Delayed plasticity during nanoindentation of single-phase CoCrFeMnNi high-entropy alloy

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ABSTRACT
Spherical nanoindentation was performed at room temperature to characterize the time-dependent plasticity behavior of the single-phase CoCrFeMnNi high-entropy alloy (HEA). It was observed that incipient plasticity occurred after a period of waiting time in the apparent elastic regime. Through the experimental data, an activation energy $\sim 0.74$ eV and an activation volume $\sim 1.54b^3$ ($b =$ Burgers vector) were extracted for the delayed plasticity. Our results indicate that heterogeneous dislocation nucleation governs the delayed plasticity in the single-phase CoCrFeMnNi, and also provide quantitative insights into viscoplastic behavior and creep mechanisms in HEAs.

IMPACT STATEMENT
The delayed plasticity behavior was studied in single-phase FCC CoCrFeMnNi HEA. Our results indicate that heterogeneous dislocation nucleation governs the delayed plasticity behavior.

The elastoplastic transition or yielding in crystalline materials is usually marked by a displacement burst, also termed as displacement ‘pop-in’, in a spherical nanoindentation experiment [1–4]. In general, occurrence of the first pop-in is ascribed to dislocation nucleation under a spherical indenter when the applied load reaches a critical value, below which elasticity is commonly perceived to prevail [4,5]. However, the pop-in behavior of crystalline materials is essentially a stress-assisted and thermally activated defect nucleation process at a finite temperature [1–4,6]; therefore, the pop-in load is both temperature and time dependent [1,7,8]. Schuh et al. performed nanoindentation experiments on single crystal platinum at elevated temperatures and found that displacement pop-in occurred at a lower stress level as the temperature was increased [6,9]. The time dependence of the pop-in behavior was also reported by a number of researchers [7,8,10–13]. Furthermore, it was observed that, even when the applied load was held constant in the apparent elastic regime, pop-in could still occur in crystalline metals after some waiting time [12], i.e. in a delayed fashion.

High-entropy alloys (HEAs) are a new type of alloys that usually comprise five or more elements mixed in an equi- or nearly equimolar ratio [14]. In spite of the complexity of alloy compositions, a number of HEAs exhibit a simple crystalline structure, such as single-phase face-centered cubic (FCC) or body-centered cubic (BCC), rather than complex intermetallic compounds [15–19]. However, it is expected that the atom size difference among the constituent elements can induce an intrinsic residual strain field [20,21] and distort the lattice [22,23] in HEAs, which hinders dislocation nucleation and movement in these alloys. As a result, HEAs have shown superior wear and creep resistance [24–26] as well as excellent high temperature strength [16,27].
These superb properties make them attractive candidates for structural applications, especially at high temperatures. In principle, the delayed yielding behavior is closely related to the creep behavior of HEAs; therefore, it would be of interest to study their delayed yielding behavior, the result of which, in turn, could provide useful insights into the creep mechanisms in HEAs. In this work, we chose the single-phase FCC CoCrFeMnNi HEA as the model system to investigate the delayed yielding behavior of HEAs.

The CoCrFeMnNi alloy used in this study was prepared by arc-melting of pure constituent metals (purity > 99%) in a high-purity argon atmosphere. Detailed sample preparation procedures can be found in the previous work of Zhu et al. [1]. After a series of cold rolling and heat treatment processes, the equiaxed structure was obtained, which exhibited an average grain size of about 30–50 μm. The crystal structure was identified as a single-phase FCC structure by the X-ray diffraction (XRD), the same as that reported by Zhu et al. [1]. Nanoindentation experiments were subsequently performed using the Hysitron TI950 nanoindentation system with a Berkovich tip. The tip radius $R_t$ was calibrated to be 370 nm on a standard quartz sample based on the Hertzian contact law [28]. According to the work of Zhu et al. [1], the pop-in load can be estimated to be about 210 μN by taking the tip radius as 370 nm. Thus, the delayed yielding behavior of the CoCrFeMnNi alloy was studied by holding the applied load at four different values, namely, 125, 150, 175 and 200 μN. Figure 1(a) shows the typical load function with the maximum holding load of 200 μN. The loading, holding and unloading times were set at 3, 50 and 3 s respectively. As shown in Figure 1(b), there is no displacement burst observed in the loading period, indicating that the maximum load value chosen here is within the apparent elastic regime. However, after some waiting time, a distinct displacement burst occurs during the holding period. To obtain a statistical distribution of the waiting time, more than 50 indents were performed at each load value. To avoid the influence of grain boundary and any possible interference of the plasticity zone from adjacent indents, more than 200 grains were selected randomly and only one indent was made on each grain at its central region.

