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INCIPIENT PLASTICITY OF METALS AND ALLOYS USING NANO-INDENTATION TECHNIQUE

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INCIPIENT PLASTICITY OF METALS AND ALLOYS USING NANO-INDENTATION TECHNIQUE

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Dong Wu
August 2015
DEDICATION

To My Parents
Hanzhang Wu and Yuzhen Li

To My Wife
Taotao Long
ACKNOWLEDGEMENT

At the end of the long journey pursuing a Ph.D degree, I can still recollect my immaturity and inexperience at the beginning of this journey when I just arrived in the US. It is not easy for a newcomer to grow up and get mature. In my first two years in the program, I staggered and stumbled forward, and then I learned to walk, and now I can run towards the final goal. After five-year studying and training, I found myself well equipped with sufficient knowledge, ways of thinking and experiences in the field of materials science for the future career. On the threshold that connects graduate student life and professional career, I feel grateful to those who has encouraged and helped me to move forward.

First of all, I would like to give thanks to my parents who have supported me without reservation throughout 30 years. I also would like to thank my wife Taotao Long, who encouraged and supported me when I was frustrated in these years.

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ABSTRACT

The incipient plasticity indicates the nucleation or activation of defects in materials and enables us to study the intrinsic mechanical properties of materials. In this dissertation, instrumented indentation technique was employed to study the incipient plasticity of metals (bcc-Cr, fcc-Ni, fcc-Au) and a fcc-structured high entropy alloy (HEA) NiFeCoMnCr. The critical shear stresses for pop-in in these materials were all within the range of theoretical strength of materials, indicating the nucleation of dislocations in perfect crystals.

In Chapter 3 and 4, indentation tests were conducted at elevated temperatures to study the pop-in behavior in bcc-Cr and fcc-Au. The pop-in load was found to drop with increasing temperature. Activation energy for pop-in was found too low to form a dislocation loop homogeneously in the lattice. The heterogeneous nucleation of dislocations at point defects in the lattice might be responsible for the pop-in events. Atomistic simulations of indentations were also performed in the Au(100) lattice with/without point defects at different temperatures. A good agreement was found between simulations and the experiments. Using an atomistic model, the activation parameters for the incipient plasticity were calculated from the simulation results, which were comparable with experimental results.

In Chapter 5, a broad range of tip radii of indenters were used to investigate the effect of indentation volume on pop-in behavior in the indentation experiments on bcc-Cr. The critical shear stress was found to increase with decreasing the tip radius. The cumulative pop-in probability on load was successfully described by a combined model over the full range of tip radius, indicating
the incipient plasticity might be triggered either by the nucleation of dislocation or the multiplication of existing dislocations underneath the indenter.

In Chapter 6, I found the combined model can also well described the pop-in behavior of fcc-Ni, and fcc-NiFeCoMnCr under three different tip radii (80, 255, 759 nm). The effect of tip radius on the elastic/plastic responses of Ni and HEA were evaluated quantitatively.

From the above studies, I tentatively make a conclusion in Chapter 7 and also presented a future perspective based on my research experience in the past five years.
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Chapter 1. Introduction

1.1 Plastic deformation and microstructure of the metals and alloys

By definition, plastic deformation is a permanent deformation process of materials under a significant load, which results in nucleation and motion (or propagation) of some deformation carrier in the materials. The deformation carriers are usually defects in the materials, for example, dislocations and twins in metals, shear bands in BMG, cracks in ceramics.

In this dissertation, we will focus on the plastic deformation process of metals and alloys. The plastic deformation process of metals is greatly affected as a result of the barriers in the lattice that hinder the motion of dislocation [1,2], e.g. solutes or precipitates in the aged alloy, grain boundaries in polycrystalline metals, twin boundaries in the nano-twin materials, dislocation forest in the heavily-worked metals, as shown in Figure 1-1.

![Figure 1-1 Relation between strength and microstructure in the metals and alloys [1,2]](image-url)

\[ \tau = \tau_0 + \frac{\alpha Gb}{L} \]

Particles, precipitates

\[ \sigma = \sigma_0 + k_{\text{gb}} \ell^{0.5} \]

Grain Boundaries

\[ \sigma = \sigma_0 + k_{\text{tb}} \lambda^{0.5} \]

Twin boundaries

Figure 1-1 Relation between strength and microstructure in the metals and alloys [1,2]
Empirical relations have been summarized in the following equations to quantitatively describe the strengthening effect for each interaction mechanism mentioned above:

\[
\tau = \tau_0 + \frac{\alpha Gb}{L} \quad \text{or} \quad \tau = \tau_0 + \frac{\alpha Gb}{l} \tag{1.1}
\]

\[
\sigma = \sigma_0 + k_{HP} d^{-0.5} \quad \text{or} \quad \sigma = \sigma_0 + k_{HP} \lambda^{-0.5} \tag{1.2}
\]

In these equations, a characterization length that describes the spacing or distance between the barriers can be identified, like particle distance \(L\), dislocation spacing \(l\), grain size \(d\), twin spacing \(\lambda\), and this characterization length has a significant effect on the strength of materials.

Figure 1-2 Sample size effect on the strength of materials in the presence of lattice imperfections: grain boundaries, precipitates, twins, dislocations.
In principle, these empirical relations work well at the macro scale, to be more specific, sample size >> $L$ (or $l$, $d$, or $\lambda$), however, they will break down when the sample size shrinks to a comparable value as or below these characterization lengths, as indicated in Figure 1-2. Under those circumstances, the intrinsic strength of material will be revealed. The plastic behaviors of the metals and alloys at the macro scale and their dependence on the sample size have been thoroughly studied so far. On the other hand, the size effect on the intrinsic strength of material at the micro/nano scale is still not well understood. It is one aim of this dissertation to shed some light on this topic.

1.2 Compression/tension test of micro/nano pillars

To study the mechanical property at small scale (micro/nano), two major techniques have been adopted. One is to perform tension/compression tests on the micropillars, which were fabricated by the Focused Ion Beam (FIB). This straightforward technique ensures us to derive the plastic stress-strain response from the load-displacement data easily. J.Y. Kim et al [3] have observed the increasing of yielding strength with the decreasing of the pillar diameter in the tension/compression tests of bcc metals (see Figure 1-4), while similar increasing trend in strength was also found in fcc metals [4], as indicated in Figure 1-5. This increasing trend probably results from less and less defects in the smaller sample, the strength of which approaches to the theoretical strength of materials.
Figure 1-3 SEM images of (a) nanopillar before compression, (b) and (c) severely compressed nanopillars including pronounced crystallographic slip lines, and (d) tension sample, (e) front and (f) side views of fractured sample after tension [5]

Figure 1-4 Flow stresses at 8% strain in compression and at 5% strain in tension and 0.2% offset yield strength vs. sample size for (a) W, (b) Mo, (c) Ta (d) Nb [3]
Figure 1-5 Shear flow stress normalized by shear modulus on appropriate slip system for most face-centered cubic (fcc) metallic micro- and nano-pillars tested in compression and tension [4]
Though microtension/compression technique gives us a general idea of how the strength evolves as the sample size shrinks, it can’t provide more precise results. Here are some of the reasons. First of all, perfect pillar shape can’t be obtained by FIB, and a taper shape is inevitable as a result of the beam fabrication process. The irregular shape of the pillar affects the accuracy of the stress. Another thing is surface effect. The pillar has a large surface fabricated by FIB, and a smaller pillar diameter is, a larger surface/volume ratio becomes. Since the surface may act as dislocation sources/sink [6,7], the intrinsic mechanical properties of material may not be evaluated from a small pillar.

1.3 Nanoindentation technique

1.3.1 Contact mechanics of indentation

Nanoindentation is another technique to evaluate the mechanical properties of materials at micro/nano scale. According to the Hertzian contact theory, the stress field underneath a spherical indenter can be described in cylindrical coordinates \((r, \theta, z)\) by

\[
\frac{\sigma_{rr}(r,z)}{\sigma_{0}} = \frac{3}{2} \left[ 1 - 2\nu \frac{a^2}{r^2} \left( \frac{z}{u^{\nu/2}} \right)^3 + \frac{a^2 u}{u^2 + a^2 z^2} + \frac{z}{u^{\nu/2}} \left( \frac{u}{a^2 + u} \right) + (1 + \nu) \frac{u^{\nu/2}}{a} \tan^{-1} \left( \frac{a}{u^{\nu/2}} \right) \right]
\]

(1.3)

\[
\frac{\sigma_{\theta\theta}(r,z)}{\sigma_{0}} = \frac{3}{2} \left[ 1 + 2\nu \frac{a^2}{r^2} \left( \frac{z}{u^{\nu/2}} \right)^3 + \frac{2\nu + 1}{u^2 + a^2 z^2} - (1 + \nu) \frac{u^{\nu/2}}{a} \tan^{-1} \left( \frac{a}{u^{\nu/2}} \right) \right]
\]

(1.4)

\[
\frac{\sigma_{zz}(r,z)}{\sigma_{0}} = -\frac{3}{2} \left( \frac{z}{u^{\nu/2}} \right)^3 \left( \frac{a^2 u}{u^2 + a^2 z^2} \right)
\]

(1.5)

\[
\frac{\tau_{rz}(r,z)}{\sigma_{0}} = -\frac{3}{2} \left( \frac{r z^2}{u^2 + a^2 z^2} \right) \left( \frac{a^2 u^{\nu/2}}{a^2 + u} \right)
\]

(1.6)
where the parameter \( u = \frac{1}{2} \left\{ (r^2 + z^2 - a^2) + \left[ (r^2 + z^2 - a^2)^2 + 4a^2z^2 \right]^{1/2} \right\} \), \( a \) is the contact radius given by \( a = (Rh)^{0.5} \), and the mean pressure \( p_m \) is given by \( p_m = \frac{P}{\pi a^2} = \left( \frac{16PE_r^2}{9\pi^3R^4} \right)^{1/3} \).

At a given point in the solid, the maximum shear stress is \( \tau_{\text{max}}(r, z) = \sqrt{\left( \frac{\sigma_r - \sigma_z}{2} \right)^2 + \tau_{\text{r}}^2} \), and a typical contour plot of \( \tau_{\text{max}} \) as a function of position within a bulk metallic glass sample[8] was shown in Figure 1-6.

![Contour plot showing the distribution of \( \tau_{\text{max}} \) in a BMG sample [8]](image)

As shown in the above contour plotting, the shear stress \( \tau_{\text{max}} \) reaches a peak value 0.445\( p_m \) directly below the center of the spherical indenter \( (r = 0) \) at a distance of about half the contact radius below the specimen surface. This feature of the stress field underneath the indenter enable
us to focus the high shear stress to an internal point inside the sample, away from the surface, thus gives us a chance to probe the bulk properties near the high-stress spot.

### 1.3.2 Pop-in event

A sudden displacement excursion or "pop-in" event during an indentation test was first observed in metals using SEM in 1968 [9]. The load-displacement response with the “pop-in” phenomenon was obtained during a continuous micro-indentation test in 1995.

![Figure 1-7 Load-displacement curve of an indentation into the <100> face of a tungsten single crystal [10]](image)

The loading part prior to the displacement excursion was found to be elastic, and it could be well described by Hertzian contact theory (see Figure 1-7):

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

(1.7)
where in the equation $R$ is tip radius of the indenter, $h$ is the penetration depth, and $E_r$ is the reduced Young’s modulus: $E_r = \left[\frac{((1-\nu^2)\/E)_{\text{Indenter}}}{1}, \frac{((1-\nu^2)\/E)_{\text{Sample}}}{1}\right]^{-1}$, $\nu$ is the Poisson’s ratio. In the early days, the researchers used to ascribe the first yielding event on the load-displacement curve to the fracture of oxide layer on the sample surface [11,12]. Another idea on the origin of pop-in was suggested to be the nucleation process of dislocation at the surface irregularities. These viewpoints then were ruled out due to further studies on this phenomenon. The pop-in (or incipient plasticity) event has been observed universally in metals (e.g. Au [13,14], Al [15], Pt [16], Ni [17], Mg [18], W [19], Ta [20,21]) and alloys (FeAl [22], a high entropy alloy NiFeCoCrMn [23] and intermetallics Ni$_3$Al [24], Fe$_3$Al [25]). Some of these metallic materials like Au, Pt have no oxide layer on the surface. The sample surface was usually electropolished prior to indentation tests, and the RMS roughness of the surface can reduced be below 1 nm [16,25]. Moreover, the stress field underneath the indenter illustrates low stress level on the surface, on the other hand, a concentrated high stressed zone at about half of the contact radius below the surface. More and more experimental data [16,26–31] have indicated the maximum shear stress for pop-in falls in the range of theoretical strength of materials. The pop-in event is more likely to arise from the dislocation nucleation process in the dislocation-free zone in the material [32].

The pop-in event was also found to be sensitive to the surface preparation process. The displacement excursion doesn’t happen in the sample with mechanical damage layer, because mobile dislocation exists in the stressed zone underneath the indenter. Z. Wang et al [33] observed the re-occurrence of pop-in event after the removal of the damaged layer by chemo-mechanical polishing process. C Zhu et al [23] found the pop-in event in polished high entropy alloy sample fully annealed in Ar. Obviously, there is a strong connection between pop-in event
Figure 1-8 Surface topography of Fe$_3$Al–0.5Cr alloy before and after indentation: (a) Surface topography prior to indentation, (b) typical matrix of indents and (c) surface profile along the line 1 in Figure (a) [25]
1.3.3 *Pop-in behavior in the viewpoints of energy and thermodynamics*

The nucleation of dislocations was discussed previously in the frame work of continuum mechanics theory by Hirth and Lothe [34]. It involves the free energy of formation for a dislocation loop in the presence of stress field. Similar discussions [35,36] have also been performed under the circumstance of indentation tests. The free energy to form a dislocation loop under stress is given by

\[
\Delta G = 2\pi r W - \pi r^2 b \tau + \pi r^2 \gamma
\]  

(1.8)

where \( W \) is the line energy for the dislocation loop, \( r \) is the radius of the loop, \( \tau \) is the applied shear stress acting on the loop, \( b \) is the Burgers vector, \( \gamma \) is the stacking fault energy. Obviously, the first term on the right-hand side of the equation shows the energy required to form a dislocation loop. The second term is the work done by the stress upon the dislocation loop, serving as a driving force to form the dislocation loop. The third term indicates an increase in energy to create a stacking fault. The line energy \( W \), which arises from the lattice strain, is given by the expression [34]:

\[
W = \frac{2 - \nu}{2(1 - \nu)} \frac{G b^2}{4\pi} (\ln \frac{4r}{r_0} - 2)
\]  

(1.9)

where \( G \) is the shear modulus, \( \nu \) is the Poisson’s ratio and \( r_0 \) is the dislocation core radius. Bei et al [26] applied this model to interpret the statistics of pop-in behavior in Mo, assuming the dislocation loop was formed in the perfect lattice.
Mason et al [16] have observed the load for pop-in event decreases with the increase of temperature. This temperature dependence could not be explained by the model above, which doesn’t contain a temperature term. The nucleation of dislocation is more likely to be a single local kinetically limiting process, which requires an activation enthalpy. The energy barrier could either be reduced through the mechanical work of indentation, or be overcome by an appropriate thermal fluctuation, or be surpassed by a combination of both thermal and mechanical energy. The rate of this process per unit volume of material can be described in an Arrhenius-type form:

\[
\dot{n} = \eta \exp\left(-\frac{\Delta G}{kT}\right)
\]  

(1.10)

where \(\Delta G = \varepsilon - \tau \nu\) is the Gibbs free energy for the pop-in event, \(\varepsilon\) is the enthalpy for the pop-in event, \(\tau\) is the applied stress over the activation volume \(\nu\), and \(\eta\) is the pre-exponential frequency factor.

Formally, the global rate \(\dot{N}\) at which pop-in would occur could be derived from the integration over the indented volume near the contact region \(\Omega\):

\[
\dot{N} = \eta \exp\left(-\frac{\varepsilon}{kT}\right) \int_{\Omega} \exp\left(\frac{\sigma \nu}{kT}\right) d\Omega
\]  

(1.11)

For the present discussion, the stress bias \(\sigma\) is approximately the maximum shear stress beneath the indenter, which is given by Hertzian contact theory:

\[
\sigma \equiv \tau_{\text{max}} = \frac{0.47}{\pi} \left(\frac{4Er}{3R}\right)^{2/3} p^{1/3}
\]  

(1.12)
Here we assume the stress $\sigma$ is independent of position within the sampling volume $\Omega$, which can be scales with the cube of the contact radius $a$: $\Omega \approx K a^3 = K\left(\frac{3PR}{4E}\right)$.

For the statistical analysis of pop-in behavior, the cumulative fraction function of pop-in $F(t)$ could be derived as follows. The rate of $F(t)$ is proportional to the number of the sample without yielding, thus

$$\dot{F}(t) = [1 - F(t)] \dot{N}(t) \quad (1.13)$$

Integrate this equation and we can have

$$F(t) = 1 - \exp\left(-\int_{0}^{t} \dot{N}(t')dt'\right) \quad (1.14)$$

Combining the equations above, we may derive the cumulative probability for pop-in $F(t)$.

