomic size between Al and Ni atoms and other constituent elements. The phase content was 77.4% and 22.6%, respectively, and the lattice parameter was 3.59 Å. To further reveal the effect of annealing treatment on CoCrFeNiAl₀.₃ HEA, JSN-7100F scanning electron microscope (SEM) was used to perform the electron backscattered diffraction (EBSD) test and TSLOIM Analysis 6 was used to process the EBSD data. The EBSD inverse polar figures of surface morphology of CoCrFeNiAl₀.₃ HEA and CoCrFeNiAl₀.₃ HEA (annealing) are shown in Figure 1b,c. It is shown that the grains of HEA are refined and grain boundaries are more abundant after annealing.

3. Results

Figure 2 shows the representative load–displacement (P–h) curves of different CoCrFeNiAlₓ HEAs at loading rates of 60 and 1500 μNs⁻¹, respectively, and the x-axis is moved in parallel for clarity of comparison. At the loading rate of 60 μNs⁻¹, the loading curves of other alloys except for CoCrFeNiAl₀.₆ all showed continuous burst displacement (pop-ins). The higher Al content leads to more severe lattice distortion, and the
stronger lattice distortion effect hinders dislocation movement during deformation.\([19]\) This is the reason why CoCrFeNiAl\(0.6\) HEAs hardly exhibit serrations flow even at low loading rate. It is well known that the faster the loading rate, the less obvious the pop-ins behavior.\([20,21]\) Therefore, CoCrFeNiAl\(0.6\) HEA is not considered in this study of pop-in behavior under other faster loading rates. As shown in Figure 2b, the three HEAs still have different characteristics of serration flow at higher loading rate, revealing that Al content has an impact on the pop-in behavior of the HEAs.

\(P-h\) curves of the other CoCrFeNiAl\(x\) HEAs at five different loading rates are shown in Figure 3. It distinctly exhibits the correlation between pop-in behavior and loading rate, that is, the lower loading rate, the more frequent pop-in behavior. Nanoscale pop-in behavior is associated with the activation of individual dislocation motion, and the deceleration of dislocation motion allows solute atoms to capture and pin the dislocation more easily, leading to increased serration.\([19]\) In addition, the first pop-in event of the three HEAs at the measured loading rate occurs under an almost constant load during the indentation depth range from 20 to 80 nm, which marks the onset of plastic deformation.

4. Discussion

The intrinsic explanation of the first indentation pop-in event is the nucleation of homogeneous or heterogeneous dislocation which follows thermal and spatial nucleation states, respectively. The activation stress of the two nucleation mechanisms is currently greater than the slip resistance of the mobile dislocations.\([22]\) Therefore, the indentation response prior to the first pop-in follows the Hertz elastic contact theory, that is, the load applied \(P\) and indentation depth \(h\) conform to the following relationship.

\[
P = \frac{4}{3} E_t R^{1/2} h^{3/2}
\]

where \(E_t\) is the reduced indentation modulus and \(R\) is tip radius of spherical indenter. The curve fitting result of elastic deformation prior to the first pop-in event is shown in Figure 4a, showing the accuracy and good applicability of Equation (1). The initial part of \(P-h\) curve follows Hertz contact theory and then shifts to plastic deformation or elastic–plastic transformation. Based on the load and displacement of each indentation at the deviation point, the 90 sets of \(P-h^{3/2}\) data of the first pop-in events of each HEAs are plotted in Figure 4b. The linear fitting results and corresponding \(R^2\) of CoCrFeNiAl\(0.1\), CoCrFeNiAl\(0.3\) (annealing), CoCrFeNiAl\(0.3\) HEAs are \(P = 13.21 h^{3/2}\), \(P = 13.84 h^{3/2}\), \(P = 13.57 h^{3/2}\) and 0.97, 0.97, 0.96; combining with Equation (1), we can obtain the reduced modulus as \(E_t = 140.16\) GPa, \(E_t = 146.75\) GPa, and \(E_t = 143.90\) GPa, respectively. Considering that the difference in the composition of the grains and intragrain perhaps affects the local properties of HEAs in

Figure 2. \(P-h\) curves of CoCrFeNiAl\(x\) HEAs at different loading rates: a) 60 \(\mu\)N s\(^{-1}\) and b) 1500 \(\mu\)N s\(^{-1}\).