Figure 2(a,b) shows the statistical distribution of the waiting time and displacement burst obtained at different holding loads. As seen in Figure 2(a), the waiting time appears to exhibit a random distribution over a wide range from 0.5 to 47 s at the lowest holding load of 125 μN. As the holding load is increased, the distribution of the waiting time gradually becomes exponentially decayed, and specifically with more short waiting times observed at the higher holding load. On the other hand, the distribution of displacement bursts shows a reverse trend as compared to that of the waiting time. It is evidenced in Figure 2(b) that almost all displacement bursts observed at the lowest holding load of 125 μN are less than 4 nm, and they display an exponential-like distribution. As the holding load is increased, large displacement bursts are more frequently observed. Interestingly, the distribution of displacement bursts finally display in a random fashion at the holding load of 200 μN. For the sake of comparison, the averaged values of the waiting time and displacement burst are summarized in Table 1. Despite a relatively large data variation (Figure 2), a general trend begins to emerge, that is, the higher the holding load is, the shorter the waiting time is and the larger the displacement burst is. Notably, the current results obtained from the CoCrFeMnNi alloy are similar to these observed by Bahr et al. [7] on Fe–3%Si and Wo et al. [12] on Ni$_3$Al. Here, it is worth noting that the local reduced moduli of the individual grains were also obtained from the indentation unloading curves based on the Oliver–Pharr method [28]. The reduced moduli

![Figure 1](image1.png)

**Figure 1.** (a) a typical load function used in the delayed yielding nanoindentation experiments. (b) load-displacement curve showing displacement burst occurs at load holding period.
Figure 2. Statistical distribution of (a) the waiting time before pop-in occurs and (b) displacement burst at different holding load.

Table 1. The averaged waiting time, displacement burst and reduced modulus at different holding load.

| Holding load (μN) | 125    | 150    | 175    | 200    |
|-------------------|--------|--------|--------|--------|
| Waiting time (s)  | 18.53 ± 13.90 | 9.36 ± 12.42 | 9.23 ± 11.51 | 2.44 ± 4.56 |
| Displacement burst (nm) | 1.67 ± 1.22 | 2.89 ± 1.97 | 4.39 ± 2.89 | 5.51 ± 3.29 |
| Reduced modulus (GPa) | 175.79 ± 16.80 | 167.16 ± 13.74 | 158.31 ± 11.00 | 165.75 ± 14.90 |

obtained at different holding loads with an average locate within a narrow range between 160 and 175 GPa, as seen from Table 1. These important results indicate a dominant grain orientation or a texture for the grains indented, which is consistent with the XRD pattern of the CoCrFeMnNi alloy [1]. In other words, the grain orientation effect on the delayed pop-in behavior is negligible which is also consistent with the analysis of Zhu et al. [1].

To understand the incipient plasticity behavior of crystalline materials, Schuh et al. [4] attributed the pop-in events as observed in SiC to a stress-assisted, thermal-activated dislocation nucleation process, in which the defect nucleation rate is governed by the instantaneous load and thereby independent of the loading history, which is in sharp contrast to our current findings. Alternatively, Ngan et al. proposed a theory based on heterogeneous dislocation nucleation to rationalize the delayed incipient plasticity observed in Ni₃Al [8]. In theory, a significant chemical potential gradient can be induced underneath an indenter when it is pressured into a sample surface [29]. Consequently, this gradient significantly enhances the vacancy diffusion process in the direction perpendicular to the contour line of the chemical potentials. According to Li et al. [29], the chemical potential for vacancy formation is the highest just under the indenter [30]. Therefore, it is reasonable to envision that a dislocation loop might nucleate just under the indenter as a result of vacancy diffusion, as illustrated in Figure 3,
which leads to delayed plasticity, being fundamentally different from the scenario of homogeneous dislocation nucleation at the position of the maximum shear stress located at a depth of about 0.48 of the indenter–sample contact radius [4,10]. During the heterogeneous dislocation nucleation process, there are two possible paths for vacancies to be absorbed into the growing dislocation loop. One is the interfacial diffusion of vacancies from nearby free surfaces along the indenter–sample interface, and the other is the bulk diffusion of intrinsic vacancies or vacancies from nearby free surfaces. During this subcritical process of heterogeneous dislocation nucleation, the dislocation loop would be unzipped and disappear due to the imaging force if the applied load is removed before the dislocation loop grows up to a critical size. Incipient plasticity events only occur in a delayed fashion when the dislocation loop grows progressively beyond the critical size, after which a cascading process of dislocation nucleation might be also triggered.