If we apply a constant loading rate $\dot{P}$ during the indentation tests, we can evaluate the cumulative fraction function $F(P)$ to be

$$F(P) = 1 - \exp\left[-\frac{9KR\eta}{4E,\dot{P}\alpha^6} \exp(-\frac{\epsilon}{kT}) \left[120 + \exp(P^{13}\alpha) \cdot (P^{13}\alpha^5 - 5P^{13}\alpha^4 + 20P\alpha^3 - 60P^{2/3}\alpha^2 + 120P^{13\alpha - 120})\right]\right]$$

Here the parameter $\alpha$ shows a group of time-independent terms: $\alpha = \frac{0.47}{\pi} \left(\frac{4E}{3R}\right)^{2/3} \frac{\nu}{kT}$.

The equation above could be re-arranged in a linear form:

$$\ln[-\ln(1 - F)] = \alpha P^{13} + \ln\left[\frac{9KR\eta}{4E,\dot{P}\alpha^6} \exp(-\frac{\epsilon + \tau \nu}{kT})\beta\right] \quad (1.15)$$

where the parameter $\ln(\beta)$ is a weak function of $P$ compared to the first term, and is given by

$$\beta = 120 + (P^{5/3}\alpha^5 - 5P^{4/3}\alpha^4 + 20P\alpha^3 - 60P^{2/3}\alpha^2 + 120P^{13\alpha - 120}) \exp(P^{13}/\alpha) \quad (1.16)$$
Mason et al [16] analyzed the pop-in behavior of single crystal Pt using this model, and abstracted the activation volume for pop-in from the slope of the linear fitting $\ln[-\ln(1-F(P))]$ versus $P^{1/3}$. The equation can be re-written in the following form:

$$P^{1/3} = \gamma kT + \frac{\pi}{0.47} \left( \frac{3R}{4E_v} \right)^{2/3} \frac{E}{\nu}$$

(1.17)

where $\gamma$ is a unimportant complex function. The activation enthalpy $\varepsilon$ could be extracted from the intercept of the above equation. Mason et al [16] performed indentation tests on Pt at elevated temperatures, and determine the activation enthalpy $\varepsilon$ for the pop-in event in Pt. According to their results, the activation volume and activation enthalpy for pop-in in Pt are $\nu = 0.5 b^3$, $\varepsilon = 0.28$ eV, respectively, both of which are significantly lower than those to form a critical-sized homogeneous dislocation loop. Relatively low activation parameters were also observed in GaN (0.85 eV) [37] and hexagonal-close-packed (hcp) Mg (0.2 $b^3$) [18].

These low activation parameters indicate the dislocation may nucleate from zero-dimension defect like vacancies, solutes, interstitials etc.

1.3.4 Effect of indented volume on pop-in behavior

So far, it is well accepted that pop-in event is related to the nucleation of dislocations in the highly stressed zone beneath the indenter. During the indentation test, the size of the stressed zone is scaled by the contact radius $a$, which is the square root of tip radius times penetration depth. Therefore, a series of indenters with different tip radii could be used to study the effect of stressed zone size on the incipient plasticity of materials. Schuh et al [38] compared the cumulative distribution of pop-in stress for two indenters with different tip radii. They found the blunt tip
results in a broader distribution of critical stresses, and the stress level for sharp tip is higher than that for blunt one. Shim et al [27] performed indentation tests on Ni using 10 different spherical indenter tips. They found the critical stress decreases with the increase of tip radius, as shown in Figure 1-9. The smallest indenter produced reproducible results, and larger indenter radii produced a strongly stochastic component in the pop-in strength. The dislocations in the annealed Ni was proposed to cause the decrease of critical shear stress, but a stochastic model is required to evaluate the indenter tip radius effect quantitatively.

![Figure 1-9](image)

Figure 1-9 The maximum shear stress determined from the pop-in loads as a function of indenter radius for annealed Ni(100)

Shin et al. [39] revealed a power-law relationship between the critical shear stress and the tip radius in the blunt tip region, but the relationship doesn’t apply to the sharp tip. Morris et al [40] suggested a statistical model for pop-in initiated at pre-existing dislocations during
nanoindentation. In their model, the volume $V(\tau > \tau_{\text{pop-in}})$ is defined as the region where the local resolved shear stress $\tau$ is larger than the critical shear stress for pop-in $\tau_{\text{pop-in}}$. If there is at least one defect in this volume, pop-in will occur. Otherwise, pop-in won’t occur until the maximum shear stress approaches the theoretical strength. The scaled volume could be calculated from the previous Hertzian analysis, and it is plotted as a function of normalized critical shear stress in Figure 1-10. Assuming the distribution of defects obeys Poisson statistics, the probability $P_0$ that pop-in has not occurred in the sample was given by

$$P_0(V) = \exp(-\rho_{\text{def}} V)$$  \hspace{1cm} (1.18)

where $\rho_{\text{def}}$ is the density of defects in the material. The cumulative probability for pop-in was then

$$P_{\text{pop-in}} = 1 - P_0(V) = 1 - \exp(-\rho_{\text{def}} V)$$  \hspace{1cm} (1.19)

This model was applied to describe the pop-in behavior of single crystal Mo when spherical indenters with radii from 115 nm to 700 μm. The comparison between experimental data and modeling was displayed in Figure 1-11, and the model agrees with the data well for the blunt indenters ($R > 3.75 \mu m$), but could not extend to sharp indenters. There is probably no defect in the small stressed zone underneath the sharp indenter, and Morris’s model doesn’t apply under this circumstance. Maybe a model that combines dislocation nucleation and the activation of pre-existing defect can describe the pop-in behavior using tip radii in a broad range.

Recently the pop-in behavior of single-crystal Mo(001) was reanalyzed [41,42] following this idea, and the experimental data were found well described.
Figure 1-10 Calculated volume of the highly stressed region, where the shear stress exceeds the defect-driven pop-in strength.

Figure 1-11 Cumulative probability of pop in, as a function of maximum stress under the indenter, for a series of indenter radii (points) Smooth curves show the predicted behavior, the dashed vertical line indicates the theoretical strength, where dislocation generation may occur without a preexisting defect.
Figure 1-12 Homogeneous defect nucleation in Al (a) Indentation response to the point of initial load relaxation (b) Corresponding atomic structure, indicating subsurface homogeneous dislocation nucleation at a depth $z = 0.51a$, where $z$ and $a$ are depth and contact radius, respectively. (c) Plan view from within the crystal, oriented along the loading axis toward the free surface [44]

As a result of the limitation of the current experimental technique, the researchers are unable to confirm whether the dislocation nucleate homogeneously or heterogeneously in the stressed zone beneath the indenter. Molecular dynamics (MD) simulation may give us some clues about the nucleation process, since it can visualize the atomistic structure of defect and shows how the defect evolves during the deformation of materials [43]. J. Li et al [44] observed homogeneous nucleation of defect in the stressed atomic lattice underneath the spherical indenter, as displayed in Figure 1-12. The formation of lattice defect was found to correspond to the sudden drop of the load.
Figure 1-13 Molecular dynamics simulation of spherical indentation of \{111\} single-crystal Al thin film, (a)–(f) Key transitions in the load-displacement (P–h) response, with snapshots of atomic activities within the crystal (only atoms whose coordination number differs from 12 are shown). [44,46]
The evolution of dislocation structure in the process of indentation was shown by a series of snapshots in Figure 1-13. Dislocation loops were found to nucleate heterogeneously from the defects formed previously. These dislocations interact with each other and propagate forward to the inner part of material. Load drops from (b) to (f) are triggered by these dislocation activities. Similar atomistic processes have also been observed in Au [45].

Figure 1-14 Load–displacement curve with snapshots of atomistic configuration at several stages of nanoindentation, including the nucleation of dislocations from the defect and the onset of plasticity (marked with *) [47]

The MD simulation of indentation tests mainly focused on the perfect lattice at very low temperature ~ 0K in the early days. However, defects inevitably exist in the lattice at ambient temperature to lower the free energy of the system according to thermodynamics. The defects may play roles in the dislocation activities. Recently point-like defects (e.g., vacancies, di-vacancies,
tri-vacancies, and interstitial atoms [47–49]) were introduced into the lattice in the atomistic simulations to show their effect on the incipient plasticity, as shown in Figure 1-14. Salehinia et al [48,50] has studied the effect of vacancies on the incipient plasticity of Ni during indentation by MD simulation. The impacts of a variety of point defects (vacancies, di-vacancies, self-interstitials and stacking fault tetrahedra) on inception of plasticity were also discussed in Cu [47]. It was found that all these defects facilitate the onset of plasticity and lower the yielding load, but these phenomena were observed at very low temperature (~0 K), different atomistic processes probably occur at higher temperature. Recently, the onset of plasticity of copper containing point defects at finite temperature were studied [51]. It mainly focused on the simulation of asymmetry phenomena and orientation effect in uniaxial loading tests, but didn't provide information about the coupling of lattice vibration and point defects in dislocation nucleation processes at higher temperature. Solid solute impurity is another common kind of point defect in metallic materials. An active promoting role of hydrogen solute has been not only observed in the pop-in behaviors in FeAl [52], bcc-V [53], but also in the dislocation nucleation process in MD simulations [54,55]. So far, substitutional solid solutes have been found to raise the pop-in load in Mo-Ir system [56] and Fe₃Al [25], but not in Ni-Cu system [57], and Mg [18].

1.4 Motivations and outline of this dissertation

According the literature review above, we have found studies of incipient plasticity of the body-centered cubic (bcc) metals [21,58] are limited, compared with face-centered cubic (fcc) metals [15,27,30,59]. It will be intriguing to evaluate the activation parameters for the incipient plasticity of bcc-metals to shed lights on the dislocation nucleation, since the nucleation kinetics in bcc-metals are expected to be different from that in the fcc-metals, in which partial dislocations...
tend to dominate [31]. In Chapter 3, we carried out nanoindentation tests at elevated temperature on bcc-Cr and explored the nature of incipient plasticity in the material.

Mason et al [16] analyzed the drop of pop-in load with the increasing temperature statistically, and indicated the heterogeneous nucleation of dislocation for pop-in. However, so far the MD simulation work on the deformation process of lattice with defects at elevated temperatures is still lacking. Besides, the role of substitutional impurities in dislocation processes is unclear, and relevant simulation is rare. In previous studies, the effect of loading rate on incipient plasticity in nanoindentation has been observed in Pt [16] and Mg [18], but this effect was not found in some bcc and fcc metals [28,31]. It would be interesting to investigate and compare the rate effect employing both experimental technique and simulation method. In view that the effect of tip radius on incipient plasticity has been intensively studied by experiments [17,27,39,40,60,61], but rare simulation studies [47,48,62] were reported, the tip radius effect is another interesting topic to study. In Chapter 4, the onset of yielding in gold was studied using instrumental indentation technique at elevated temperature and varied loading rates. The reason we choose to use gold is its excellent resistance to oxidization at higher temperature, and reliable potentials for gold has been developed and applied in MD simulations [63–65]. The deformation of gold sample by indentation was also simulated at finite temperatures and varied indentation velocities using molecular dynamics method. Vacancies and impurities were introduced into the lattice, and their effect on dislocation nucleation were observed and qualified. Two tip radii were used in both the indentation tests and modeling to investigate the tip radius effect. In summary, the experimental results and simulation were compared, and the mechanism of dislocation nucleation underneath the indenter was discussed.
The incipient plasticity of pure metals (e.g. Al [15], Pt [16], Ni [17], Mg [18], W [19], Ta [20,21]) and alloys (e.g., a high entropy alloy FeCoCrNiMn [23] and Ni$_3$Al [24] intermetallics) have been characterized by nanoindentation, and the tip radius used in these studies ranges from 113 nm to 1300 nm. However, no more than two tip radii were used in each of these studies, thus studies on the effect of tip radius were still limited. All the available quantitative discussions [39,41,42] on the tip radius effect above were based on the same set of experimental data on single-crystal Mo [40]. It is interesting to study the tip radius effect on the incipient plasticity in other metals and alloys. In Chapter 5, we performed indentation tests on bcc-Cr using indenters with a series of different tip radii, and discussed the mechanisms for pop-in in the stressed zones with different sizes. A model combining two statistical models, one based on dislocation nucleation in a perfect crystal [16] and another on pre-existing dislocation sources in the crystal [40] was proposed to describe the pop-in behavior for different tip radii.

In Chapter 6, we probed the tip radius effect on the pop-in behaviors in single crystal Ni and fcc-structured high entropy alloy NiFeCoCrMn, and discussed the influence of alloying on the elastic/plastic responses using different tip radii.
Chapter 2. Methodology

2.1 Sample preparation

In our study, we conducted indentation tests on the metals (Cr, Au, Ni . etc) and alloy (NiFeCrCoMn) with low dislocation density. The preparation procedures for each sample were described as below:

A piece of Cr sample was sliced from a coarse-grained Cr bulk prepared by arc melting method (purity > 99.99%). The surface of the Cr sample was ground using 1200 and 2400-grit SiC, and then mechanically polished using alumina of 0.06 μm in grit size. To reduce existing dislocations and minimize possible surface damage resulting from the mechanical polish, the Cr specimen was initially sealed in a fused silica tube filled with pure Ar gas and, then, annealed at 1250°C for 4 hr [66]. As the final procedure, the annealed Cr was additionally electropolished in a solution (H₃PO₄:H₂SO₄ = 4:1) to remove possible oxidization layer during annealing.

A high-purity (> 99.999%) single crystal Au(100) purchased from Goodfellow was used. The gold sample was mechanical polished to remove the scratches on the surface, and electropolished in the electrolyte solution (glycerol: hydrochloric acid = 2.5:1.5) in a two-electrode cell.

The high entropy alloy sample with the nominal composition of NiFeCrCoMn (in atomic proportion) in this study was 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-casted ingots were homogenized at 1200 °C for 4 h, and then cold rolled by 50% reduction in thickness. Rectangular samples were sliced from the rolled plate, then ground and polished to a mirror finish. The sample was annealed at 1000 °C for 2 h to induce recrystallization and grain growth, and to remove any surface stress resulting from the mechanical polishing.

The Ni sample was prepared using a directional floating zone melting technique [27] in Oak Ridge National laboratory. The surface of the sample was ground and electropolished in a solution of 40% sulfuric acid and water for the indentation tests.

2.2 Microstructure Characterization

Figure 2-1 Characterization techniques to exam the microstructure and surface of samples: (a) Optical Microscope (b) Scanning Electron Microscope equipped with electron backscatter diffraction (EBSD) (c) Atomic Force Microscope
In our study, multiple techniques have been adopted to exam the surface of samples, as shown in Figure 2-1. The surface of the electropolished sample can be observed by Nikon EPIPHOT reflected light optical microscope. The microstructure of the polycrystalline metallic materials could be examined using Zeiss Auriga scanning electron microscope equipped with EBSD function. The shape of indent after indentation tests were visualized using atomic force microscope. An Atomic Force Microscope MFP-3DTM (Asylum Research Inc, Santa Barbara, CA) was utilized at the air image mode to evaluate the surface quality of the samples before indentation tests. The probe (AC160TS-R3) used for imaging has tip radius of about 9 ± 2 nm.

2.3 Nanoindentation tests at ambient temperature

Figure 2-2 Configuration of Triboindenter (Hysitron. Inc.) for indentation test at ambient temperature (a) and two typical geometries of indenter tip: cube corner (b) and Berkovich (c)
Instrumented indentation tests were performed using Hysitron Triboindenter (Hysitron Inc, Minneapolis, MN) machine, as shown in Figure 2-2. The advantages of having high resolution in both displacement (~nm) and load (~μN) enables a nanoindentation system to capture pop-in events while probing a small volume of sample that is free of lattice defects, in particular, dislocations. Two typical geometries of the indenter tips are Berkovich and cube corner, both of which are three-sided pyramids. In principle, the three sides of the pyramids end as a sharp point, however, as a result of the fabrication limit, these sides end as a round sphere. The tip radii of the indenters we used in this study were calibrated on single crystal tungsten, and they fell in the range of 60 ~ 759 nm.

2.4 Nanoindentation tests at elevated temperature

Figure 2-3 Hysitron Triboindenter system equipped with heating stage and heating shield for the indentation test at elevated temperatures
The Hysitron Triboindenter machine we used is also equipped with accessories that enable us to conduct indentation tests at elevated temperatures. These accessories include a heating stage to heat the sample up to 200 °C, and a heating shield to protect the transducer away from the hot sample and stage below. Since the temperature gradient around the sample results in thermo expansion of components like shaft of indenter, serious thermal drift will occur and the experimental data is significantly affected. We usually heat up the sample to the set temperature and hold it for 30 min, the tip is then brought to contact with the sample surface and equilibrate for another 30 min. The temperature of the sample surface was monitored and controlled within ±0.2 K using a J-type thermocouple in direct contact with the surface.