Figure 3. \(P-h\) curves of different CoCrFeNiAl\(x\) HEAs.
micrometer levels, the data points on the fitted line are recorded for the subsequent analyses in Figure 4b.

For the cylindrical indenter, the contact area during the indentation test process is constant and equal to the indenter cross-sectional area, the elastic unloading process is theoretically linear and can be used to determine the reduced modulus \( E_r \), namely

\[
dP/dh = 2E_r a
\]

Herein \( P \) and \( h \) are the indentation load and depth during unloading and \( a = 2.75 \mu m \) is the radius of the cylindrical indenter. Based on Equation (2) and unloading data (in Figure 4c), the average \( E_r \) of CoCrFeNiAl\(_{0.1}\), CoCrFeNiAl\(_{0.3}\) (annealing), and CoCrFeNiAl\(_{0.3}\) HEAs are obtained as 150.62 ± 3.17, 158.03 ± 5.28, and 152.98 ± 2.94 GPa. The \( E_r \) measured via the spherical and cylindrical indentation test is nearly identical, manifesting the availability of determining the \( E_r \) through elastic deformation prior to the first pop-in event.

The first pop-in event marks the elastic–plastic transition. Figure 5 shows the occurrence depth \( h \) and bursting width \( \Delta h \) of the first pop-in under different loading rates of CoCrFeNiAl\(_x\) HEAs. The higher Al content hinders dislocation movement and deformation, making the first pop-in event of CoCrFeNiAl\(_{0.3}\) HEA in indentation test later than that of CoCrFeNiAl\(_{0.1}\) HEA. The CoCrFeNiAl\(_{0.3}\) HEA with annealing treatment has grain refinement and abundant grain boundaries, which impede the motion of dislocation and result in the lagged emergence of the first pop-in depth. For the lower strain rate \((10^{-5}–1 \text{ s}^{-1})\), with increasing strain rate the propagation speed of dislocations increases and the frequency of serrations decreases. The experimental strain rate calculated by \( \dot{\varepsilon} = \frac{1}{h} \frac{dh}{dt} \) is in the range of 1.5 × 10\(^{-3}\)–0.84 s\(^{-1}\); in the circumstances, dislocation pinning is the primary mechanism of pop-in events.

The strain rate sensitivity (SRS) exponent \( m \) is defined as the slope of the double logarithmic curve of yield stress versus loading strain rate, that is

\[
m = \frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}}
\]

where \( \dot{\varepsilon} \) is the loading strain rate and \( \sigma \) is the yield stress. The linear relation between hardness and yield stress can be determined by Tabor D.\(^{[26]}\) It can be assumed that the indentation hardness \( H \) and indentation strain rate \( \dot{\varepsilon} \) are proportional to yield stress \( \sigma \) and loading strain rate \( \dot{\varepsilon} \) respectively. Then SRS can be written as

**Figure 4.** Indentation test results of CoCrFeNiAl\(_x\) HEA. a) Spherical indentation \( P-h \) curve with the Hertzian. b) Statistics of 90 \( P-h^{3/2} \) data points under different loading rates and the linear fitting result. c) Cylindrical indentation \( P-h \) curve and linear fitting result of the unloading process.
Hence, the strain rate sensitivity exponent $m$ estimated by the slope of the fitted curve, as shown in Figure 6. For a thermally activated process, the activation volume $V$ of dislocation nucleation is the determinant of strain rate sensitivity, which can be estimated by strain rate sensitivity and shear stress.[27]

$$V = \frac{kT}{\tau m}$$  \hspace{1cm} (5)

