

**Mechanical behavior of body-centered cubic high-
entropy alloys**

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Degree

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DEDICATION

This doctoral dissertation is dedicated to my parents Fangwang Ye and Wenxiu Chen, my parents-in-law Shunxiang Liu and Yunhua Chen, my wife Chenze Liu, my daughter Celina Ye, and my sister Xueping Ye.

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ABSTRACT

The objective of this dissertation is to provide a fundamental understanding of mechanical behavior of body-centered cubic (BCC) high-entropy alloys (HEAs).

Incipient plasticity in metallic alloys is of great interest to the scientific community. In my research, I selected a NbTiZrHf-HEA for the initial study using nanoindentation. The critical shear stress was found to approach the theoretical strength, indicating a dislocation nucleation-controlled process. The activation volume was much larger than that for pure metals, suggesting cooperative migration of multiple atoms. The activation energy was also found to be higher than that in a typical face-centered cubic HEA, which is attributable to the nucleation of full dislocations in the former but partial dislocations in the latter.

In view of the pronounced effect of interstitials on the strengthening of traditional BCC-metals, oxygen or nitrogen was further added into the BCC-HEA to study their effect on the incipient plasticity. Both interstitial elements increased the critical stress, and nitrogen produced a larger hardening effect than oxygen. The calculated activation volumes were similar in magnitude, implying a similar aforementioned mechanism governing the dislocation nucleation in the studied HEAs. First-principle calculations revealed that the presence of interstitials induced charge transfer between the interstitial and its surrounding metals, resulting in the increased critical stresses for incipient plasticity.

I further investigated the incipient yielding under dynamic loading via nanoscratching and found that it occurred at lower stresses compared to the static loading during nanoindentation. Concurrently, tribological behavior of the HEA was studied and

compared with its conventional counterparts using nanoscratch tests. The HEA exhibited improved wear resistance and reduced friction coefficient. Wear resistance scaled linearly with hardness, but friction behavior exhibited elastic and plastic regimes. The reduced friction coefficient was discussed in lights of the acting plowing and adhesion mechanisms during nanoscratching.

Elastic properties of the HEA were also evaluated via both experiments and first-principle calculations, and their results agreed excellently. Additionally, rule-of-mixtures based on lower-bound prediction could be conveniently used to reasonably estimate elastic moduli of single-phase HEAs.

Finally, I also made several suggestions of possible future research topics based on the above results and my experiences.

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Chapter 1. Introduction

1.1 Incipient plasticity of high-entropy alloys during nanoindentation

High-entropy alloys (HEAs), also known as multi-principal element alloys, have attracted significant research attention since they were first introduced [1, 2], not only due to their outstanding properties, such as high strength-ductility combination [3-10], excellent resistance to fracture [11, 12], creep [13], and wear [14-16] etc., but also because they expands the composition space for alloy design. Unlike conventional alloys with a major element, HEAs comprise of multiple equiatomic or nearly equiatomic metallic elements. The high configurational entropy over the mixing enthalpy promotes HEAs to form a simple solution-like phase, usually face-centered cubic (FCC) [11, 17, 18] or body-centered cubic (BCC) [19-21], instead of brittle intermetallics. This has been shown before [17] that, because the lack of a major diffusing element, atomic (or vacancy) migration in HEAs is expected to involve cooperative motion of several atoms in order to maintain proper composition portioning.

Instrumented nanoindentation has been demonstrated previously to be able to quantitatively assess the onset of yielding in crystals [17, 22-26]. Experimentally, plastic yielding is associated with distinct displacement bursts, or pop-ins, in the load-displacement curve. The first pop-in is often attributed to dislocation nucleation triggered by the applied shear stress near the theoretical strength ($\sim G/10$, where G is shear modulus) [17, 22-26]. Schuh et al. [22, 23] first proposed a statistical approach to quantitatively

evaluate the temperature and rate dependence on the dislocation nucleation and extract related activation energy and volume in the single-crystal FCC-Pt. Recently, Zhu et al. [17] studied the nanoindentation pop-in behavior of a single-phase FCC-NiCoCrFeMn HEA and found the activation volume for dislocation nucleation is much larger than that in the conventional metals. It was also reported [26] that the pop-in behavior was quite different between FCC-Ni and BCC-Mo, indicating the effect of structure on dislocation nucleation. It is, therefore, of interest to investigate the atomic processes for dislocation nucleation in BCC-HEAs. In this thesis, we performed instrumented nanoindentation to explore dislocation nucleation process in a BCC-NbTiZrHf HEA to compare it with that in conventional metals as well as FCC HEAs.