2.5 MD simulation method

The molecular dynamics simulations with the embedded atom method (EAM) potentials were performed to simulate the nanoindentation processes in our studies. The velocity form of the Verlet algorithm was implemented to evolve the system using LAMMPS code [67]. The EAM potentials for gold used in this study was developed by Grochola et al. [63]. The EAM potential for Au-Ag alloy [68] was also applied to model the effect of silver impurity in gold. The Au single crystal chosen for simulation is $20 \times 20 \times 10 \text{ nm}^3$ in size, and contains about 255,000 atoms. The point defects (vacancies, impurities) were introduced randomly in the atomistic structures. The bottom face was fixed, while the top face was allowed to move. Periodical boundary condition was applied to the side faces. The simulation box is large enough to neglect the effect of indentation from neighboring simulation box.

In the simulation, a quadratic force was applied to model a rigid spherical indenter: $F(r) = -K(r-R)^2$, where $r$ is the distance from the atom to the center of the indenter, $R$ is the radius of the
indenter, K is the force constant. The force is repulsive and \( F(r) = 0 \) for \( r > R \). The indentation process was performed along the Z-axis, and the motion of the indenter was prescribed at a constant velocity. In this study, simulations were performed at 1K, 300K, 400K, 500K, respectively, to study the effect of temperature on the dislocation nucleation process.

The atomistic configuration in the simulation was visualized by the free software OVITO[69]. The centrosymmetry parameter for each atom was calculated and used to pick up the atoms adjacent to defects [43].
Chapter 3. Effect of temperature on the pop-in behavior in Cr

3.1 Pop-in event and surface condition

In this study, a piece of Cr sample was sliced from a coarse-grained Cr bulk prepared by arc melting method (purity > 99.99%). The surface of the Cr sample was ground using 1200 and 2400-grit SiC, and then mechanically polished using alumina of 0.06 μm in grit size. To reduce existing dislocations and minimize possible surface damage resulting from the mechanical polish, the Cr specimen was initially sealed in a fused silica tube filled with pure Ar gas and, then, annealed at 1250°C for 4 hr [66]. As the final procedure, the annealed Cr was additionally electropolished in a solution (H₃PO₄:H₂SO₄ = 4:1) to remove possible oxidization layer during annealing. To measure the grain size and dislocation population in the Cr sample, an etchant consisting of 6 wt% nitric acid, 16 wt% ceric ammonium nitrate, and 78 wt% water was used and an etched surface is shown in Figure 3-1. Dislocation density is estimated from the number of etched pits to be about $1 \times 10^{10}$ m⁻² and the grain size is determined to be about 0.5 mm.

Figure 3-1 Etched pits on the surface of the annealed Cr sample gives an averaged dislocation density of about $1 \times 10^{10}$ m⁻².
Nanoindentation was performed in only one single Cr grain, the crystal orientation of which was determined by electron backscattering diffraction (EBSD), as indicated in the inverse pole figure (inset of Figure 3-2). Indentation tests were all conducted on a Triboindenter (Hysitron, Minneapolis, MN). A Berkovich indenter tip supported by a low-thermal-expansion shaft was used in this study. The tip radius of this Berkovich indenter was estimated from the calibration tests on W single-crystal to be 210 nm. A maximum load of 1 mN was used in all tests. Indentation tests at various loading rates (0.02 mN/s, 0.1 mN/s, 0.5 mN/s, 2 mN/s) were conducted to examine the effect of loading rate on incipient plasticity. Indentation tests were also performed at elevated temperatures (295 K, 333 K, 373 K, 423 K) at a constant loading rate of 2 mN/s to access the
activation enthalpy for the incipient plasticity. To carry out indentation tests at elevated temperatures, a commercial heating stage was installed and the displacement transducer was shielded from the hot specimen and stage with a cooled copper fixture [70]. Before indentation, the sample was heated to the set temperature and held for at least 30 min and the tip was, then, brought to contact with the sample surface and equilibrated for another 30 min. The temperature of the specimen surface was monitored and controlled (± 0.2 K) using a J-type thermocouple in direct contact with the sample surface. At least 60 indentations were performed at each test temperature and loading rate. The distance between adjacent indents was set at 10 μm to minimize possible overlap of the indented zone. Thermal drift was estimated to be within 0.5 nm/s.

![Graph](image)

Figure 3-3 Pop-in events during the indentation of Cr prepared under different surface conditions (a) and the statistics of 184 \( P-h^{1.5} \) pairs at pop-ins (b). The reduced elastic modulus of 236.12 ± 1.59 GPa is obtained.

Representative \( P-h \) curves with apparent pop-in events during indentation are presented in Figure 3-3(a). The elastic part of the \( P-h \) curves can be well described by the Hertzian relation [71]:

\[
P = \frac{4}{3} E_r R^2 h^{1.5}
\]

where \( E_r \) is the reduced elastic modulus and \( h \) is the indentation depth.
\[ P = \frac{4}{3} E_r R^\frac{1}{2} h^\frac{3}{2}, \]
where in the equation \( R \) is tip radius of the indenter, \( h \) is the penetration depth, and \( E_r \) is the reduced Young’s modulus. Insert proper parameters into the Hertzian relation, namely,

\[ E_r = \left[ \frac{((1-\nu^2)/E_{\text{Diamond}} + ((1-\nu^2)/E_{\text{Cr}})^{-1}} \right], \]

where the Poisson's ratio \( \nu \) for Cr is 0.21 [72], and the diamond properties [73] are \( E = 1141 \) GPa and \( \nu = 0.07 \), we can plot a \( P-h^{1.5} \) graph using a collection of \( P-h \) pairs at the pop-in obtained from a series of 184 indentations; this is shown in Figure 3-3(b). The slope of the fitted curve is 4.509, from which \( E_r \) is deduced to be \( 236.12 \pm 1.59 \) GPa. The elastic modulus of Cr sample is thereafter determined to be \( 284.30 \pm 1.52 \) GPa, which is slightly higher (2%) than the literature value of 279 GPa [74].

It has been reported that the occurrence of pop-in events is highly sensitive to the surface condition of a test sample [21,75]. In the present study, it is also demonstrated in Figure 3-3(a) in which load-displacement (\( P-h \)) curves obtained from Cr samples prepared by both mechanical polishing and electropolishing are shown. It is evident that pop-in events occur in the electropolished Cr, but are absent in the mechanical polished sample. Similar results were also observed in single-crystal Mo [75], indicating that a mechanically damaged surface layer can artificially eliminate the pop-in events during indentation.

It is worthy to note that the size of the plastic zone beneath the Berkovich tip is scaled with the contact radius \( a \) (= 71 nm), which is \( a = (Rh)^{1/2} \), according to the Hertzian theory [71]. In the current Cr sample, the dislocation spacing, estimated from the dislocation density (Figure 3-1) is about 10 \( \mu \)m, which is much larger than the size of plastic zone. It suggests that the observed pop-in is unlikely triggered by preexisting dislocations.
Figure 3-4 Cumulative pop-in probability $F$ as a function of normalized maximum shear stress $\tau_{\text{max}}/\mu$ for the pop-in events in the Cr sample at varied loading rates.

3.2 Effect of loading rate and temperature

To perform the pop-in analysis with data obtained at different loading rates, cumulative probability of pop-in events $F$ as a function of normalized maximum shear stress $\tau_{\text{max}}/\mu$ is plotted in Figure 3-4. The maximum shear stress beneath the indenter, from the Hertzian contact theory, is

$$\tau_{\text{max}} = \frac{0.47}{\pi} \left( \frac{4E}{3R} \right)^{2/3} \mu^{1/3}$$

(3.1)

occurring approximately at a depth of 0.48 of the contact radius $a$. For the current Cr sample, $\tau_{\text{max}}$ is observed to range from $\mu/9$ to $\mu/7$, which is close to the expected theoretical strength ($\tau_{\text{th}} \sim \mu/2\pi$). Also noted in Figure 3-4 is the fact that the $F-(\tau_{\text{max}}/\mu)$ curves do not vary significantly under
different loading rates, indicating a weak rate dependence of the pop-in behavior in Cr. This insensitive rate dependence was also observed in bcc-Mo and fcc-Ni [31], although the opposite was reported in bcc-Ta [21], hcp-Mg [18] and fcc-Pt [16].

Figure 3-5 Pop-in load drop as the temperature increases in representative $P-h$ curves (a) and the cumulative pop-in probability $F$ as a function of critical load at various temperatures (b).
To investigate the temperature effect on the pop-in stress, tests were carried out at high temperatures. As shown in Figure 3-5(a), pop-in events are observed at all test temperatures and the cumulative pop-in probabilities of critical load for various temperatures are summarized in Figure 3-5(b). It is apparent in both figures that, when the ambient temperature increases the critical load that is necessary to trigger the pop-in decreases. This thermal softening has also been reported in several other materials, such as the fcc-Pt [16], a fcc-high entropy alloy FeCoCrNiMn [23], and GaN thin film [37].

3.3 Homogeneous nucleation versus heterogeneous nucleation

3.3.1 Activation volume and activation enthalpy for pop-in

It is generally recognized that incipient plasticity is caused by dislocation nucleation [32]. Although in situ TEM experiments have been effectively employed to investigate dislocation activities in the early stage of plastic deformation [59], it is still challenging to identify the dislocation nucleation process beneath the indenter using such technique. On the other hand, Schuh et al [16] cleverly combined the transition-state theory [76,77] and Weibull-type statistics [78] to develop a model [16,79] to determine the activation parameters for the pop-in events during nanoindentation. According to the model, the rate of pop-in events per unit volume can be described by a stress-biased, Arrhenius-type equation

\[ \dot{n} = \eta \exp\left(-\frac{\Delta G}{kT}\right) \]  

(3.2)

where $\Delta G = \varepsilon - \tau \nu$ is the Gibbs free energy for the pop-in event, $\varepsilon$ is the enthalpy for the pop-in event, $\tau$ is the applied stress over the activation volume $\nu$, and $\eta$ is the pre-exponential frequency
factor. The key significance of the equation is that an applied stress can effectively reduce the energy barrier via the activation volume term in a pop-in event.

Figure 3-6 Replotted Fig. 4 in a form of ln[-ln(1-F)] versus $\tau_{\text{max}}$ in order to deduce the activation volume by the linear least-squares fitting procedure

Activation volume physically reveals the type of defects and their roles during plastic deformation. It can be effectively deduced from fitting experimental data to the statistical model. According to the model[16], the cumulative distribution function of nanoindentation pop-in event, $F$, can be written in an analytical form as

$$F = 1 - \exp\left[-\frac{9KR\eta}{4E_{\text{P}}\alpha^6} \exp\left(-\frac{\varepsilon}{kT}\beta\right)\right]$$

(3.3)
where $\alpha = \frac{0.47}{\pi} \left( \frac{4E_r}{3R} \right)^{2/3} \frac{\nu}{kT}$, $\beta$ is a power-law function of $(\tau_0/kT)$, $K$ is a proportionality constant ($\sim \pi$), and $\dot{P}$ is the loading rate. Rearrange Eq. 3.3 we have

$$\ln[-\ln(1-F)] = \frac{\nu}{kT} \tau + \ln\left[ \frac{9KR\eta}{4E_r \dot{P} \alpha^6} \exp\left(-\frac{\varepsilon + \tau_0}{kT}\right)\beta \right] \quad (3.4)$$

Neglecting the weak dependence of the logarithmic term on $\tau$, this equation clearly reveals a linear correlation between $\ln[-\ln(1-F)]$ and $\tau$. In the present pop-in case, $\tau$ corresponds to the maximum shear stress underneath the indenter $\tau_{max}$. The linear correlation is shown in Figure 3-6, in which the activation volume $\upsilon$ can be readily deduced from the slope of the curve. The overlap of the data at different loading rates, particularly in the high-probability region, indicates, again, that the activation volume is insensitive to the loading rate.

Use the data sets measured (at four loading rates and four temperatures in the current study), the average activation volume for pop-ins in Cr is determined to be $0.308 \pm 0.015 \ b^3 \ (4.81 \ \text{Å}^3)$, which falls within a similar range for fcc-Pt ($0.5 \ b^3$) [16] and hcp-Mg ($0.2 \ b^3$) [18]. To the authors’ knowledge, no activation volume measurement is available from nanoindentation pop-in of bcc-metals. However, a small activation volume ($\sim 1 \ b^3$) for dislocation nucleation was also measured from compressive deformation of 200 nm-diameter single-crystal Mo nanopillars [3]. The activation volumes measured in this study is noted to be less than one atomic volume, suggesting the pop-in (or incipient plasticity) is probably caused by the motion of point-like defects such as vacancies, impurities, or their clusters.
Figure 3-7 The activation enthalpy can be obtained from the slope of the $P^{1/3} - T$ or $\tau_{\text{max}} - T$ curve according to Eq. (3.5).

Activation enthalpy is considered to be a measure of thermal barrier for a kinetic reaction (e.g., incipient plasticity). In nanoindentation experiments, it is correlated with the indentation parameters, and particularly the indentation load, through the following equation [16]

$$P^{1/3} = \gamma kT + \frac{\pi}{0.47} \left( \frac{3R}{4E_r} \right)^2 \varepsilon \frac{\varepsilon}{\nu}$$  \hspace{1cm} (3.5)

where $\varepsilon$ is the activation enthalpy, $\gamma$ is a complex but insignificant function, which incorporates a dependence on both $f$ and $P$. Thus, the activation enthalpy $\varepsilon$ can be determined from the intercept of the $y$-axis in a linear $P^{1/3} - T$ graph, and specifically, $\frac{\pi}{0.47} \left( \frac{3R}{4E_r} \right)^2 \varepsilon \frac{\varepsilon}{\nu}$; the graph is presented in
Figure 3-7. Substitute Eq. (3.1) into Eq. (3.5), a linear correlation between the maximum shear stress \( \tau_{\text{max}} \) and the temperature can be obtained as

\[
\tau_{\text{max}} = \frac{0.47}{\pi} \left( \frac{4E_k}{3R} \right)^{\frac{2}{3}} \gamma kT + \frac{\varepsilon}{\nu},
\]

(3.6)

This correlation is also included in Figure 3-7. Apply either Eq. (3.5) or (3.6) and take into account of the activation volume of 4.81 Å\(^3\), the activation enthalpy is determined to be 0.505 ± 0.034 eV. This value is noted to be less than the migration energy for vacancy (0.88 eV) [80] and the activation energies for the diffusion of interstitials (1.05 eV for N [81], 1.13 eV for C [82]) in Cr.

With the values of \( \varepsilon \) and \( \nu \) derived from the above procedures, frequency factor \( \eta \) can then be calculated from the intercept of each individual data set according to Eq. 4. An average attempt frequency \( \eta_{\text{ave}} = 5.045 \times 10^{22} \text{ s}^{-1} \text{ m}^{-3} \) is subsequently obtained from a logarithmic averaging procedure (i.e., \( \eta_{\text{ave}} = \exp\left(M^{-1} \sum_{i=1}^{M} \ln \eta_i\right) \)). With the frequency factor, the rate equation Eq. (3.2) for pop-in events per unit volume in Cr is now fully established. In the following, we discuss the possible nucleation mechanisms based on the above measurements.

### 3.3.2 Homogeneous dislocation nucleation mechanism

Homogeneous dislocation nucleation has been often invoked to explain the pop-in events during nanoindentation[26,83–85] and its associated atomistic simulations [44,45,86,87]. In this framework, the activation energy for the formation of a circular dislocation loop in perfect lattice is given by [34,88]
\[ \Delta G = 2\pi rW - \pi r^2 b(\tau_a - \tau_p) \]  \hspace{1cm} (3.7)

where \( r \) is the radius of dislocation loop, \( b \) is the Burgers vector, \( \tau_a \) is the applied shear stress on the slip plane where the dislocation loop forms (usually taken as a half of the maximum shear stress \( \tau_{\text{max}} \) underneath the indenter), \( \tau_p \approx 10^{-2} \mu \) [89] is the Peierls-Nabarro stress due to lattice disregistry, and \( W = \frac{\alpha \mu b^2}{4\pi(1-\nu)} \) is the mean energy per unit length of a circular dislocation loop [34], where \( \alpha = \frac{2-\nu}{2} \left[ \ln\left(\frac{4r}{r_0}\right) - 2 \right] \) or \( \ln\left(\frac{4r}{r_0}\right) - 1 \), depending on whether the Burgers vector parallel or normal to the circular dislocation loop, \( r_0 \) is the cutoff radius of the dislocation core, and \( \nu \) is the Poisson's ratio of the material studied.