In theory, the volume rate of atomic transportation from the indenter to a nearby free surface along the indenter–sample interface can be derived as $V_i = (16/3)(1 + \nu)PPD_i\Omega/2a^2 kT$ [8], where $P$ is the Poisson ratio, $P$ the applied load and $D_i$ the self-diffusion coefficient along the indenter–sample interface, $\Omega$ the atomic volume, $\delta$ the thickness of the diffusion path along the indenter–sample interface (as illustrated in Figure 3), $a$ the contact radius, $k$ the Boltzmann constant and $T$ the absolute temperature. Likewise, the volume rate of atomic transportation rate through bulk diffusion can be derived as $V_v = 3\pi(1 + \nu)PPD_{vd}\Omega/2akT$ [8], where $D_{vd}$ is the bulk diffusion coefficient. Assuming the total volume rate of atomic transportation $V = V_i + V_v$, one can arrive at the following important relations as derived previously by Ngan et al. [8]. If the diffusion along the indenter–sample interface is dominant, one would obtain:

$$p^{1/2}t_c^{1/2} = (p^{1/6}t_c^{1/2})^{p^{1/3}} + \sqrt{A}$$  \hspace{1cm} (1)

where $t_c$ is the critical waiting time before pop-in occurs; $P_i$ is the constant applied stress and $A' = (3\pi^2\alpha^2 G^2 b^3 kT R_t^2/128(1 + \nu)\Omega D_i \delta m E^2)$ in which $G$ is the sample’s shear modulus, $b$ the Burgers vector, $R_t$ the indenter tip radius and $E$, the sample’s reduced modulus. The physical meaning of $\alpha$ is given by the relationship of $\tau - \tau_i \approx \alpha Gb/R$ where $\tau$ is the applied shear stress; $\tau_i$ is the resistance stress to dislocation gliding; $\alpha$ is a geometric factor and $R$ is the radius of a dislocation loop. Here, $m$ is a scaling factor given by $\tau = mp_0$ where $p_0 = (6PE^2/\pi \gamma R_t^2)^{1/3}$ is the mean pressure under the indenter. On the other hand, if bulk diffusion dominates the diffusion process, one would have:

$$p^{2/3}t_c^{1/2} = (p^{1/3}t_c^{1/2})^{p^{1/3}} + \sqrt{A},$$

where

$$A = \frac{\pi \alpha^2 G^2 b^3 kT}{6\sqrt{6}(1 + \nu)\Omega D_{vd} m^2}(R_t/E) \frac{5/3}{\Omega_1}.\]

As shown in Figure 4(a) and (b), it appears that our experimental data can be fitted equally well to Equations (1) and (2). Through data fitting, the constant $A'$ can be estimated as $3.41 \times 10^{-5} \text{Ns}$ and $A$ as $2.00 \times 10^{-6} \text{N}^{4/3} \text{s}$. Since the reduced modulus $E_r$ of the CoCrFeMnNi alloy is about 166.7 GPa on average, the shear modulus $G$ can be estimated as $\sim 68.3$ GPa with a Poisson’s ratio $\nu = 0.3$. Meanwhile, the Burgers vector of the CoCrFeMnNi alloy is estimated to be $2.55 \text{Å}$. [1]. According to Ref. [28], the shear stress $\tau$ under the indenter is about $0.1p_0$ and therefore, we can take $m = 0.1$. According to Ref. [31], the geometric factor $\alpha$ is on the order of unity and hence we may take $\alpha \approx 1$. As for the thickness $\delta$ of the diffusion path, a minimum value can be estimated as on the order of one Burgers vector for atom diffusion to occur. Finally, the diffusion coefficient $D_i$ can be expressed as $D_i \approx k^2/\nu_0 \exp(-Q_i/kT)$ where $\nu_0$ is atomic vibration frequency ($\nu_0 \approx 10^{13} \text{s}^{-1}$). If we take $\delta = b = 2.55 \text{Å}$ as the minimum value, the interfacial diffusion coefficient and activation energy can be obtained from Figure 4(a) as: $D_i \approx 1.92 \times 10^{-19} \text{m}^2 \text{s}^{-1}$ and $Q_i \approx 0.74$ eV. However, if we take $\delta = 10b = 25.5 \text{nm}$ as an upper bound estimate, which might be unrealistic, the interfacial diffusion coefficient and activation energy would be: $D_i \approx 1.92 \times 10^{-20} \text{m}^2 \text{s}^{-1}$ and $Q_i \approx 0.74$ eV. Comparing these two estimates, one can see the extracted interfacial diffusion activation energy is not sensitive to the choice of the $\delta$ value. For simplicity, we herein take $\delta = b$, which leads to an interfacial diffusion activation energy $Q_i \approx 0.74$ eV. In a similar way, the bulk diffusion coefficient $D_{vd}$ and the corresponding activation energy $Q_{vd}$ can be extracted from Figure 4(b) as $D_{vd} \approx 7.97 \times 10^{-22} \text{m}^2 \text{s}^{-1}$ and $Q_{vd} \approx 0.88$ eV.