1.2 Effect of interstitial solutes on incipient plasticity

Recently, a new category of HEAs by incorporating additional interstitial elements, in light of interstitial solid-solution strengthening mechanism, have been developed [3, 27-29]. For example, Wang et al. [27] investigated the effect of interstitial carbon addition (up to 1.1 at.%) on mechanical properties and dislocation substructure evolution in tension in a face-centered cubic (FCC) $\text{Fe}_{40.4}\text{Ni}_{11.3}\text{Mn}_{34.8}\text{Al}_{7.5}\text{Cr}_6$ HEA. Another study also demonstrated that 0.5 at.-%-nitrogen addition to FCC NiCoCr medium entropy alloy (MEA) could increase its yield strength without losing the ductility [28]. It is especially noted that Lei et al. [3] have reported an unprecedented enhancement in both strength and ductility in an interstitial oxygen doped (2 at.%) body-centered cubic (BCC) NbTiZrHf HEA, surmounting the interstitial-induced embrittlement in conventional BCC alloys [30].

In the study of interstitial-containing HEAs, the majority of published works focused on the effect of interstitial additions on the macroscopically plastic deformation in which the interstitial solutes act as obstacles to impede dislocation motions [31]. Only limited data were reported pertinent to the effect of interstitial atoms on the onset of yielding in HEAs [32, 33]. For example, interstitial hydrogen was recently found to reduce the critical load for incipient plasticity (or pop-in) during nanoindentation in FCC-NiCoCrFeMn [32, 33]. On the other hand, interstitial carbon were found to increase the pop-in load during nanoindentation in an ultralow-carbon steel [34]. However, both interstitial hydrogen and carbon could enhance the tensile yield strength of their individual alloy matrices [34, 35]. Apparently, the traditional wisdom that interstitial solute addition can lead to solid-solution hardening may not be applicable to the incipient plasticity measured by nanoindentation; the role of interstitial atoms on the incipient plasticity appears to be different. Therefore, it will be intriguing to differentiate the two processes and to identify their individual mechanism. In this study, we employed instrumented nanoindentation, in combination with quantitative statistical analysis and density functional theory (DFT) calculations, to systematically examine the effect of interstitial oxygen and nitrogen additions on the incipient plasticity in BCC-NbTiZrHf HEAs, in an attempt to identify the origin for hardening during the incipient plasticity.

1.3 Tribological behavior of high-entropy alloys during nanoscratching

In the literature, the aforementioned incipient plasticity was generally investigated using nanoindentation with normal force applied only, which can be regarded as a “static loading”. By contrast, very few efforts have been made on such topic under a “dynamic loading” during nanoscratching, in which an additional tangential force was also introduced besides the normal force. Wasmer et al. [36] performed both nanoindentation and nanoscratch tests on a single-crystal indium phosphide (InP) semiconductor surface and found that load threshold to generate the first dislocations is twice lower in nanoscratching compared to indentation. Therefore, it is of interest to investigate whether it is a common phenomenon for other materials, such as HEAs.

Concurrently, nanoscratch technique has also been demonstrated to be a viable method for characterizing the tribological behavior, i.e., friction and wear, of various materials under dry wear [37-42]. The precise measurement of load and displacement in both normal and tangential directions at the microscale or even nanoscale is useful for quantitative analysis of the mechanical/tribological responses.

Since HEAs contain several (usually > 4 -5) metallic elements in equiatomic or nearly equiatomic ratio and the “high-entropy” effect promotes the formation of disordered solid-solution structures, e.g., FCC and BCC structures, the lattice of these alloys is usually distorted because of different atomic sizes and chemical bonds of the constituent elements [43-45]. As a result, HEAs are stronger than their conventional counterparts [46, 47]. Since for wear resistance, it is known that the wear rate of a material is inversely proportional to

its hardness (or strength), according to the Archard equation for dry wear [48], HEAs are anticipated having good wear resistance.

In fact, several studies [16, 49-57] have reported that HEAs are wear resistant. However, tribological improvement reported in these studies was mainly in materials with two-phase or multi-phase structures [16, 49-55], in which the strengthening effect was relying on the hard second phases. For example, Wu et al. [52] investigated the adhesive wear behavior of $\text{Al}_x\text{CoCrCuFeNi}$ HEAs and found that volume fraction of the harder BCC phase increased with increasing Al content, thus resulted in better wear resistance. There were also studies reporting the formation of boride [54] or carbide phases [50] in the HEA matrices which significantly improved the hardness, thus wear resistance. However, friction and wear behavior and their related mechanisms in single-phase HEAs have not yet been well addressed and remain elusive.

Up to date, wear testing methods adopted in previous studies of HEAs [16, 49-57] were based on macroscopic experiments, such as pin-on-disc and ball-on-disc. However, studies of tribology and related mechanisms of HEAs at micro/nanoscale have not yet been reported. In this thesis, nanoscratch technique was employed to systematically investigate the friction and wear mechanisms of a single-phase BCC, equiatomic NbTiZrHf under both ramping and constant load modes to address the response of the alloy under wear. A direct comparison of the friction and wear behavior between this BCC-HEA and the traditional Nb-based alloys are also made.