Figure 3-8 Variation of formation energy \( \Delta G \) of dislocation loop with the loop radius \( r \) for the homogeneous nucleation mechanism under stress
Insert the parameters [72] for Cr ($\mu = 115$ GPa, $\nu = 0.21$, $b = 0.25$ nm, $r_0 \sim b$) and assume the dislocation line energy $W$ is an average value for the two types of dislocation, the formation energy of circular dislocation loop $\Delta G$ is plotted as a function of loop radius $r$ and is shown in Figure 3-8. $\Delta G$ is expected to reach a maximum value of 4.02 eV at a loop radius of $r = 4b$ (or 1 nm). This estimated $\Delta G$ value is obviously much higher than $0.505 \pm 0.034$ eV obtained in our current study.

It is particularly noted that the slightly negative $\Delta G$ value at $r \sim 0$ in Figure 3-8 is attributable to the inherent singularity of the dislocation line energy in the continuum mechanics framework [34], which can be overcome by combining the Peierls-Nabarro (P-N) model [87,90] in an analytical nonlinear elastic solution. However, even under the P-N framework, the activation energies of homogeneous dislocation nucleation in fcc metals are generally estimated to be high ($> 10$ eV) [87,91]. The activation energy for bcc-metals is anticipated to be higher than that for fcc-metals since the nucleation of partial dislocations is energetically favored in fcc, in contrast to bcc, where the nucleation of full dislocations is necessary [31].

### 3.3.3 Heterogeneous dislocation nucleation mechanism

Several recent simulations [47,48,50] indicated that the presence of point-like defects, such as vacancy, di-vacancy, tri-vacancy, and impurity, could produce significant effect on the pop-in stress. Although the exact atomic process for dislocation nucleation is still unclear, simulations usually favor a heterogeneous process. In the present study, considering the small magnitude of $\varepsilon$ and $\nu$ for the incipient plasticity, dislocation is probably nucleated heterogeneously from point-like defects. In such a case, the number of dislocation nucleation sites, in principle, cannot exceed
the number of point defects. The number of vacancy sites $n_o$ in the stressed zone underneath an indenter tip is estimated to be

$$n_o = \frac{\pi a^3}{a_o^3} \times 2 \text{ (atoms per unit cell)} \times c \text{ (vacancy concentration)}$$  \hspace{1cm} (3.8)$$

where $a_o$ is the lattice parameter, the stressed volume is scaled with the contact radius $a$, i.e., $Ka^3$, where $K \sim \pi$. In Eq. (3.8), the vacancy concentration $c$ in the sample prior to the indentation can be estimated by a critical temperature at which atoms become essentially immobile during cooling from 1523K. It is reasonable to assume that it is the critical temperature, $T_c$, at which the atomic diffusion distance is of the same dimension as the stressed zone, namely, $a \sim (Dt)^{1/2}$, where $D = D_0 \exp\left(-\frac{Q_v}{kT_c}\right)$ is the diffusion coefficient, $Q_v$ is the migration energy for vacancies (~0.88 eV for Cr [80]) and $t$ is the cooling time (~1800 s) for the sample. The pre-exponential coefficient $D_0$ in the equation is [92]

$$D_0 = \frac{d^2}{6} z v_0 \exp\left(\frac{S_M}{k}\right)$$  \hspace{1cm} (3.9)$$

where $d = 0.25$ nm is the atomic jump distance, $z = 8$ is the coordination number, and $v_0 = 5 \times 10^{13}$ s$^{-1}$ is the jump frequency for vacancies [93]. Generally, the migration entropy $S_M$ is small that the exponential term is near unity. The characteristic temperature $T_c$ is thus calculated to be 364 K. Given the vacancy formation enthalpy of $H_{vf} = 2$ eV for Cr [94], the equilibrium vacancy concentration at this temperature is about $2.08 \times 10^{-28}$, which further yields the number of vacancy sites in the stressed zone to be $1.94 \times 10^{-20}$ (Eq. (3.8)). Obviously, this value is too small to induce a notable effect on the nucleation of dislocations in Cr.
On the other hand, bcc-Cr is noted to have an open structure, thus is susceptible to interstitial contamination. Typical impurity contents in a “high-purity” Cr sample are carbon (10 ppm) and nitrogen (50 ppm) by weight [95] (GoodFellow supplies “high-purity” Cr foils at <100 ppm impurities [96]). As the first approximation, assuming carbon and nitrogen impurities remain as interstitials in the Cr lattice after annealing, there would be approximately 4,000 carbon and 17,000 nitrogen interstitial atoms in the stressed zone, which might be sufficient to contribute to pop-in events underneath the indenter. This appears to be consistent with the notion that some recent simulations [47,97] demonstrated that the presence of interstitials can significantly reduce the pressure (or stress) necessary to nucleate dislocation during indentation.

3.4 Summary

In the present study, the pop-in behavior (or incipient plasticity) of Cr was characterized as a function of temperature using nanoindentation method. The maximum shear stress required for the incipient plasticity was observed to be within 1/9 to 1/7 of the shear modulus, well corresponding to the theoretical strength of a dislocation-free material (\(\tau_{th} \sim \mu/2\pi\)). This value also appeared to be insensitive to the loading rates. Based on a statistical model, the activation volume and the activation energy for dislocation nucleation were determined to be 0.308 \(b^3\) and 0.505 eV, respectively. These activation parameters are much lower than those required for forming a dislocation loop homogeneously, which suggests dislocations are probably nucleated heterogeneously at point-like defects. Analysis of the point-defect contents indicates that interstitials rather than vacancies might be the main contributors to the nucleation processes.
Chapter 4. Effect of temperature and point defects on the pop-in in single crystal Au

4.1 Effect of tip radius, loading rate and temperature on the pop-in event in Au

4.1.1 Pop-in behavior in Au

In this study, a high-purity (> 99.999%) single crystal Au(100) from Goodfellow was used. The gold sample was mechanical polished to remove the scratches on the surface, and electropolished in the electrolyte solution (glycerol: hydrochloric acid = 2.5:1.5) in a two-electrode cell. Nanoindentation tests were performed on the sample using a Hysitron triboindenter (Hysitron Inc. Minneapolis, MN). Two Berkovich indenters were used, and the tip radii of these two indenters were calibrated to be 211 ± 12 nm and 759 ± 54 nm, respectively, from the indentation tests on single crystal tungsten. A maximum load of 0.6 mN was applied in the indentation tests, and a series of loading rates were used to study the effect of loading rate on the incipient plasticity. Indentation tests were also conducted at elevated temperatures (296 K, 365 K, 429 K, 465 K) at a constant loading rate of 2 mN/s. To carry out indentation tests at elevated temperatures, a commercial heating stage was installed and the displacement transducer was shielded from the hot specimen and stage with a cooled copper fixture [70]. Before indentation, the sample was heated to the set temperature and held for at least 30 min. The tip was, then, brought to touch the sample surface for another 30 min to achieve thermal equilibrium. A J-type thermocouple, which was in direct contact with the sample surface, was used to monitor and control the temperature of the specimen surface (± 0.2 K). At least 60 indentations were performed at each test temperature and loading rate. The distance between adjacent indents was set at 8 µm to minimize possible overlap of the indented zone. Thermal drift was estimated to be within 0.5 nm/s.
The onset of yielding during the indentation tests was identified by the pop-in event, which is usually observed in the loading part of the load-displacement curves. Typical pop-in events occurring underneath diamond indenters in Au(100) were shown in Figure 4-1. The elastic loading part can be described by Hertzian relation: $P = 4E_r R^{0.5} h^{1.5}/3$, where $R$ is the tip radius of the indenter, $h$ is the indentation depth and $E_r$ is the reduced elastic modulus given by $E_r = [(1-v^2)/E_{Diamond} + ((1-v^2)/E_{Au})^{-1}]$, where the Poisson's ratio $v$ is 0.44 for Au and 0.07 for diamond, and the elastic moduli are 78.5 GPa and 1141 GPa for Au and diamond, respectively.

The pop-in events in the indentation tests usually occur when the maximum shear stress $\tau_{\text{max}}$ underneath the indenter exceeds a critical value. According to the theory of contact mechanics, the maximum shear stress $\tau_{\text{max}}$ is given by

$$\tau_{\text{max}} = \frac{0.47}{\pi} \left(\frac{4E_r}{3R}\right)^{2/3} P^{1/3}$$ (4.1)
where \( P \) is the applied load. \( \tau_{\text{max}} \) is usually found at about half of the contact radius \( a \) underneath the indenter and the contact radius is \( a = \frac{3PR}{4E} \) for an indenter.

### 4.1.2 Tip radius effect

![Figure 4-2 Cumulative probability of pop-in in Au(100) at varied loading rate using two different indenters (R = 211 nm, 759 nm), respectively.](image)

Repeated indentation tests were performed on Au sample using two different tip radii (R = 211 nm, 759 nm), respectively. The cumulative probability for pop-in event was then counted, and plotted as a function of the maximum shear stress, which is calculated by Eq. (4.1) for each tip radius under the pop-in load, as shown in Figure 4-2. The pop-in shear stress for blunt tip 2.243 ± 0.268 GPa is significant lower than 3.418 ± 0.193 GPa for the sharp one. Since the shear modulus of Au is 26 GPa, the measured \( \tau_{\text{max}} \) is around \( G/12 \) and \( G/8 \), respectively, both of which are in the range of theoretical strength of crystalline materials (~\( G/5 \) - \( G/30 \)). It has been reported that the tail of \( F \) function deviate to lower load end as a result of pre-existing dislocation [61], but no such tail was observed in this study.
4.1.3 Loading rate effect

Varied loading rates (up to 100 times) were applied in the indentation tests for both two tip radii. The critical stress for pop-in was found to weakly depend on loading rate in Figure 4-2. This phenomena is similar to those reported in Ni [31], Mo [31] and Cr [28], but different from Pt [16] and Mg [18].

4.1.4 Temperature effect

Figure 4-3 As the temperature increases from 296 K to 465 K, the pop-in load drops in representative P-h curves (a) and the cumulative pop-in probability $F$ as a function of $\tau_{\text{max}}$ for pop-in shift to the low stress end (b)
To investigate the effect of temperature on the pop-in behavior in Au(100), indentation tests were performed at elevated temperatures (296 K, 365 K, 429 K, 465 K). As displayed in Figure 4-3(a), Pop-in events were observed at all test temperatures, and the pop-in load was found to decrease with the increasing of temperature. This decreasing trend can also be discerned from the shift of the cumulative pop-in probability to the low stress end as the temperature increases. This thermal softening has also been observed in other metallic materials, such as fcc-Pt [16], bcc-Cr [28], bcc-Ta [98] and fcc high entropy alloy FeCoCrNiMn [23].

4.1.5 Activation volume and activation energy for pop-in

It is generally accepted that the onset of yielding is caused by dislocation nucleation processes. Combining the transition-state theory and Weibull-type statistics [78], Mason et al [16] developed a statistical model to determine the activation parameters for pop-in events during nanoindentation. In the framework of that model, the rate of pop-in events per unit volume can be described by a stress-biased, Arrhenius-type equation

$$\dot{n} = \eta \exp\left(-\frac{\Delta G}{kT}\right)$$

where $\Delta G = \varepsilon - \tau \nu$ is the Gibbs free energy for the pop-in event, $\varepsilon$ is the enthalpy for the pop-in event, $\tau$ is the applied shear stress over the activation volume $\nu$, and $\eta$ is the pre-exponential frequency factor. Among these parameters above, the activation volume reveals the scale of defects that involves in the deformation process.

According to the model, the cumulative probability distribution for pop-in in nanoindentation, $F$, can be derived in an analytical form as
Figure 4-4  Replotted Fig.4-2 and Fig.4-3(b) in the form of $\ln(-\ln(1-F))$ versus $\tau_{\text{max}}$ in order to deduce the activation volume by the linear least-square fitting procedure.
\[ F = 1 - \exp\left[- \frac{9KR\eta}{4E,\dot{P}\alpha^6} \exp\left(- \frac{\varepsilon}{kT}\right) \beta \right] \]  
(4.3)

where \( \alpha = \frac{0.47}{\pi} \left( \frac{4E,\dot{P}}{3R} \right)^{2/3} \frac{\nu}{kT} \), \( \beta \) is a power-law function of \( \left( \frac{\nu}{kT} \right) \), \( K \sim \pi \) is a proportionality constant, and \( \dot{P} \) is the loading rate. Rearrange Eq.(4.3) in the form:

\[
\ln[-\ln(1-F)] = \frac{\nu}{kT}\tau + \ln\left[ \frac{9KR\eta}{4E,\dot{P}\alpha^6} \exp\left(- \frac{\varepsilon + \nu\tau}{kT}\right) \beta \right]
\]  
(4.4)

and a simple linear correlation between \( \ln[-\ln(1-F)] \) and \( \tau \) can be obtained, the weak dependence of the logarithmic term on \( \tau \) is neglected. \( \tau \) corresponds to the maximum shear stress underneath the tip in nanoindentation. The experimental pop-in data in Figure 4-2 and Figure 4-3(b) could be replotted in the form of \( \ln[-\ln(1-F)] \) versus \( \tau_{\text{max}} \) in Figure 4-4. Compared with the separated pop-in probability at different temperature in Figure 4-4(b), the data at different loading rate almost overlap with each other, which, again, indicates that the activation volume is insensitive to the loading rate. According to Eq.(4.4), the activation volume for each case is readily extracted from the slope of the curves, as listed in Table.4.1.

Table 4.1 Activation volume for pop-in event during nanoindentation tests on Au(100)

<table>
<thead>
<tr>
<th>Indenter</th>
<th>Loading rate (mN/s)</th>
<th>Temperature (K)</th>
<th>Activation volume (b^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = 759 nm</td>
<td>0.02</td>
<td>296</td>
<td>0.813</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>296</td>
<td>0.845</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>296</td>
<td>0.746</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>365</td>
<td>0.850</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>429</td>
<td>1.001</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>465</td>
<td>1.355</td>
</tr>
<tr>
<td>R = 211 nm</td>
<td>0.01</td>
<td>296</td>
<td>0.984</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>296</td>
<td>1.072</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>296</td>
<td>0.740</td>
</tr>
</tbody>
</table>
In Table 4.1, all the activation volumes for pop-in in Au(100) are found to be \( \sim 1 \text{ b}^3 \). Averaging the determined value from all the data sets in Table 4.1, and the activation volume could be calculated as \( 0.934 \pm 0.196 \text{ b}^3 \). This value falls within a similar range for fcc-Pt (0.5 b\(^3\)) [16], bcc-Cr (0.308 b\(^3\)) [28], and hcp-Mg(0.2 b\(^3\)) [18]. The activation volume in this study is close to one atomic volume (~0.707 b\(^3\) for fcc structure), indicating the pop-in may result from the activities of point defects such as vacancies, impurities and their clusters in metals.

Figure 4-5 The activation enthalpy can be extracted from the intercept of the linear plotting \( \tau_{\text{max}} - T \) according to Eq.(4.5)

In Eq. (4.2), the activation energy acts as an energy barrier for the pop-in event, more specifically, the dislocation nucleation process underneath the indenter. According to Schuh's model, it can be extracted from the linear correlation between \( \tau_{\text{max}} \) and temperature in the equation below:

\[
\tau_{\text{max}} = \frac{0.47}{\pi} \left( \frac{4E_i}{3R} \right)^{\frac{2}{3}} \gamma kT + \frac{\varepsilon}{\nu}
\]  

(4.5)
where $\gamma$ is a complex but unimportant function in terms of $f$ and $F$, and the activation enthalpy $\varepsilon$ is contained in the intercept of Eq.(4.5). Perform a linear fitting on the average value of $\tau_{\text{max}}$ as a function of temperature, the ratio $\varepsilon/\nu$ is determined to be about 3.03 GPa. Introduce the average activation volume we obtained earlier in this section, and we can determine the activation enthalpy $0.424 \pm 0.089$ eV for the pop-in events in the indentation tests on Au(100).

4.2 Effect of loading rate, temperature, tip radius and point defects by MD simulation

The molecular dynamics simulations with the embedded atom method (EAM) potentials for gold with point defects were performed to simulate the nanoindentation processes on Au(100) single crystal. The velocity form of the Verlet algorithm was implemented to evolve the system using LAMMPS code [67]. The EAM potentials for gold used in this study was developed by Grochola et al. [63]. The EAM potential for Au-Ag alloy [68] was also applied to model the effect of silver impurity in gold. The Au single crystal chosen for simulation is $20 \times 20 \times 10$ nm$^3$ in size, and contains about 255,000 atoms. The point defects (vacancies, impurities) were introduced randomly in the atomistic structures. The bottom face was fixed, while the top face was allowed to move. Periodical boundary condition was applied to the side faces. The simulation box is large enough to neglect the effect of indentation from neighboring simulation box.