where $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\tau$ is the shear stress roughly estimated by empirical formula $\tau \approx H/3\sqrt{3}$. By inserting the current value of $m$, it can be estimated that the activation volume $V$ of CoCrFeNiAl$_{0.1}$ HEA, CoCrFeNiAl$_{0.3}$ (annealing) HEA, and CoCrFeNiAl$_{0.3}$ HEA are 153.53, 55.78, and 47.28 Å$^3$, respectively, and the lattice parameters of the corresponding specimens are 45.89, 46.38, and 46.31 Å$^3$. Activation volume is a vital indicator to reveal the atomic process for dislocation nucleation, and the activation volume data of some FCC and BCC materials[28] are summarized in Table 1. The activation volumes of pop-in events in conventional FCC and BCC metals are on the order of single atoms, revealing the migration of individual point-like defects (e.g., vacancy or impurity).[7] In contrast, the activation volume measured in both FCC-HEA and BCC-HEA is above 4 Ω, manifesting that dislocation nucleation in HEAs is relatively difficult and involves the coordinated migration of multiple atoms. Unlike the conventional FCC/BCC alloys, the size and chemical properties of the constituent atoms of HEAs render the crystal structures to be distorted. Therefore, regardless of the Al content, the vacancy migration in Al-based HEAs requires the coordinated movement of several atoms to maintain reasonable composition distribution due to the absence of major diffusion elements, rather than relying on simple one-to-one exchange of atomic vacancies.

The collective movement of atoms results in the activation volume larger than 1 Ω. Figure 7 shows a schematic diagram of the dislocation pinning–unpinning cycle. Dislocations are pinned by diffusion solute atoms, and with the increasing indentation load the dislocation remains pinned until a critical stress is reached, which provides sufficient energy for dislocation to unpin. After escaping the solute atom, dislocation moves until it is immobilized again by the migrating solute atom and the process repeats, forming subsequent serration flow.[29]

Previous studies[21] have shown that the first indentation pop-in event of HEAs has significant three-stage characteristics: 1) elastic stage prior to pop-in, 2) linear bursting stage, and 3) deceleration stage after pop-in. The typical relationship between indentation depth and time is shown in Figure 8a. Based on this three-stage feature, a phenomenological model is proposed to represent the first pop-in event and is plotted in Figure 8b.

The phenomenological model can be described by

$$\varepsilon = \frac{\sigma}{E_0} + \frac{f(\sigma - \sigma_y)}{n_1} t - \frac{f(\sigma - \sigma_y)}{E_1} \left(1 - e^{-\frac{t}{t_1}}\right)$$  \hspace{1cm} (6)

expression[30,31], therein, $\varepsilon$ is the strain, $\sigma$ is the stress, $E_0$ and $E_1$ are the elastic modulus of different Hook Solids, $n_1$ and $\eta_1$ are the viscous coefficient of different Newtonian fluids, $\sigma_y$ is the yield strength of St Venant body, $t$ is the indentation time and $t_1$ is a time constant, $f(x-x^\star)$ is a piecewise function where $x < x^\star$. 

![Figure 5. Indentation depth and bursting width of the first pop-in event.](image)

![Figure 6. Double logarithmic plots of hardness versus the indentation strain rate.](image)
\[ f(x - x^*) = 0 \text{ or } x \geq x^*, \quad f(x - x) = x - x^*. \]

For nanoindentation tests, the indentation stress \( \sigma \) and strain \( \varepsilon_i \) are expressed as \( \sigma = H \) and \( \varepsilon_i = h/h_{in} \), respectively (\( h \) is indentation pop-in depth and \( h_{in} \) is the maximum indentation elastic depth prior to the first pop-in event). Then the phenomenological model can be rewritten as

\[
\frac{h}{h_{in}} = \frac{H}{E_0} + \frac{f(H - H_0)}{n_1} t + \frac{f(H - H_0)}{E_1} \left(1 - e^{-\frac{E_1}{\eta_2} \frac{f(t - t_1)}}\right) \quad (6)
\]

\( H_0 \) is the indentation hardness at the maximum elastic depth prior to the first pop-in; further, by substituting \( h_{in} H/E_0 = h_0 \), \( h_{in}(H - H_0)/\eta_1 = h_1 \), \( h_{in}(H - H_0)/E_1 = h_3 \), and \( E_1/\eta_2 = \varphi \).
the phenomenological model around the first pop-in event may be given as follows.

\[ h(t) = h_0 + h_1 t + h_2 \left( 1 - e^{-\phi t/h_1} \right) \]  

(7)

Data points on the fitting line in Figure 4b were selected, and for the sake of effective analysis, the indentation time was reset to the starting point of first pop-in event. Curve fitting was carried out through Equation (7) and relevant fitting parameters are listed in Table 2. In addition, the indentation elastic deformation energy of the CoCrFeNiAl\(_x\) HEA at different loading rates prior to first pop-in event is calculated from loading curve area (the inset in Figure 9a), as shown in Figure 9a.