According to Ref. [32], the self-diffusion activation energies of the constituent elements Co, Cr, Fe, Mn and Ni in the CoCrFeMnNi HEA matrix were measured as 3.18, 3.04, 3.21, 2.99 and 3.29 eV respectively. Thus, it is therefore unlikely that the activation energy $Q_{vd}$ can be as low as 0.88 eV for bulk diffusion to occur in the HEA. However, the activation energy can reduce significantly when diffusion occurs along defects, such as dislocations, surface and grain boundaries. In general, it is well known that the activation energy for self-diffusion $Q_{vd}$, grain-boundary diffusion $Q_{gb}$ and surface diffusion $Q_{surf}$ follows a relationship $Q_{gb} > Q_{vd} > Q_{surf}$. For example, the activation energy for bulk diffusion of Ni in Ni$_3$Al is about 3.2 eV; however, the activation energy reduces to 1.68 eV when Ni diffuses along the grain boundary in
Ni$_3$Al [33,34]. In light of these earlier observations, we consider that, unlike the activation energy $Q_{sd}$ for bulk diffusion, the activation energy for interfacial diffusion $Q_i \approx 0.74$ eV is reasonable. In other words, the growth of the dislocation loop in our study is probably governed by the vacancy diffusion along the indenter-sample interface rather than through the bulk.

Next, let us estimate the activation volume of the heterogeneous dislocation nucleation in the HEA. It is generally believed that the dislocation nucleation rate in incipient plasticity follows an Arrhenius equation, that is,

$$\dot{N} = N_0 \exp\left(-\frac{(H - \tau V^\star)}{kT}\right),$$

where $N_0$ is the pre-exponential constant; $H$ is the activation enthalpy; $\tau$ is applied shear stress and $V^\star$ is activation volume. To back out the activation volume, the applied shear stress under the indenter can be estimated as $\tau = 0.1 \left(6PE_i^2/\pi^3 R_i^2\right)^{1/3}$ [28]. As a first-order approximation, the waiting time for a pop-in event to occur can be estimated through a linear correlation with the reciprocal of the dislocation nucleation rate, namely: $t = C/\dot{N}$ where $C$ is a constant [35]. Thus, we obtain:

$$\ln(t) = -\frac{0.1V^\star}{kT} \left(\frac{6E_i^2}{\pi^3 R_i^2}\right)^{1/3} \cdot P^{1/3} + \frac{H}{kT} - \ln\left(\frac{N_0}{C}\right).$$

(3)

As shown in Figure 4(c), the experimental data can be fitted to Equation (3) very well. The activation volume can be extracted from the slope of the curve of $\ln(t)$ versus $P^{1/3}$. Consequently, we obtain the activation volume $V^\star \approx 25.6 \text{Å}^3 \approx 1.54b^3$ which is lower than the activation volume of $34 \text{Å}^3$ obtained by Zhu et al. [1]. This is also consistent with our assumption that the delayed pop-in events are caused by heterogeneous rather than homogeneous dislocation nucleation.

To summarize, the delayed incipient plasticity is first studied for the CoCrFeMnNi HEA. Despite the data scattering, a clear trend can be perceived that the average waiting time decreases with the increasing holding load. According to our analyses, the activation energy for the interfacial diffusion along the indenter-sample interface is extracted as 0.74 eV while the activation volume for the delayed incipient plasticity is extracted to be $1.54b^3$. All our findings suggest a heterogeneous dislocation nucleation mechanism that governs the delayed yielding behavior of the single-phase CoCrFeMnNi alloy, which should be useful to deepen our understanding of viscoplastic behavior and creep mechanisms in HEAs.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by Research Grant Council, Hong Kong government: [grant number CityU11207215]; US NSF: [grant number DMR-0905979].

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