In the simulation, a quadratic force was applied to model a rigid spherical indenter: $F(r) = -K(r-R)^2$, where $r$ is the distance from the atom to the center of the indenter, $R$ is the radius of the indenter, $K$ is the force constant. The force is repulsive and $F(r) = 0$ for $r > R$. In this study, $K = 16$ nN/Å, and two tip radii: 5, 10 nm was applied. The indentation process was performed along the Z-axis, and the motion of the indenter was prescribed at a constant velocity. The time step is 1
The beginning of each indentation simulation, a dynamic relaxation for 10 ps using isothermal-isobaric ensemble (NPT) was done following the energy minimization. During the indentation process, canonical ensemble (NVT) was applied to the system, and the velocity of atoms were rescaled to control the system temperature. In this study, simulations were performed at 1K, 300K, 400K, 500K, respectively, to study the effect of temperature on the dislocation nucleation process.

The atomistic configuration in the simulation was visualized by the free software OVITO[69]. The centrosymmetry parameter for each atom was calculated and used to pick up the atoms adjacent to defects [43]. The defects like vacancies, dislocations, stacking faults in the single crystal were displayed by hiding the atoms in the perfect lattice structure.

Molecular dynamics (MD) method was applied to study the indentation process on single crystal Au(100). The simulations were performed at different indentation velocities at elevated temperature. The effect of tip velocity and temperature on the dislocation nucleation processes were investigated, respectively. Two different tip radii were used to see possible indentation size effect. Point defects (vacancies and impurities) were introduced into Au(100) lattice in the simulation, and their effect on yielding were discussed. The dislocation nucleation process and relevant atomic motions underneath the indenter were visualized in the snapshots.

4.2.1 Onset of yielding and dislocation nucleation

The load-displacement responses of indentation on Au(100) by MD simulation were shown in Figure 4-6 are quite similar to the experimental data in Figure 4-1. At the beginning of the indentation process, elastic deformation occurs in the gold lattice. The mean pressure underneath the indenter was calculated using
Figure 4-6 Load-displacement curves and snapshots of atomistic simulation using MD method for the simulated indentation process at 1 K on perfect gold single crystal (a), (b) and gold crystalline containing vacancies (c),(d), respectively. Two different tip radii: R = 5 nm for (a),(c); R = 10 nm for (b), (d) were used in the simulation.
Figure 4-6 continued
Figure 4-6 continued
\[ p_m = \frac{P}{\pi Rh} \]  

(4.6)

where \( P \) is the applied load, \( R \) is the tip radius, \( h \) is the indentation depth. Since the elastic part of the \( P-h \) curve follows the Hertzian relation: \( P \propto h^{1.5} \), \( p_m \) increases with the increasing of indentation depth \( h \). When the \( p_m \) reach a critical value \( p_Y \), a deviation from elastic deformation could be found on the \( P-h \) curve and dislocation nucleation process was observed on the snapshot of atomistic view. Once the dislocation nucleates, the dislocation loop expands rapidly to the sample surface (snapshot b-4, d-4 in Figure 4-6), which corresponds to the onset plasticity of the material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tip radius R (nm)</th>
<th>Temperature T (K)</th>
<th>Yielding load ( P ) (eV/Å)</th>
<th>Yielding depth ( h ) (Å)</th>
<th>Yielding stress ( p_Y ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect Au(100)</td>
<td>5</td>
<td>1</td>
<td>56.2</td>
<td>4.2</td>
<td>13.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>38.0</td>
<td>3.4</td>
<td>11.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>35.6</td>
<td>3.2</td>
<td>11.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>29.9</td>
<td>3.0</td>
<td>10.22</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>158</td>
<td>6.6</td>
<td>12.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>112.5</td>
<td>5.3</td>
<td>10.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>102.2</td>
<td>5.2</td>
<td>10.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>102</td>
<td>5.1</td>
<td>10.19</td>
</tr>
<tr>
<td>Au(100) with vacancies</td>
<td>5</td>
<td>1</td>
<td>45.6</td>
<td>3.8</td>
<td>12.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>34.1</td>
<td>3.3</td>
<td>10.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>31.6</td>
<td>3.1</td>
<td>10.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>25.1</td>
<td>2.7</td>
<td>9.48</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>140</td>
<td>6.1</td>
<td>11.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>93.3</td>
<td>4.8</td>
<td>9.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>78.6</td>
<td>4.4</td>
<td>9.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>66</td>
<td>4.0</td>
<td>8.48</td>
</tr>
</tbody>
</table>
The yielding stresses corresponding to dislocation nucleation under various conditions were calculated from Eq. (4.6), as listed in Table 4.2. It should be noted that the determined $p_Y$ ranges from 9.85 to 11.38 GPa at 300 K, or 1/8~1/7 of the elastic modulus of gold ($E = 79$ GPa), indicating that a high level of stress up to theoretical strength of material is required for dislocation nucleation process. Another thing should be mentioned is that the yielding stress for 5 nm tip radius is higher than that for 10 nm tip radius, similar tip radius effect has been observed in previous experiments and reported in simulation work on Ni [48].

4.2.2 Indentation velocity effect

Varied indentation velocities (5 m/s, 0.5 m/s, 0.05 m/s) were applied in the simulation to investigate the effect of indentation velocity on the incipient plasticity in Au(100). The critical load for dislocation nucleation was found to slightly increase with the indenter velocity in perfect Au(100) at 1 K and 300 K, as shown in Figure 4-7(a) and (c), respectively. However, this velocity dependence was also found to become insignificant in Au(100) with vacancies, as displayed in Figure 4-7(b) and (d), respectively. It seems that the dislocation nucleation process depends weakly on the indentation velocity in perfect lattice at 1 K, and the vacancy defects in the material probably eliminate this velocity effect at higher temperature. The simulation results agree with our previous experimental data.
Figure 4-7 Load-displacement curves for the simulated indentation process on perfect Au(100) ((a), (c)) and Au(100) with vacancies ((b),(d)) using different indentation velocities (5 m/s, 0.5 m/s, 0.05 m/s) at 1 K ((a),(b)) and 300 K ((c),(d))
Figure 4.7 continued

(a) Perfect Au(100)
- $T = 1 \text{ K}$
- $R = 5 \text{ nm}$

(b) Au(100) with vacancies
- $T = 1 \text{ K}$
- $R = 5 \text{ nm}$
Figure 4-7 continued

(c) Load eV/Å vs. Depth (Å) for Perfect Au(100) at different velocities: 5 m/s, 0.5 m/s, and 0.05 m/s. Conditions: T = 300 K, R = 5 nm.

(d) Load eV/Å vs. Depth (Å) for Au(100) with vacancies at different velocities: 5 m/s, 0.5 m/s, and 0.05 m/s. Conditions: T = 300 K, R = 5 nm.
4.2.3 Temperature effect

The indentation process at a series of elevated temperatures (300 K, 400 K, 500 K) were also modeled to study the effect of temperature on the incipient plasticity of gold. The P-h curves for the simulated indentation at different temperatures were plotted in Figure 4-8. It was found that the elastic part of P-h curves for different temperatures almost overlap, and these curves separate from each other beyond the yielding point. The yielding point on each P-h curve was identified by

Figure 4-8 Load-displacement curves for the simulated indentation tests on (a) the perfect Au(100), and (b) Au(100) with vacancies at elevated temperatures (1 K, 300 K, 400 K, 500 K)
the atomistic configuration underneath the indenters, as shown in Figure 4-9. In these snapshots, some blue atoms show up in the lattice, because the atoms vibrate in the lattice at higher temperature. A defect embryo grows out in the highly stress zone underneath the indenter when the load reaches a critical value (e-2 in Figure 4-9). This critical load is much lower than the yielding load (e-3 in Figure 4-9), at which the dislocation nucleates from the embryo and expands up to the top surface at the yielding point. The defect embryo arises because the exchange rate of atoms increases as a result of the stress gradient $\nabla \sigma$ underneath the indenter. In Figure 4-8, the yielding load is found to drop with the increasing of temperature, and a similar decreasing trend in critical stress can also be found in Table 4.2. This phenomenon occurs probably because the lattice vibrates more intensive at higher temperature. Under this circumstance, the defect embryo forms earlier with the assistance of stress field underneath the indenter, and finally results in the drop of the yielding load/stress as the temperature increases.

![Figure 4-9 Load-displacement curve and atomic configuration before and after yielding point for the simulated indentation process on perfect Au(100) at 300 K](image)

Figure 4-9 Load-displacement curve and atomic configuration before and after yielding point for the simulated indentation process on perfect Au(100) at 300 K
4.2.4 Effect of vacancies

Figure 4-10 Load-displacement curves and snapshots of atomistic simulation using MD method for the simulated indentation process on Au(100) with vacancies at 300 K

The vacancies are inevitable found in materials, and they are introduced into the Au(100) lattice during the simulation to see their effect on the yielding of gold. In total, ten atoms were removed randomly underneath the indenter in the simulation box. The results of simulated indentation on Au(100) with vacancies at temperatures and varied indentation velocities were shown in Figure 4-7 and Figure 4-8, respectively. Under all the circumstances, the yielding loads of the Au(100) with vacancies are lower than those of perfect gold lattice. The vacancies in the lattice were found to act as the preferred sites for dislocation nucleation at 1 K, as shown in the snapshots in Figure 4-6c and d. In the snapshots in Figure 4-10 when the indentation on Au(100) with vacancies at higher temperature was simulated, an vacancy was observed to diffuse to the defect embryo in the highly stressed zone underneath the indenter, and dislocation nucleate at the embryo thereafter. The preference of dislocation nucleation at vacancies cooperates with the thermal vibration behavior of crystalline lattice to facilitate incipient plasticity. The critical yielding load in this case is lower than that when either raising the temperature or adding vacancies.
4.2.5 Effect of impurities

In this study, Ag atoms were added into the Au(100) lattice to investigate the effect of impurities on the dislocation nucleation process. Typical load-displacement curves and snapshots for the simulated indentation processes on impure Au(100) at 1 K and 300K were shown in Figure 4-11. From the snapshots, dislocation is found to nucleate homogeneously in lattice at 1 K or from...
the defect embryo at 300 K, however, in either case, Ag impurities seem not to involve in the dislocation nucleation. No significant drop of yielding load was found in the impure Au(100), compared with the perfect pure Au(100). It may indicate the impurities may not affect dislocation nucleation processes in fcc alloys.

4.2.6 Activation volume and Activation energy from MD simulation

The onset of yielding simulated in the small crystalline lattice system by MD method could also be described by a rate equation similar to Eq.(4.2):

\[ \nu = Nv_0 \exp\left(-\frac{Q(T, \tau)}{k_BT}\right) \] (4.7)

where \( v_0 \) is the attempt jump frequency, \( N \) is the number of equivalent nucleation sites in the lattice, \( Q(T, \tau) \) is the activation energy for dislocation nucleation which depends on temperature \( T \) and shear stress \( \tau \). At a given temperature \( T \), the activation energy \( Q \) can be approximated by a linear relation: \( Q(\tau) = Q^* - \pi \Omega \), where \( Q^* \) corresponds to the nucleation barrier in the absence of applied stress. Ting Zhu et al.[99] has derived an expression for the nucleation stress at constant temperature and strain rate in an axial loading test. This stress expression has been applied to extract the activation volume and activation energy for dislocation nucleation from the nucleation stresses, which were determined in single crystal Cu under the uniaxial loading by MD simulation at different temperatures.

In the case of indentation deformation, a similar expression could be derived. The shear stress underneath the indenter is given by \( \tau = 0.47 \frac{P_m}{\pi Rh} \). For a displacement controlled indentation test, the indentation depth \( h = kt \), where \( k \) is velocity of indenter motion, \( t \) is the loading
time. Plug in the Hertzian relation $P = 4E_rR^{0.5}h^{1.5}/3$, and a relationship between shear stress $\tau$ and time $t$ could be written as $\tau = \frac{1.88E_r\sqrt{kt}}{3\pi\sqrt{R}}$ or $t = \frac{9\pi^2R}{3.53E_r^2k}\tau^2$. Let constant $C = \frac{9\pi^2R}{3.53E_r^2k}$, we can have $t = C\tau^2$.

Define $f$ to be the survival probability of an indentation (no dislocation nucleation occurs in this case), $\frac{dF(t)}{dt} = -vF(t)$, and replace the time $t$ by shear stress $\tau$, this equation becomes

$$\frac{dF(C\tau^2)}{d\tau} = -2C\tau vF(C\tau^2)$$

(4.8)

As $\tau$ increases, $F(\tau)$ decreases and $v(\tau)$ increases, giving rise to a maximum of $dF(\tau)/d\tau$. The most probable nucleation stress is defined by the peak of $dF(\tau)/d\tau$, thus $\frac{d^2F(\tau)}{d\tau^2} = 0$. Let us differentiate Eq. (4.8) with respect to $\tau$, and we can find

$$\frac{d^2F}{d\tau^2} = -2C(vF + \tau F \frac{dv}{d\tau}) - 2C\tau^2v^2F = 0$$

(4.9)

From Eq.(4.7), we can find: $\frac{dv}{d\tau} = -\frac{v}{k_BT} \frac{dQ}{dt}$. For a given temperature, the activation volume is defined as $\Omega(\tau) = -\left(\frac{\partial Q}{\partial \tau}\right)_T$. Then Eq. (4.9) could be rewritten and simplified to be

$$\frac{k_BT + \tau \Omega}{k_BT} = 2C\tau v$$. Since $\tau \Omega \gg k_BT$, thus $k_BT$ is negligible compared with $\tau \Omega$, the above relation could be further reduced to be $\frac{\Omega}{k_BT} = 2C\tau v$. Plug this relation into Eq.(4.7), we can obtain
an expression for the nucleation stress when the indentation is performed at constant temperature and indentation velocity

\[
\frac{Q(\tau, T)}{k_B T} = \ln\left(\frac{2k_B T N \nu_0}{\pi \Omega}\right)
\]  \hspace{1cm} (4.10)

If we recollect the linear dependence of activation energy on stress: \(Q(\sigma) = Q^* - \tau \Omega\), the shear stress for dislocation nucleation could be written as

\[
\tau = \frac{Q^*}{\Omega} - \frac{k_B T}{\Omega} \ln\left[\frac{k_B T N \nu_0}{\tau \Omega/(2t)}\right]
\]  \hspace{1cm} (4.11)

In Eq.(4.11), the first term \(Q^*/\Omega\) is the athermal nucleation shear stress causing dislocation nucleation in the linear model of stress-dependent activation energy. \(k_B T/\Omega\) in the second term acts as a stress unit. In the logarithmic term, \(k_B T N \nu_0\) corresponds to the rate of energy exchange between candidate nucleation sites and the thermal bath, and \(\frac{\tau \Omega}{2t}\) stands for the rate of activation energy reduced by mechanical work. The ratio of these two terms indicates the competition of thermal and mechanical effects in reducing the stress level for the nucleation event at limited temperature during indentation.

The nucleation shear stress \(\tau_Y\) at various temperatures in previous MD simulation could be calculated from the yielding stress \(p_Y\), according to \(\tau_Y = 0.47 p_Y\). The critical stress calculated at 1 K was taken as the athermal nucleation stress \(Q^*/\Omega\). The indentation time \(t\) is about 70 ps and 120 ps for small tip radius (\(R = 5\) nm) and larger tip radius (\(R = 10\) nm), respectively. The attempt frequency in crystalline lattice can be described by \(\nu_0 = \frac{1}{2\pi} \sqrt{\frac{C}{m}}\), where \(C\) is assumed to be a
constant for fcc metals, and m is the mass of a atom. The attempt frequency in gold $\nu_0 = 1.78 \times 10^{11}$ s$^{-1}$ is estimated from the frequency value for Cu: $3.14 \times 10^{11}$ s$^{-1}$ [99]. The number of potential nucleation sites N in perfect gold lattice could be estimated from the volume of stressed volume underneath the indenter:

$$N = \frac{1}{2} \times \frac{4}{3} \pi a^3 \times \frac{4}{a_0^3}$$

(4.12)

where $a$ is the contact radius, $a_0$ is the lattice parameter of fcc-Au. The N value for the lattice with vacancies should be the number of atoms neighboring to the vacancies, thus 120 in this study. Use these simulation parameters above, the activation volume for dislocation nucleation at different temperatures could be calculated from Eq. (4.11) and listed in Table 4.3.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tip radius (nm)</th>
<th>Temperature (K)</th>
<th>Activation volume ($b^3$)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfect Au(100)</td>
<td>5</td>
<td>300</td>
<td>0.91</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>1.17</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>1.05</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>300</td>
<td>1.93</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>1.75</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>2.31</td>
<td>1.98</td>
</tr>
<tr>
<td>Au(100) with vacancies</td>
<td>5</td>
<td>300</td>
<td>0.97</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>1.22</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.98</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>300</td>
<td>1.05</td>
<td>0.90</td>
</tr>
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<td></td>
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<td>400</td>
<td>1.07</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>1.12</td>
<td>0.96</td>
</tr>
<tr>
<td>Au(100) with impurities</td>
<td>5</td>
<td>300</td>
<td>1.01</td>
<td>0.95</td>
</tr>
</tbody>
</table>
It is found that all the calculated activation volumes from MD simulation are around 1~2 $b^3$, which agree well with the activation volume for homogeneous dislocation nucleation in single crystal copper under uniaxial loading (0.5 ~ 2 $b^3$) [100], and fall in the range of the activation volume for heterogeneous dislocation nucleation at surface (1 ~ 10 $b^3$) [99]. It is not surprising to find the activation volumes for perfect gold are similar to those for gold with vacancies. The atomistic snapshots in Figure 4-10 have shown that dislocation actually nucleates from the defect embryo at higher temperature (T >> 0 K), no matter there exist point defects nearby or not. On the other hand, the atoms neighboring to a vacancy are weaker in bonding compare with those in perfect lattice, the involvement of vacancies is likely to facilitate the nucleation process and reduce the yielding load. The diffusion of vacancy to defect embryo and load drop have been observed in Figure 4-10.