Table 2. Relevant parameters fit from Equation (7) for the first pop-in event.

| Loading rate [\(\mu N \cdot s^{-1}\)] | \(h_0\) [nm] | \(h_1\) [nm \cdot s^{-1}] | \(h_2\) [nm] | \(t_1\) [s] | \(\phi\) [1 \cdot s^{-1}] |
|-------------------------------------|-------------|-----------------|-------------|-------------|-----------------|
| 60                                  | 23.76       | 2.77            | 1.25        | 0.31        | 1.65            |
| 150                                 | 24.07       | 7.98            | 1.31        | 0.09        | 3.65            |
| 375                                 | 29.39       | 22.80           | 1.86        | 0.06        | 10.99           |
| 750                                 | 35.55       | 31.73           | 2.39        | 0.05        | 11.31           |
| 1500                                | 62.55       | 48.75           | 5.19        | 0.04        | 12.55           |

For CoCrFeNiAl\(_{0.1}\) (annealing):

| Loading rate [\(\mu N \cdot s^{-1}\)] | \(h_0\) [nm] | \(h_1\) [nm \cdot s^{-1}] | \(h_2\) [nm] | \(t_1\) [s] | \(\phi\) [1 \cdot s^{-1}] |
|-------------------------------------|-------------|-----------------|-------------|-------------|-----------------|
| 60                                  | 34.62       | 4.36            | 0.81        | 0.19        | 1.88            |
| 150                                 | 39.09       | 11.99           | 1.17        | 0.10        | 5.54            |
| 375                                 | 46.19       | 19.24           | 1.25        | 0.06        | 8.10            |
| 750                                 | 56.39       | 25.29           | 2.44        | 0.05        | 11.28           |
| 1500                                | 77.99       | 33.40           | 3.00        | 0.04        | 12.34           |

For CoCrFeNiAl\(_{0.3}\):

| Loading rate [\(\mu N \cdot s^{-1}\)] | \(h_0\) [nm] | \(h_1\) [nm \cdot s^{-1}] | \(h_2\) [nm] | \(t_1\) [s] | \(\phi\) [1 \cdot s^{-1}] |
|-------------------------------------|-------------|-----------------|-------------|-------------|-----------------|
| 60                                  | 28.49       | 3.65            | 0.69        | 0.24        | 1.96            |
| 150                                 | 33.30       | 9.18            | 1.11        | 0.13        | 5.60            |
| 375                                 | 36.37       | 15.62           | 1.21        | 0.06        | 11.55           |
| 750                                 | 44.02       | 27.92           | 1.45        | 0.05        | 12.54           |
| 1500                                | 66.48       | 38.69           | 1.91        | 0.04        | 13.09           |

It can be observed that the prior to first pop-in in Figure 8a corresponds to part I of the phenomenological model in Figure 8b. As the loading rate increases, the fitting parameter \(h_0\) increases and stores more elastic deformation energy (Figure 9a). When the maximum shear stress under the indenter exceeds the critical, that is, when solute atoms capture or pin motion dislocation occurs, the first pop-in occurs with the release of elastic energy stored in stage I and then starts to enter the stage II. For stage II, the rapid increase in plastic deformation is accompanied by the linear bursting displacement, corresponding to part II (Figure 8b). Under the condition of higher loading rate, the release of larger elastic energy leads to the occurrence of larger bursting width \(h_1\) in a shorter burst time \(t_1\). For stage III, as most of the stored elastic energy was released in stage II, the indentation elastic deformation energy of the CoCrFeNiAl\(_x\) HEA at different loading rates prior to first pop-in event is calculated from loading curve area (the inset in Figure 9a), as shown in Figure 9a.