According to the first term in Eq.(4.11), The activation energy for dislocation nucleation in MD simulation could be estimated by $Q^* \sim \tau \Omega$. Use the activation volume and shear stress obtained before, the activation energy $Q^*$ was calculated and as listed in Table 4.3. All values of $Q^*$ are found to range around 1~2 eV in good agreement with $h_m = 0.83$~0.89 eV the activation enthalpy for vacancy diffusion in Au [101]. It is also noted that $Q^*$ for perfect lattice is slightly higher than that for defective lattice, indicating more energy is required to nucleate the dislocation without assistance of vacancies. Generally, similar values of activation parameters indicate the similar physical processes of dislocation nucleation in the lattice with or without point defects.

Though the results from simulation and experiments agree well with each other, it should be noted that orders of discrepancy in tip radius (5 nm vs 759 nm) and sample scale (10⁴ atoms vs 10⁸ atoms) between them may result in different physical processes. The length of the first pop-in in indentation experiments was found to range from several to tens of nm, which correlates to
multiple dislocations bursting out in one pop-in event. This phenomenon doesn't agree with the nucleation process of single dislocation loop in simulation. Since the indentation machine technically is incapable to distinguish the event of one single dislocation, which is easy to be overwhelmed by the noise. The dislocation activities have been observed by in situ TEM prior to the first displacement excursion during indentation test [59,102]. Nonetheless, the out-burst of multiple dislocations may nucleate from the heterogeneous sites produced by the activities of pre-existing defects (e.g. vacancies, dislocations). It is no wonder to find the calculated activation volumes in Table 4.3 are also very close to our previous determined value from experimental data.

4.3 Summary

Instrumented indentation tests and molecular dynamics simulations have been performed to study the coupling effect of temperature, point defects on the onset of yielding of fcc-Au single crystal. Effect of tip radius and loading rate/indentation velocity were also evaluated and discussed, respectively. Several conclusions can be drawn from the results:

1. Pop-in events were observed in single crystal gold during the indentation tests, and the critical shear stress was found to increase with the decrease of tip radius we used. The critical stress for pop-in is insensitive to the loading rate, while decreases significantly with the increasing temperature.

2. Using a statistical analytical model, the activation volume and activation energy for pop-in in Au were determined to be about $1 \, \text{b}^3$ and 0.424 eV, respectively. These small-value parameters indicate the pop-ins may arise from a small-scale event like nucleation of dislocation at a point defect.
3. The indentation processes were simulated in Au(100) using MD method. Nucleation processes of dislocations occurred underneath the indenter in the lattice, which corresponds to the plastic response on the load-displacement curve. The onset of plasticity was facilitated either by the introduction of vacancies in lattice or an increase in temperature. However, the indentation velocity and Ag impurities have little effect on the pop-in in Au. The simulation generally agrees with the experimental results.

4. Using an atomistic model, the activation volume and activation energy for pop-in in MD simulation were extracted to be $1 \sim 2 \text{ b}^3$ and $1 \sim 2 \text{ eV}$, respectively. Both of them were close to the experimental results. No significant difference between the dislocation nucleation process in perfect lattice and in defective lattice at elevated temperature was observed, because the thermal vibration of lattice is also a kind of lattice defect.
Chapter 5. Effect of tip radius on the pop-in behavior in Cr

5.1 Pop-in event in Cr using different tip radii

The Cr sample was sliced from a coarse-grained Cr bulk prepared by arc melting method (purity > 99.99%). The surface of the Cr sample was ground using 1200 and 2400-grit SiC, and then mechanically polished using alumina of 0.06 μm in grit size. To reduce existing dislocations and minimize possible surface damage resulting from the mechanical polish, the Cr specimen was initially sealed in a fused silica tube filled with pure argon gas and, then, annealed at 1250 °C for 4 hr [66]. As the final procedure, the annealed Cr was additionally electropolished in a solution (H₃PO₄:H₂SO₄ = 4:1) to remove a possible oxide layer resulting from annealing. The sample was immediately tested under nanoindentation. The grain size was determined to be about 0.5 mm by optical observation.

Nanoindentation tests were performed using a Triboindenter (Hysitron Inc. Minneapolis, MN) equipped with a Berkovich or cube corner diamond indenter. Single-crystal tungsten was used for calibration and the tip radii of the indenters used in the current study were determined to be 60.3±6.7 nm, 80.3±10.7 nm, 211±12 nm, 303±25 nm, 601±20 nm and 759±54 nm. At least 50 indentation tests were performed with each indenter. For valid comparison, all the indentation tests were conducted on the same Cr grain at the loading rate of 2 mN/s.

Typical load-displacement curves showing the pop-in event obtained from the indentation tests on Cr using the Berkovich indenters with the tip radii, R, of 211 and 759 nm, and cube corner indenters (R = 60 nm and 80 nm) are shown in Figure 5-1. The elastic loading part of the P-h curve
is well described by the Hertzian relation [103]: \( P = 4E_r R^{0.5} h^{1.5} / 3 \), where \( R \) is the tip radius of the indenter, \( h \) is the indentation depth, and \( E_r \) is the reduced elastic modulus given by \( E_r = [(1-\nu^2)/E_{\text{Diamond}} + (1-\nu^2)/E_{\text{Cr}}]^{-1} \), where the Poisson's ratio \( \nu \) is 0.21 for Cr and 0.07 for diamond, and the elastic moduli are 279 and 1141 GPa for Cr [74] and diamond [73], respectively. Due to a smaller tip radius of the cubic corner indenter, pop-in occurs at a much shallower depth (<10 nm).

Due to a smaller tip radius of the cubic corner indenter, pop-in occurs at a much shallower depth (<10 nm).

Figure 5-1 Typical load-displacement curves from nanoindentation tests on annealed Cr using indenters with various tip radii. The elastic part of loading curves is well predicted by the Hertzian relation.

In general, these pop-in events are triggered when the maximum shear stress \( \tau_{\text{max}} \) underneath the indenter exceeds a critical value. According to contact mechanics [103], \( \tau_{\text{max}} \) occurs at about half of the contact radius \( a \) and is given by \( \tau_{\text{max}} = 0.47[16E_r^2 P/(9\pi^3 R^2)]^{1/3} \), where \( P \) is the applied load, and \( R \) is the tip radius of the indenter. For an indenter, the contact radius is \( a = (3PR/4E_r)^{1/3} \).
5.2 Nucleation and activation processes of dislocation

According to the statistical analysis for a dislocation-free crystal [16], pop-in events is caused by the nucleation of dislocation assisted by stress, and the rate at which the pop-in events occur per material volume is given by $\dot{n} = \eta \exp[-(\varepsilon - \tau \nu)/kT]$, where $\varepsilon$ is the activation barrier for the pop-in event, $\tau$ is the applied stress over the activation volume $\nu$, and $\eta$ is the pre-exponential frequency factor. This must be integrated over the volume of stressed material underneath each indenter ($\Omega$) to give the displacement burst rate. As a good approximation, the maximum shear stress $\tau_{\text{max}}$ is assumed to be the stress bias $\tau$, and the sampling volume $\Omega$ is scaled with $a^3$, specifically $\Omega = 3KPR/4E_r \approx 3\pi PR/4E_r$. Thus, the global pop-in rate $\dot{N}$ over the stressed volume is expressed as

$$\dot{N} = \eta \int_{\Omega} \exp\left(-\frac{\varepsilon - \tau \nu}{kT}\right) d\Omega = \eta \cdot \frac{3\pi P R}{4E_r} \exp\left(-\frac{\varepsilon - \tau_{\text{max}} \nu}{kT}\right)$$ (5.1)

Following the Weibull statistics[78], the cumulative probability function $F$ obeys the equation: $dF/dt = (1 - F) \dot{N}(t)$ or in its integral form: $\ln[1 - F(t)] = -\int_{0}^{t} \dot{N}(t')dt'$. In the current study, the analytical form of $F(P)$ could be derived by combining Eq. (5.1) with the Weibull statistical equation:

$$F_{\text{nucleation}}(P) = 1 - \exp\left[-\frac{9\pi R \eta}{4E_r P a^6} \exp\left(-\frac{\varepsilon}{kT}\right)\beta\right]$$ (5.2)

where $\alpha = 0.47[16E_r^2/(9\pi^3 R^2)]^{1/3} \nu/kT$ and $\beta$ is a complex but weak function [16] of load $P$. 
Figure 5-2 The cumulative probability of pop-in events underneath indentation with various tip radii. Solid lines are predictions based on (a) heterogeneous dislocation nucleation model [16] and (b) a combined model of dislocation nucleation and activation processes.

The cumulative probability of pop-in $F$ is shown in Figure 5-2(a) as a function of applied load $P$ at various indenter tip radii. Each $F$ curve is noted to exhibit a “tail” toward the low-load side and the tail becomes more pronounced when a blunter tip is used. The tail is the region where the pop-in occurs at a lower pop-in load (or stress). Using the activation volume $v$ (0.287 b$^3$) and
the activation energy (0.505 eV) determined previously for the pop-in events in a coarse-grained Cr [28], the cumulative probability of pop-in $F$ can be calculated using the theoretical model [16] and directly compared with the experimental data. It is apparent in Figure 5-2(a) that the model predictions generally fit the data well, except a gradual deviation in the tail region. The deviation becomes more significant when the tip radius is larger.

Schuh’s model [16] was based on the assumption that a material had no prior defects, in particular, dislocations. On the other hand, Morris et al. [40] proposed a statistical model to describe the stochastic behavior of nanoindentation pop-in in single crystals. However, his model was based on the fact that there were preexisting defects, such as Frank-Read sources; thus, heterogeneous dislocation nucleation was not necessary for the onset of plasticity. In this case, pop-in occurs when at least one defect is activated in the high-stressed volume of material beneath the indenter. The probability $q$ for the absence of the pop-in in the highly stressed region is predicted as $q = \exp[-\rho_{\text{defect}}V(\tau > \tau_{\text{pop-in}})]$, where $\rho_{\text{defect}}$ is the density of pre-existing defect in the material, and $\tau_{\text{pop-in}}$ is the assumed stress required to activate a source at the defects. $\tau_{\text{pop-in}}$ is assumed to be single-valued, for mathematical convenience, though more generally one would expect, which would depend on specific defect structure and orientation. Phani et al. [42] demonstrated that a similar model with orientation effects had only a minor effect on pop-in distribution. $V(\tau > \tau_{\text{pop-in}})$ is the high-stressed volume where the local shear stress $\tau > \tau_{\text{pop-in}}$ in the stress field, in which the maximum shear stress $\tau_{\text{max}}$ beneath the indenter is determined by the tip radius $R$ and applied load. As the applied load $P$ increases, a higher $\tau_{\text{max}}$ is attained in the stressed zone and the stressed volume $V$ expands rapidly.
The stressed volume $V$ underneath an indenter and its variation with $\tau_{\text{max}}/\tau_{\text{pop-in}}$ according to the Hertzian theory

The functional relationship between $V$ and $\tau_{\text{max}}/\tau_{\text{pop-in}}$ could be fitted in a power-law as

$$V/a^3 = -2.105 \times 10^{-4} x^3 + 0.128 x^2 + 5.695 x$$

where $x = (\tau_{\text{max}}/\tau_{\text{pop-in}}) - 1$, as shown in Figure 5-3. It is noted that the $V$ approaches zero as $x$ approaches zero. This power-law relation is valid within the range of material strength, namely, $\tau_{\text{max}} < \mu/2\pi$.

The cumulative probability for pop-in in Morris’ model [40] is, therefore,

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

For a material with fixed $\rho_{\text{defect}}$ and $\tau_{\text{pop-in}}$, the $F$ function can be derived for any pairs of indenter tip radius $R$ and the maximum shear stress $\tau_{\text{max}}$ below the indenter. Morris’s model has been successfully applied to describe the pop-in behavior in single crystal Mo for blunt indenters ($R > \ldots$
3.75 \mu m), but showed large deviation for sharper indenters. When the tip radius decreases below 1.5 \mu m, the cumulative pop-in probability begins to converge to the limit of theoretical strength [40], suggesting a transition from dislocation activation to dislocation nucleation. It appears, therefore, a complete description of the cumulative pop-in probability over a broad range of tip radii should include both Schuh’s and Morris’ models. In the following, we present a model that combines these two models.

The survival probability for dislocation nucleation mechanism during indentation is

\[
\exp\left\{ -9KR\eta \exp\left[-\varepsilon/(kT)\right] \beta /\left(4E,\dot{\rho}\alpha^6\right) \right\} \quad \text{(Eq. (5.2))}
\]

When this combines with the survival probability \( q \) for the activation of pre-existing defect, it leads to the total survival probability as

\[
\exp\left\{ -\rho_{\text{defect}} V -9\pi R\eta \exp\left[-\varepsilon/(kT)\right] \beta /\left(4E,\dot{\rho}\alpha^6\right) \right\} \quad \text{during nanoindentation. Consequently, the total cumulative probability of pop-in is modified as}
\]

\[
F_{\text{total}} = 1 - \exp\left\{ -\rho_{\text{defect}} V -\frac{9\pi R\eta}{4E,\dot{\rho}\alpha^6} \exp\left(-\frac{\varepsilon}{kT}\right) \beta \right\} \quad \text{(5.5)}
\]

The modified model can apparently describe quite well the cumulative probability of pop-in at various tip radii, as shown in Figure 5-2(b). In this study, the pre-existing defects are considered pinned in the lattice, and a critical shear stress \( \tau_{\text{pop-in}} \) is required for activation. For the modeling, the theoretical shear stress for the obstacle-controlled dislocation glide in single-crystal Cr (0.2 GPa [89,95,104]) was used for the yield strength. A defect density of \( \rho = 1-1.5 \times 10^{17} \text{ m}^{-3} \) is selected for the fitting, indicating that defect-driven pop-in will be important when the highly stressed region under the indenter has a volume of \( \sim 1/\rho \) (\( \sim 8 \mu m^3 \)). This density corresponds to a mean free distance of 2 \mu m for defects. If we assume an equally spaced cubic array of dislocation
lines, the dislocation density would be about $10^{11}$ m$^{-2}$, which is a typical dislocation density in a fully annealed metal [105].

Assume that the mean value of $\tau_{\text{max}}$ is $\tau_{1/2}$, namely, the value of maximum shear stress when $F$ function is 0.5, and insert $\alpha$, then for each radius, we have the following relationship between $\tau_{1/2}$ and the tip radius $R$:

$$
\gamma \exp(-\frac{\varepsilon}{kT}) \beta R^5 + \rho_{\text{defect}} V(\tau > \tau_{\text{pop-in}}) = \ln 2 \quad (5.6)
$$

where $\gamma = 264.2 \pi^2 \eta (kT)^6 / (E_s \dot{\gamma} u^6)$.

Figure 5-4 Comparison of experimental data with the prediction of modified model in the $\tau_{1/2}$-R relationship (Eq. (6))
From the experimental measurements, $\tau_{1/2}$ is plotted as a function of the indenter tip radius, as shown in Figure 5-4. Evidently, $\tau_{1/2}$ decreases with increasing tip radius. To carry out the model prediction, the average activation parameters ($\nu = 0.287$ b$^3$, $\varepsilon = 0.505$ eV, $\eta_{ave} = 8.9 \times 10^{23}$ s$^{-1}$m$^{-3}$) and material parameters for Cr ($b = 0.25$ nm, $E_r = 232.61$ GPa, $\rho = 1.5 \times 10^{17}$ m$^{-3}$) are inserted into Eq. (5.6). Evidently, the model prediction agrees well with the decreasing trend of critical shear stress with the tip radius as shown in Figure 5-4. The strength for the sharp indenter ($R = 60$ nm) begins to deviate from the model prediction, because the upper bound of the theoretical strength is reached. On the other hand, when the tip radius is larger than 0.6 ~ 0.8 $\mu$m, the yielding strength begins to drop faster as a result of possible presence of pre-existing defect in the stressed volume. For the blunt tip ($R > 1$ $\mu$m), the predicted pop-in stress drops with tip radius following a power law of $\tau \sim R^{-2/3}$, which is consistent with the results reported in single-crystal Mo(100) [39].