Figure 9. Loading rate versus a) indentation elastic deformation energy prior to first pop-in and b) energy dissipation fraction for CoCrFeNiAl\(_x\) HEA.
the increasing rate of the indentation plastic deformation gradually declines causing the displacement to increase slowly, corresponding to part III in Figure 8b. The fitting parameter $h_d$ and $\phi$ increase with the increase in loading rate. To the end, with the occurrence of pop-in event and successive release of stored indentation elastic energy, the indenter needs to be continuously loaded to store energy to implement the next pop-in event. In conclusion, the greater the indentation depth corresponding to the first pop-in event, the higher the elastic deformation energy accumulated, and the larger the bursting width. However, the increase in Al content hinders dislocation movement, resulting in the fact that the bursting width of CoCrFeNiAl$_{0.3}$ is only slightly higher than that of CoCrFeNiAl$_{0.1}$ at low loading rate and even lower than that of CoCrFeNiAl$_{0.1}$ at high loading rate under the same conditions, as shown in Figure 5.

The energy dissipated $E_d$ during the indentation process is determined by dividing the area within the indentation $P$-$h$ curve (representing the plastic deformation energy containing pop-in events and the elastic energy stored in the specimen material in the form of residual stress) by the area under the loading curve. The equation is as follows\cite{32}

$$E_d = \frac{U_p}{U_p + U_e} \cdot \frac{1}{E_0}$$ \hspace{1cm} (8)

where $U_p$ is the net area enclosed via the $P$-$h$ curve and the coordinate axis and $U_e$ is the area under the unloading curve, as shown in the inset in Figure 9b. Pure plastic deformation portion is dissipated as heat, and the energy dissipation fraction $E_d$ of CoCrFeNiAl$_x$ HEAs at different loading rates is plotted in Figure 9b. It is clear that the loading rate has almost no effect on energy dissipation fraction. The calculated value of $E_d$ varies along with different CoCrFeNiAl$_x$ HEAs, the discrepancy of which is visible within the range of 74–88%.

Combining the above characteristics of pop-in events of CoCrFeNiAl$_x$ HEA, the CoCrFeNiAl$_{0.1}$ HEA has the earliest occurrence of pop-in event and the most frequent serration behavior, so the dissipated energy fraction is highest. The increase in the Al content to 0.3 leads to the enhancement of lattice distortion of the alloy system and hindrance of dislocation motion in the deformation process; thereby, first pop-in event lags, the serration behavior frequency decreases, and the material dissipation energy fraction is lower than CoCrFeNiAl$_{0.1}$ HEA. Annealing treatment reduces the microstress and mechanical residual stress of CoCrFeNiAl$_{0.3}$ (annealing) HEA, and abundant grain boundaries as additional media of plastic deformation hinder the dislocation motion, weakening serration and reducing energy dissipation fraction.

The indentation mechanical properties of different HEAs measured in the test are summarized in Table 3. Results show that the indentation hardness of alloys increases with the increase in Al content and loading rate. The atomic radius of the four components of Co, Cr, Fe, Ni are similar to occupy the lattice vacancies equally, while the larger atomic radius of Al leads to an increase in the lattice distortion energy of the alloy system.\cite{19} With the increase in Al content, the solid-solution strengthening effect is further enhanced, so the measured indentation hardness is greater. $E_i$ is the elastic modulus of specimen material defined by\cite{22}

$$\frac{1}{E_i} = \frac{1}{E_1} + \frac{1}{E_2}$$ \hspace{1cm} (9)

thereinto, $E_i = 1141 \text{ GPa}$ and $v_i = 0.07$ are the elastic modulus and Poisson’s ratio of diamond indenter, respectively, $v_i$ is the Poisson’s ratio of CoCrFeNiAl$_x$ HEA and is set to be 0.26. The results manifest the elastic modulus of CoCrFeNiAl$_x$ HEA with the increase in Al atomic radius. The interaction force among the crystal structure elements of the multiprincipal HEA is proportional to its absolute value of mixing enthalpy, which increases with the increase in Al content, resulting in the increase in elastic modulus.\cite{33} There is a unique and inherent relationship between the reduced modulus $E_s$, hardness $H_s$, and recovery resistance $R_s$ of solid materials\cite{34}