5.3 Summary

In summary, the stress required for incipient plasticity in Cr with a broad range of tip radii (from 60 nm to 759 nm) was determined. The pop-in stress was found to increase with the reduction of tip radius and saturated at a tip radius less than 80 nm. The cumulative probability of pop-in measured from using a sharp tip ($R < 300$ nm) can be well described by model based on the assumption of testing a perfect crystal, originally proposed by Schuh et al [16]. However, data from using a blunt tip ($R > 300$ nm) appear to fit better with a model assuming the test sample has preexisting dislocations, proposed by Morris et al [40]. We demonstrated that a modified model, specifically, a combination of these two models, can predict the pop-in behavior in Cr over the entire range of tip radii. This indicates a mechanistic transition from a dislocation nucleation to pre-existing defect activation when the tip radius increases. The transition is attributable to the
fact that when the stressed volume underneath an indenter increases, the probability to encounter a dislocation also increases.
Chapter 6.  Effect of the tip radius on elastic and plastic responses in HEA and Nickel

6.1 Microstructure of NiFeCrCoMn and indentation method

The microstructure of the annealed alloy was observed by the optical microscope and SEM (Figure 6-1), and the grain size was found to be ~ 60 - 120 μm. Previous studies [23,106] have shown a single FCC-structured phase in the NiFeCrCoMn alloy with lattice parameter of about 3.61 Å. For the purpose of comparison, a single crystal Ni sample was also tested in this study. The Ni sample was prepared using a directional floating zone melting technique [27], ground and electropolished in a solution of 40% sulfuric acid and water for the indentation tests.

Figure 6-1 Microstructure of the annealed NiFeCrCoMn alloy
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. A typical indentation pattern was shown in Figure 6-2. The spacing between the indents ensures the plastic zone underneath the indenter doesn’t overlap with each other. During each indentation test, the loading rate 400 μN/s was applied to avoid loading rate effect, and the maximum load was held for 1s before unloading. Indentation tests were also performed with the maximum load of 10 mN and a 20 μm interval to investigate the global plasticity in the samples, and a Berkovich indenter (R = 255 nm) was used. The area function of this Berkovich indenter was carefully calibrated on fused silica.

An atomic force microscope MFP-3D™ (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. The residual indented marks from a blunt cube corner indenter (R = 80 nm) and a blunt Berkovich indenter (R = 759 nm) on NiFeCoCrMn were also examined by AFM. The 2-D profiles of these indented marks are all found to agree with the tip radii used (Figure 6-3).
Figure 6-2 Typical indentation pattern on NiFeCrCoMn alloy using Berkovich tip (R = 759 nm) observed by AFM.

Figure 6-3 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 $R = 80$ nm and $759$ nm, respectively.
6.2 Elastic response of NiFeCrCoMn and Ni

Figure 6-4 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.

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 6-4a and 6-4b, 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 elastic part of the loading curve prior to a pop-in event is described by the Hertzian relation,

$$P = \frac{4}{3} E \sqrt{R h^3}$$  \hspace{1cm} (6.1)
where $R$ is the tip radius of the indenter, $h$ is the indentation depth, and $E_r = \left[\frac{(1-\nu_{in}^2)}{E_{in}}+(1-\nu_s^2)/E_s\right]^{-1}$ is the reduced elastic modulus of the tested sample, $(\nu_{in}, E_{in})$ and $(\nu_s, E_s)$ 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 are plotted in Figure 6-4c and 6-4d. The reduced elastic moduli for NiFeCoCrMn and Ni are calculated to be $190.21 \pm 1.22$ and $187.18 \pm 1.59$ GPa, respectively. Using these $E_i$ values, the elastic loading curves for other tip radii $R = 80$ and $759$ nm are also found to agree with the Hertzian relation (Eq.(6.1)). Using the mechanical parameters for the diamond indenter ($\nu_{in} = 0.07$, $E_{in} = 1141$ GPa) [73] and samples ($\nu_{HEA} = 0.26$, $\nu_{Ni} = 0.31$) [107], 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 ($0.361$ nm for NiFeCoCrMn and $0.352$ nm for Ni) suggests a stronger bond in the alloy.

6.3 Plastic response of NiFeCoCrMn and Ni

Load-displacement curves from indentation tests of NiFeCoCrMn and single crystal Ni at a high load of $10$ mN are shown in Figure 6-5a. A shallower indentation depth indicates the HEA is harder than Ni. In Figure 6-5b, 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.,

$$H_{HEA} = H_{Ni} + \Delta H$$

(6.2)

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 [108,109], and Nix and Gao [110] proposed the depth dependence of the hardness $H$ as:
\[ H^2 = H_o^2 (1 + h^* / h) \] (6.3)

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 [111,112].

Figure 6-5 Typical load-displacement curves (a) produced from the Berkovich indenter \((R = 255 \text{ nm})\) on single-crystal Ni and NiFeCoCrMn. Hardening effect \( \Delta H \) was determined from indentation size effect revealed from hardness \( H \) vs indentation depth \( h \) (b). This term was incorporated in the Nix-Gao model 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 \( h < 30 \text{ nm} \) probably results from the spherical geometry of indenter.
The breakdown of self-similar indenter geometry and incorrect size of plastic zone have been suggested to be the main causes of such deviation [113]. It is apparent that, in Figure 6-5c, the \( H^2 \) value slightly deviates from the linear correlation when \( h < 100 \) nm, but 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 6-5c, data fit well at \( h > 100 \) nm according to the Nix-Gao model (Eq. (6.3)), and the depth-independent hardness \( H_o \) is extrapolated from the intercept of the fitting, as listed in Table 6.1. 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 6.1 Parameters in the Nix-Gao model for the indentation size effect in Ni single crystal and high-entropy alloy NiFeCoCrMn

<table>
<thead>
<tr>
<th>Materials</th>
<th>( E_r ) (GPa)</th>
<th>( H_0 ) (GPa)</th>
<th>( 3\sigma_f ) (GPa)</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>187.18 ± 1.59</td>
<td>0.90 ±0.04</td>
<td>1.02[28]</td>
<td>2.35</td>
</tr>
<tr>
<td>NiFeCoCrMn</td>
<td>190.21 ± 1.22</td>
<td>1.88 ± 0.08</td>
<td>1.56[23]</td>
<td>2.45</td>
</tr>
</tbody>
</table>

According to the Nix-Gao model, \( H_o \) 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 [115], \( H_o \) 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:
\[ H_{o,\text{Ni}} = C \sigma_f = CM \alpha Gb \sqrt{\rho_{\text{SSD}}} \]  

(6.4)

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 stress, 76 GPa for Ni, \( b \) is the Burgers vector, 0.249 nm for Ni. The value of \( \rho_{\text{SSD}} \) is, thus, estimated to be about \( 1.065 \times 10^{14} \) m\(^{-2} \), which is close to \( \rho_{\text{SSD}} = 1 \times 10^{13} \) m\(^{-2} \) reported in a fully annealed aluminum [116].

Under indentation, \( \chi = \tan \theta / a \) is defined as a measure of the strain gradient underneath the indenter [110]. At a fixed indenter angle and when \( a \rightarrow \infty \), corresponding to infinite indentation depth, the strain gradient goes to zero. Under this circumstance, the strain \( \varepsilon \) is fixed and only depends on the shape of the indenter. Since Ni and NiFeCoCrMn alloy have the same fcc structure and similar Burgers vector (0.249 nm vs 0.255 nm), the same strain \( \varepsilon \) at the infinite indentation depth essentially would give the same \( \rho_{\text{SSD}} \) value in these two materials. However, NiFeCoCrMn has a much higher \( H_o \) value than Ni (\( H_{o,\text{HEA}} = 1.88 \) GPa, \( H_{o,\text{Ni}} = 0.9 \) GPa) and the difference is \( \Delta H = H_{o,\text{HEA}} - H_{o,\text{Ni}} = 0.98 \) GPa. The hardness values for the two materials are consistent with the classical Tabor relation, namely, \( H = 3 \sigma_f \), where \( \sigma_f \) is the flow strength [107, 114].

This strengthening difference has been ascribe to be solid solution hardening before [117], 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 in 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 [118].
Figure 6-6 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 and spherical tip geometry of Berkovich indenter are shown by the extracted 2-D profiles (c)-(e). A modified area function of Berkovich indenter $A_c = 24.5(h+0.06R)^2$ is therefore proposed (f).

Figure 6-7 Diagram for the plastic zone underneath conical indenter (a) and spherical indenter (b)
The residual impressions on NiFeCoCrMn and Ni under a maximum load of 10 mN were extracted from AFM topography in Figure 6-6, which show the general shape of a Berkovich indenter. The bottom of the residual indents agrees with the applied tip radius \( R = 255 \) nm, and the area function of the ideal Berkovich indenter is then modified as \( A_c = 24.5(h+0.06R)^2 \).

Generally, a plastic zone is formed underneath the indenter during the indentation test, and the size and shape of this zone depend on the indenter geometry, as shown in Figure 6-7. According to Nix-Gao gradient plasticity model, the hardness \( H \) at a given depth of indentation is related to the density of geometrically necessary dislocation \( \rho_{GND} \) through the Taylor’s relation:

\[
H = \Delta H + CM \alpha Gb \sqrt{\rho_{SSD} + \rho_{GND}}
\]  
(6.5)

where \( \Delta H \) is the hardness enhancement contributed by alloying, \( C \approx 3 \) is the Tabor factor, \( M = 3.06 \) is the Taylor factor that relates the shear flow stress to the tensile flow stress in fcc metals, \( G \) is the elastic shear modulus, \( b \) is the Burgers vector, \( \rho_{SSD} \) is the density of statistically stored dislocations, \( \rho_{GND} \) is the density of the geometric necessary dislocations in the plastic zone. According to the definition of hardness \( H = P/A_c \), where \( A_c \) is the projected contact area or the area function of the indenter, the load-displacement response is derived to be

\[
P = (\Delta H + CM \alpha Gb \sqrt{\rho_{SSD} + \rho_{GND}})A_c
\]  
(6.6)

Use the value of \( \rho_{SSD} \) and \( \Delta H \) for each material, the load-displacement responses can be well modeled by Eq. (6.6) and are shown in Figure 6-5a. The scaling factor \( f \) that described the effective size of plastic zone with respect to the contact radius is about 2.4, \( \rho_{GND} = \frac{3\tan^2 \theta}{2 f^2 bh} \), \( \theta = 19.7^\circ \) is the angle between the sample surface and the equivalent conical indenter surface, \( h \) is the indentation...
depth. It should be noted that this analytical model only describes the load-displacement curves at large indentation depth \((h > 25 \text{ nm})\) as a result of inadequate area function. A more accurate description for shallow indentation will be discussed in the sections below.

6.4 Statistical analysis of the incipient plasticity of NiFeCoCrMn

In general, a pop-in event is triggered when the maximum shear stress \(\tau_{\text{max}}\) underneath the indenter exceeds a critical value. The event usually consists of the nucleation and subsequent propagation of dislocations. According to contact mechanics, \(\tau_{\text{max}}\) occurs at about half of the contact radius \(a\) underneath the indenter and is given by [38]

\[
\tau_{\text{max}} = 0.47 p_m = 0.47 \frac{P}{\pi Rh} \tag{6.7}
\]

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

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 \(\tau_{\text{max}}\) in Figure 6-8a and 6-8b. 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 [27] (G/30~ G/5, where \(G\) is the elastic shear modulus of the material, 80 GPa for NiFeCoCrMn [107] and 76 GPa for Ni). As the tip radius increases, the \(\tau_{\text{max}}\) 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 [40,41], 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.

Figure 6-8 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 pop-in is deduced from the slope of the plot of ln[-ln(1-$F$)] against of $\tau_{\text{max}}$ underneath indenters with the tip radii $R = 80$ nm for NiFeCoCrMn (c) and single-crystal Ni (d).

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 $\tau$ [16] can be written as

$$\dot{n} = n_0 \exp\left(-\frac{\varepsilon - \tau_0}{kT}\right)$$  \hspace{1cm} (6.8)
where \( n_0 \) is the pre-exponential attempt frequency, \( \varepsilon \) is the energy barrier for dislocation nucleation, and \( \nu \) is the activation volume. Assume \( F \) is the cumulative probability for pop-ins, then, the population of indentations available to pop-in is \( 1 - F \), and the rate of change in \( F \) can be described by the following equation:

\[
\dot{F} = (1 - F) \dot{n}
\]  

(6.9)

Insert Eq. (6.8) into Eq. (6.9), and take an integration over the highly stressed volume underneath the indenter (scales with the contact radius, \( \Omega \sim \pi a^2 \)), the cumulative probability for nucleation events within the sampling volume can be written as a function of the maximum shear stress \( \tau_{\text{max}} \) for pop-in [44]:

\[
F_{\text{nucleation}}(\tau_{\text{max}}) = 1 - \exp\left[-\frac{9\pi R \eta}{4E \dot{\rho} \alpha^\gamma} \gamma(\tau_{\text{max}}) \right]
\]  

(6.10)

where \( \dot{\rho} \) 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, \( \gamma(\tau_{\text{max}}) \) is a complex function of \( \tau_{\text{max}} \), and the parameter \( \alpha \) is a collection of time-independent terms given by

\[
\alpha = \frac{0.47}{\pi} \left( \frac{4E}{3R} \right)^{\frac{2}{3}} \frac{\nu}{kT}
\]

Eq. (6.10) 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 [40] 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 \( \rho_{\text{defect}} \) 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,

\[
F_{\text{activation}} = 1 - \exp[-\rho_{\text{defect}} V(\tau > \tau_{\text{pop-in}})]
\]  
(6.11)

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 \( \exp[-\rho_{\text{defect}} V] \exp[-\frac{9\pi R \eta}{4E_P \alpha^6} \gamma(\tau_{\text{max}})] \), and the resultant cumulative probability for pop-in is

\[
F_{\text{total}} = 1 - \exp[-\rho_{\text{defect}} V - \frac{9\pi R \eta}{4E_P \alpha^6} \gamma(\tau_{\text{max}})]
\]  
(6.12)

Table 6.2 Parameters used for modeling the cumulative probability of pop-in \( F \) in NiFeCoCrMn and Ni single crystal

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \nu ) (b(^3))</th>
<th>( \eta \times 10^{13}\text{ s}^{-1}\text{m}^{-3} )</th>
<th>( \rho_{\text{defect}} \text{ (m}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFeCoCrMn</td>
<td>0.65</td>
<td>9.92 ~ 93.2</td>
<td>4 \times 10^{16}</td>
</tr>
<tr>
<td>Ni</td>
<td>0.69</td>
<td>2.15 ~ 84.9</td>
<td>2.3 \times 10^{17}</td>
</tr>
</tbody>
</table>

Mathematically, we can rewrite Eq. (6.10) into a double logarithmic form as \( \ln[-\ln(1-F)] = \nu \tau_{\text{max}}/kT + \beta(\tau_{\text{max}}) \), where \( \beta(\tau_{\text{max}}) \) in the equation is a weak function of \( \tau_{\text{max}} \) as compared to the first term, one can deduce the activation volume \( \nu \) from the slope of the linear fitting of \( \ln[-\ln(1-F)] \) against \( \tau_{\text{max}} \). In Figure 6-8c and 6-8d, 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 6.2. To minimize data variation caused by pre-existing defects, data obtained from the sharpest indenter (\( R = 80 \text{ nm} \)) 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. (6.12) and the results are shown in Figure 6-8. 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 ($\sim$28 MPa) [119,104], and the activation of slip systems in Ni micropillars (40-60 MPa) [120]. The parameters for modeling are summarized in Table. 6.2. It is noted in the modeling that the density of pre-existing defects is set at a value of $10^{16} \sim 10^{17}$ m$^{-3}$. Assuming dislocation lines are spaced in a cubic array, the defect density is equivalent to a dislocation density of about $10^{11}$ m$^{-2}$, which is the typical value in a fully recrystallized crystal [40,28].

6.5 Plastic deformation of NiFeCoCrMn under spherical tip

6.5.1 Load-displacement response at small depth

It has been pointed out before that when a blunt pyramid-shaped indenter is used it actually produces a spherical impression at an extremely shallow indentation depth ($h < R/10$). Consequently, the Nix-Gao model, if it is still applicable, must be properly modified when the indentation depth is extremely shallow. In such a case, we applied the density of geometrically necessary dislocation $\rho_{\text{GND}} = \frac{3}{4f^3bR}$ beneath a spherical indenter [121] in the Nix-Gao gradient plasticity model (Eq. (6.6)), where $R$ is the radius of the spherical tip, and $f$ is a scale factor connecting the radius of plastic zone $a_{pz}$ and the contact radius $a_c$, namely, $a_{pz} = fa_c$ [121,122]. A linear correlation between the load $P$ and displacement $h$ can be readily deduced as

$$P = kh$$  \hspace{1cm} (6.13)
where \( k = 2\pi R \left( \Delta H + CM \alpha Gb \sqrt{\rho_{SSD} + \frac{3}{4f^3 bR}} \right) \) is constant for a given indenter with a radius of \( R \). Insert proper values for the parameters \((R, b, \Delta H, G, \alpha, \rho_{SSD})\) into this equation, we find that the load-displacement responses (Figure 6-9) agree well with this linear correlation [123]. The scaling factor \( f \) used in the modeling ranges from 2.2 to 2.54, as listed in Table 6.3, which is close to 2.4 used before for curve fitting in Figure 6-5 and values reported in the literature [121,122]. This indicates that the plastic zone is twice as large as the contact area underneath the indenter, which is also supported by some experimental observations. For example, Zhang et al [124] observed both dislocations in the indented volume and the residual indent impression after a pop-in event, and the travel distance of the leading dislocation was about 1 \( \mu \)m. If we assume the volume occupied by dense dislocations to be the plastic zone, the zone size is estimated to be twice the diameter of the plastic contact area, i.e., \( 2\sqrt{2Rh^2} \sim 475 \) nm (tip radius \( R = 650 \) nm, indentation depth \( h = 45 \) nm). In the present study, there is no significant difference in the \( f \) value between NiFeCoCrMn and Ni, thus the effective plastic zone sizes in these two materials are quite similar.

Figure 6-9 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 the Nix-Gao model using a spherical indenter tip (Eq. (6.13)).
Table 6.3 Plastic zone size factor $f$ used in the modeling of the plastic deformation during nanoindentation

<table>
<thead>
<tr>
<th>Materials</th>
<th>R/nm</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>80</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>759</td>
<td>2.4</td>
</tr>
<tr>
<td>NiFeCoCrMn</td>
<td>80</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>255</td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td>759</td>
<td>2.54</td>
</tr>
</tbody>
</table>

6.5.2 Displacement burst at the first pop-in in NiFeCoCrMn

Pop-in marks the transition from elastic to plastic deformation, the displacement burst must be caused by the avalanche of dislocations underneath the indenter, as a result of dislocation nucleation and multiplication [124]. The length of pop-in (or the excursion size) has been suggested to be attributed to the number of dislocation loops formed in a pop-in event [125,30,39] assuming a balance between the stored elastic energy prior to the pop-in and the dissipated energies (such as energy of dislocation loops, plastic work and surface energy) after the pop-in.

Durst et al [122] suggested that the Hertzian elastic loading and dislocation-based plastic loading (the Nix-Gao model) correspond to the lower and upper bound values for the indentation displacement, respectively. As an estimate, the length of pop-in represents the difference between the elastic and plastic responses at the pop-in loads. However, in actuality, the experimental pop-in length was often underestimated as compared to the prediction of the Nix-Gao model, as indicated in Figure 6-9. A possible explanation is that the pop-in event (or the 1st yielding event)
consists of dislocation nucleation followed by the avalanche of dislocations within a very short period of time. The stress for this event occurring locally under the indenter usually reaches the theoretical strength. Immediately after the 1st yielding event, new dislocations are driven by a high shear stress. However, as a result of the sudden sink-in of the indenter, the contact area increases and the applied stress drops rapidly, well below the global yield strength of the sample. This rapid decrease in stress would cause moving dislocations to decelerate and soon come to stop because the stress is no longer sufficient to assist dislocations to bypass obstacles. At the finish of the pop-in and upon further loading, sample initially responds elastically until the stress reaches the critical value for the 2nd yielding event in the new dislocation configuration. The traditional Nix-Gao model, then, becomes applicable to describe the plastic flow after the 2nd yielding event.

The plastic responses of NiFeCoCrMn and Ni after pop-in event under the indenter $R = 759$ nm were compared in Figure 6-10. It is interesting to note that the loading curve immediately after the pop-in event in Figure 6-10a is elastic, since it essentially overlaps with the unloading curve. On the $P-h$ curves with a lower pop-in load in Figure 6-10b, stable plastic deformation starts after the 2nd yielding event. This renewed yielding event after pop-in indicates a similar physical process that usually occurs in conventional mechanical tests, specifically obstacles for dislocation movements are overcome when the shear stress reaches a critical value, namely the yield strength. The Ni single crystal has a larger pop-in length than NiFeCoCrMn (Figure 6-10b), which can be rationalized from the viewpoint of energy. During a pop-in, the strain energy stored underneath the indenter is immediately released and dissipated mainly as plastic work. With very small difference in elastic properties, NiFeCoCrMn and Ni are expected to store similar amount of strain energy at the same given load. Since $f$ factors are almost the same for NiFeCoCrMn and Ni, the fact that the HE alloy has a much shorter pop-in length would indicate a smaller plastic zone or
fewer dislocations underneath the indenter. In other words, it is reasonable to tentatively conclude that NiFeCoCrMn has a higher lattice friction for dislocation motion than the pure Ni.

To measure the pop-in length, we schematically divide the $P-h$ into several segments, as marked in Figure 6-10c. In the figure, the pop-in length $l_1$ is correlated to a virtual pop-in length $l_2$ at the yielding load $P_{2nd\text{-}yield}$ through an equation, $l_1 = l_2 + \Delta h_1 - \Delta h_2 - \Delta h_y$, where $l_2$ is also given by the difference between the elastic and plastic penetration depth at load $P_{2nd\text{-}yield}$:

$$l_2 = P_{2nd\text{-}yield} / k \left( \frac{9}{16E_r^2R} \right)^{1/3} P_{2nd\text{-}yield}^{2/3}$$  \hspace{1cm} (6.14)

where $\Delta h_1$ is the increment of elastic penetration depth when the load increases from $P_{\text{pop-in}}$ to $P_{2nd\text{-}yield}$: $\Delta h_1 = (3/4 E_r \sqrt{R})^{2/3} (P_{2nd\text{-}yield}^{2/3} - P_{\text{pop-in}}^{2/3})$, $\Delta h_2$ is the elastic indentation depth after the pop-in, and $\Delta h_y$ represents the indentation depth corresponding to the yielding event. The elastic loading after pop-in can be approximated by the power law $P = k_1 (h-h_0)^{1.5}$, then $\Delta h_2$ is quantified by the equation: $\Delta h_2 = k_1^{-2/3} (P_{2nd\text{-}yield}^{2/3} - P_{\text{pop-in}}^{2/3})$. A typical fitting of the secondary elastic loading part in Figure 6-10c indicates $\Delta h_2$ is normalized to about $0.58 \Delta h_1$. Considering the significant yielding depth $\Delta h_y$ after elastic loading, $\Delta h_1 \approx \Delta h_2 + \Delta h_y$, and we have $l_1 = l_2$. 

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Figure 6-10 Overlap of the loading and unloading parts of the load-displacement curves (a) and 2nd yielding event at higher load (b) for NiFeCoCrMn and single crystal Ni indicates the plastic deformation follows an elastic loading immediately after the pop-in. For the quantitative analysis of pop-in length, an equivalent length $l_2$ was introduced at a higher load $P_{2nd-yield}$ in (c), and ratios of $P_{2nd-yield}/P_{pop-in}$ for the NiFeCoCrMn and single-crystal Ni were determined in (d).

$P_{2nd-yield}$ is expected to scale with $P_{pop-in}$, thus $P_{2nd-yield}$ against $P_{pop-in}$ for both NiFeCoCrMn alloy and Ni are plotted in Figure 6-10d. It is apparently that $P_{2nd-yield}$ is indeed proportional to $P_{pop-in}$ and the proportional constant, i.e., the ratio $\alpha_1 = P_{2nd-yield}/P_{pop-in}$ for Ni ($\alpha_{Ni} = 1.6$) is larger than that for NiFeCoCrMn ($\alpha_{HEA} = 1.33$), which is actually a direct consequence of larger pop-in length in Ni.
In general, the pop-in length linearly scales with the pop-in load. The load ratio $\alpha_1$ is taken account in the equation for $l_2$, and a general form of the pop-in length $L_{\text{pop-in}}$ can be expressed as

$$L_{\text{pop-in}} = \frac{\alpha_1}{k} P_{\text{pop-in}} - \left( \frac{3\alpha_1}{4E_r\sqrt{R}} \right)^{\frac{2}{3}} P_{\text{pop-in}}^{\frac{2}{3}}$$  \hspace{1cm} (6.15)$$

Substituting the $f$ factor and ratio factor $\alpha_1$ determined previously into the Eq. (6.15), the pop-in size in Figure 6-11 can be reasonably predicted. The data are noted to deviate from the model predictions at large pop-in length ($L_{\text{pop-in}} > 80$ nm). It is probably caused by the fact that the geometry of indenter can no longer be treated as spherical at a large indentation depth, thus Eq. (6.15) is also no longer applicable.
6.6 Pop-in length in high entropy alloy and Ni

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.

![Graphs showing mean pressure underneath the indenter before and after pop-in in NiFeCoCrMn at different tip radii](image)

Figure 6-12 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 underneath the indenter $p_m$, 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 6-7b), evolutions of mean pressure \( p_m \) throughout a pop-in event at different tip radii in NiFeCoCrMn are calculated and shown in Figure 6-12. 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 dislocation in the materials, but 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 6-13](image)

Figure 6-13  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. (6.16).

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 6-13a. 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 $\rho_{ssd} + \frac{3}{4f^3bR}$. 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 NiFeCoCrMn 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

$$p_m = \Delta H + CM \alpha Gb \sqrt{\rho_{ssd} + \frac{3}{4f^3bR}} \quad (6.16)$$

Inserting proper parameters, predicted values of mean pressure in Eq. (6.16) are found to agree well with the experimental results, as shown in Figure 6-13. 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 6-13b. Similar schematic diagrams illustrating indentation plasticity have been presented by Zhang et al [124] and Lilleodden et al [126]. In the figure, the statistically stored dislocation density $\rho_{ssd} = 1.065 \times 10^{14}$ 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-structured materials. In the current fully annealed Ni and HEA materials, the dislocation density $\rho$ is low ($10^{11}$ m$^{-2} << 10^{14}$ m$^{-2}$), the pop-in event can only be triggered under
high $p_m$. The pop-in causes an abrupt increase in $\rho$ and, meanwhile, a sudden increase in contact area, thus a rapid decrease in $p_m$ underneath the indenter. Both $p_m$ and $\rho$ are tip radius-dependent, and a power-law correlation between them is revealed in Figure 6-13b. The power index is about 0.5, which is apparently resulted from the Taylor hardening.

6.7 Summary

Onset plasticity of high entropy alloy NiFeCoMnCr and single crystal Ni were studied using instrumented indentation technique, and three different tip radii were applied. In both these two materials, the critical shear stress for pop-in increases with the decrease of tip radius. The activation volumes for pop-in in Ni and HEA are 0.69 $b^3$ and 0.65 $b^3$, respectively, both of which indicate a small-scale event to induce pop-in. The cumulative probability of pop-in in Ni and HEA were described by a combined model, and the tail in the pop-in data for Ni may result from the pre-existing defects in the highly stressed zone underneath the indenter.

Indentation size effect is observed in both NiFeCoCrMn and Ni when tests are conducted at a load of 10 mN under which the indentation depth is about 400-500 nm. The load-displacement curves can be modeled by the Nix-Gao model and the scaling factor $f$ that describes the effective size of plastic zone underneath the indenter is about 2.4. Based on the Taylor hardening relation, the density of statistically stored dislocations for continuous plastic deformation is estimated to be $1.065 \times 10^{14}$ m$^{-2}$. NiFeCoCrMn apparently has a high lattice friction ($\Delta H = 0.98$ GPa) as compared with Ni single crystal.

The pop-in length in materials was evaluated quantitatively considering the Hertzian elastic relation and the Nix-Gao strain gradient model. The pop-in length in Ni was found to be
significantly larger than that in HEA, which results from much larger lattice friction in HEA in comparison with Ni. In both NiFeCoCrMn and Ni, the mean pressure beneath the indenter decreases with increasing tip radius. It is mainly because the decrease of dislocation density in the indented volume.
Chapter 7. Concluding Remarks

In this dissertation, the onset of yielding of several metals (including bcc-Cr, fcc-Ni, fcc-Au) and a fcc-structured high entropy alloy NiFeCoMnCr have been investigated using instrumented indentation technique. The nucleation of dislocations was believed to be the main cause for the occurrence of pop-in, since the critical shear stresses for pop-in approach to the theoretical strength of materials ($\mu/20 \sim \mu/2\pi$) in these materials.

The nanoindentation tests were also performed on bcc-Cr and fcc-Au at elevated temperatures (295 K ~ 465 K), and the pop-in load was found to drop with the increase of temperature. Following statistical analysis proposed by Schuh and coworkers, the activation volumes and activation energies for pop-in were determined to be 0.308 $b^3$ and 0.505 eV for Cr, 1 $b^3$ and 0.424 eV for Au, respectively. These relatively small values of the activation parameters indicate the nucleation of dislocation at point defects (e.g., vacancies or interstitials) might be responsible for the initiation of the incipient plasticity.

To further shed lights on the role of point defects in dislocation nucleation at different temperatures, we performed atomistic simulations of indentation process on the Au(100) lattice with/without point defects at 1K, 300K, 400K, 500K. Despite the drop of load for plasticity with the increase of temperature or the introduction of vacancies in the lattice, the incipient plasticity appears to be not affected by the indentation velocity or the presence of Ag impurities. The activation volume and activation energy for the incipient plasticity in Au were calculated to be 1~2 $b^3$ and 1~2 eV, respectively, and both values are close to those obtained from experiments. There
seems no significant difference in the dislocation nucleation process between the perfect lattice and defective lattice at higher temperatures.

In the study of the effect of indenter tip radius (60 nm ~ 759 nm) on the pop-in behavior of bcc-Cr, the stress for the incipient plasticity was found to increase with the decrease of tip radius and saturated at a tip radius less than 80 nm. We demonstrated that a modified model can successfully describe the pop-in behavior in Cr over the entire range of tip radii. This indicates a mechanistic transition from dislocation nucleation in a perfect crystal to dislocation multiplication in a crystal containing pre-existing defects when the tip radius increases. The transition is attributable to the fact that when the stressed volume underneath an indenter increases, the probability to encounter a dislocation also increases.

The combined model appears to be applicable universally to other metals. For example, I examined the pop-in behavior of fcc-Ni and fcc-NiFeCoMnCr at three different tip radii (80, 255, 759 nm), and found them well described by this model. The effect of tip radius on the elastic response of Ni and HEA was evaluated based on the Hertzian elastic relation, and the plastic response based on the modified Nix-Gao strain gradient model. The fact that the pop-in length in Ni is larger than that in HEA is probably resulted from a much higher lattice friction in HEA.

In summary, I have extensively studied the effect of tip radius and temperature on the onset of yielding of bcc-Cr, also compared the experiments and simulations on the incipient plasticity of Au. Additionally, the alloying effect on the elastic and plastic deformation during nanoindentation was also briefly explored and discussed. My dissertation work is expected to provide the scientific community with better understandings of the incipient plasticity behavior in metallic materials.
Chapter 8. Perspectives

Scientific research is an unending process that people seek to discover the mysteries hidden by God. That’s how our society makes progresses. There is always something to do or to improve in future, and my research work is not an exception. From my research in the past five years, I would like tentatively make the following suggestions.

1. I have intensively studied the incipient plasticity of bcc-Cr by experimental technique, but didn’t perform any simulation work on it. The main reason for that is the unknown interatomic potential for Cr metal. So far, the simulation on the incipient plasticity of bcc metals are still limited [49,116], and it would be interesting to perform MD simulation on this topic. The dislocation activities in bcc metals are supposed to be different from those in fcc metals as a result of different slip systems and non-planar structure of screw dislocation in bcc metals. Moreover, the effect of interstitial impurities on the nucleation of dislocation in bcc-structured materials is still unclear. Even though I didn’t observe any effect of substitutional Ag impurities on the onset of yielding in Au in Chaper 4, the interstitials may significantly contribute to the dislocation nucleation in bcc metals, since they distort the lattice severely, compared with the substitutional impurities.

2. My current study mainly focused on the incipient plasticity of cubic structured (fcc, bcc) metals and alloy, but didn’t discuss the pop-in behavior of metallic material with hexagonal close packing (HCP) structure. So far, few studies have been reported on the onset of yielding in Mg[18,117] at room temperature, and indentation experiments at elevated temperature are limited to GaN[37] to my best knowledge. HCP structure has less slip systems (basal planes, prismatic planes, and pyramidal planes) than FCC and BCC
structures, and it has a large anisotropy in deformation depending on which slip system is activated under loading. In future, the researchers may investigate the incipient plasticity of hcp-metals applying both experimental and simulation techniques, and the effects of temperature, crystalline anisotropy, stressed volume, lattice defects will be interesting topics to be discussed.

3. According to the AFM image, pile-ups were observed in around the indents on Ni and HEA. We didn’t take this into consideration when we tried to model the plastic response in the dissertation. Even though it is unlikely to change our conclusions significantly, a rigorous description of the experimental result is required for a good research. I will work on it with the assistance of FEM method and proper empirical results to give a more thorough analysis.
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LIST OF PUBLICATIONS

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