$$R_s = E_s \cdot H^{-1} \cdot D^{-2}$$ \hspace{1cm} (10)

where $D = 0.6647\times 10^{-6}$ is a constant related to the indenter shape. The relationship among the three comes from rigorous theoretical derivation without any hypothesis or statistical model. $E_i$ and $H$ are both material parameters, so $R_s$ is also a material parameter with specific physical meaning, which reflects the energy dissipation of material in the process of indentation loading–unloading. The calculated recovery resistance $R_s$ of CoCrFeNiAl$_{0.3}$, CoCrFeNiAl$_{0.3}$ (annealing), CoCrFeNiAl$_{0.3}$ HEA, and CoCrFeNiAl$_{0.6}$ HEA are 42.69, 29.13, 35.95, and 28.06 Gpa, respectively. Hence, the evaluation of the local energy dissipation or plasticity of HEAs with different Al contents through material parameters may indirectly prove that the higher the Al content and the richer the grain boundary and the weaker the plastic serration behavior.

**Table 3.** Indentation mechanical properties of different CoCrFeNiAl$_x$ HEAs under different loading rates.

| Loading rate [$\mu \text{n s}^{-1}$] | CoCrFeNiAl$_{0.1}$ | CoCrFeNiAl$_{0.3}$ (Annealing) | CoCrFeNiAl$_{0.3}$ | CoCrFeNiAl$_{0.6}$ |
|-------------------------------------|---------------------|-------------------------------|---------------------|---------------------|
| Hardness [GPa]                     | $E_i$ [GPa]         | Hardness [GPa]                | $E_i$ [GPa]         | Hardness [GPa]      |
| 60                                 | 5.37               | 161.68 ± 5.43                 | 12.57               | 170.89 ± 6.2        |
| 150                                | 5.43               | 12.62                         | 8.76                | 164.60 ± 4.89       |
| 375                                | 5.48               | 12.98                         | 8.86                | 13.59               |
| 750                                | 5.69               | 13.02                         | 9.16                |                     |
| 1500                               | 5.78               | 13.86                         | 9.45                |                     |
| 3000                               | 5.59               | 13.77                         | 8.74                |                     |
5. Conclusion

The indentation pop-in behaviors of CoCrFeNiAl$_x$ HEAs with different Al contents ($x = 0.1, 0.3, 0.6$) at different loading rates were studied through instrumental indentation experiments and the following conclusions were drawn. 1) Indentation pop-in behavior was observed on the loading curve for other alloys except CoCrFeNiAl$_{0.6}$ HEAs. Higher Al content renders more severe lattice distortion effect prone to hinder dislocation movement. Thus, the high density of dislocation results in almost no serration behavior even at low loading rate. 2) The dislocation pinning–unpinning mechanism results in serration dissipation energy insensitive to the loading rate. 4) Both large bursting width and 3) The stored energy in elastic stage increases as the vacancy exchange process but a cooperative movement of multiple atoms. The vacancy migration in HEAs is not a traditional direct atom unpinning mechanism results in serration flow of the alloys during the indentation process. Unlike conventional FCC/BCC pure metal, the higher activation volume ($\approx 4 – 13 \Omega$) of pop-in events of CoCrFeNiAl$_x$ HEAs indicates that the vacancy migration in HEAs is not a traditional direct atom vacancy exchange process but a cooperative movement of multiple atoms. 3) The stored energy in elastic stage increases as the load accelerates and the large elastic energy release leads to the large bursting width $\Delta h$ in a short time. Meanwhile, the extent of serration decreases with increasing loading rate and the indentation dissipation energy is insensitive to the loading rate. 4) Both high Al content and annealing treatment impede dislocation movement, causing the alloy to trigger the first pop-in event to lag, the frequency of pop-in behavior is weakened, and the material dissipation energy is reduced. Evaluating its local energy dissipation energy through material parameters indirectly proves that the larger the Al atom, the less obvious the serration flow of the alloy.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aluminum atomic contents, high-entropy alloys, loading rates, nanoindentations, pop-in behaviors

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