1.4 Elastic properties of high-entropy alloys

Elastic moduli are one of the intrinsic material properties, which directly affect various fundamental properties such as mechanical and thermal properties [58]. For example, they govern the stress-strain relation before yielding, and the shear modulus is closely related to dislocation motion on slip planes, thus contributing to strengthening and ductility. Elastic properties are also linked to the melting point, thermal expansion and Debye temperatures. There have been several theoretical investigations of elastic properties of HEAs [59-65]. For example, alloying effects on elastic properties were explored in FCC-structured Cantor alloy (i.e., NiCoCrFeMn) and its subsystems [59, 60]; studies have also been carried out on various BCC-structured refractory HEAs using different *ab initio* based calculations, including virtual crystal approximation (VCA), coherent potential approximation (CPA) and special quasi-random structure (SQS) [61-63]. However, experimental measurements of elastic properties of HEAs are still relatively limited, especially for BCC-structured HEAs [66, 67]. In fact, many studies were cross-referenced, namely, theoretical and experimental works were carried out by different groups, data comparisons were made, nonetheless. A direct comparison between experimental measurements and theoretical calculations has not yet been made for HEAs. In this dissertation, resonant ultrasound spectroscopy (RUS) experiments and density functional theory (DFT) calculations were also performed to evaluate the elastic properties of a BCC-structured NbTiZrHf HEA and provide a direct comparison to validate the calculations.

Additionally, the applicability of the simple rule-of-mixtures (ROM) to equiatomic solid solution alloys is also explored and discussed.

Chapter 2. Incipient plasticity of a BCC NbTiZrHf HEA studied using nanoindentation technique

2.1 Experimental

A high-entropy alloy with a nominal atomic composition of Nb₂₅Ti₂₅Zr₂₅Hf₂₅ was prepared by arc-melting a mixture of the constituent elements (purity > 99.9 wt.%) in an argon atmosphere purified by a Ti-getter. The ingots were re-melted at least four times in high purity argon atmosphere to ensure the chemical homogeneity before being drop-cast into a water-cooled copper mold. The as-cast ingots were homogenized at 1290 °C for 24 h and, then, cold rolled 80% in thickness. The rolled plates were additionally annealed at 1200 °C for 30 mins to induce recrystallization and grain growth. Microstructure of the annealed samples has a grain size about 150 μm examined by optical microscope and electron backscatter diffraction (EBSD, Fig. 2.1a). Phases and lattice parameter were identified by X-ray diffraction (XRD) with Cu-Kα radiation. Instrumented nanoindentation experiments were performed using a Berkovich diamond tip with an effective tip radius of 272 nm at room temperature (22 °C) on a Hysitron Triboindenter (Hysitron, Inc., Minneapolis, MN). To prevent possible overlap of the deformed zone produced by adjacent indentations, tests were conducted at a 5-μm interval. Four randomly selected grains were tested at a fixed loading rate of 10 μN/s. Various loading rates (10, 100 and 1000 μN/s) were also carried out to investigate the rate dependence of the pop-in behavior. Testing samples for nanoindentation were prepared by initial mechanical polishing, followed by

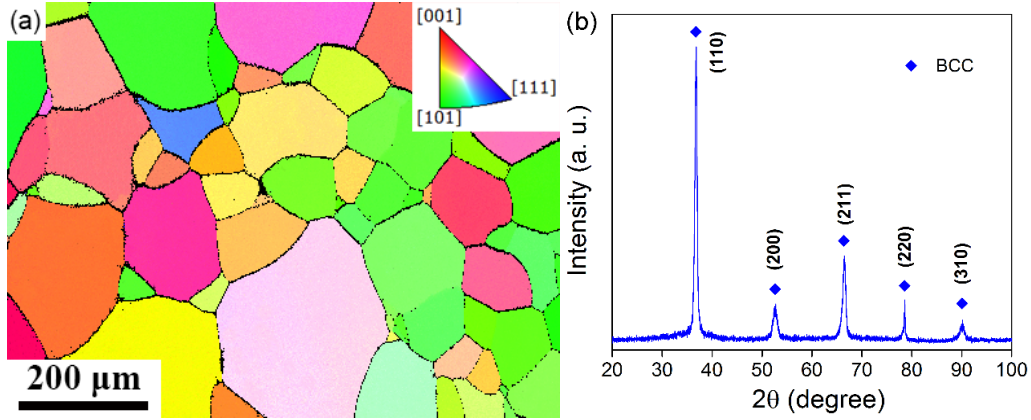


Fig. 2.1 (a) EBSD image and (b) X-ray diffraction patterns of the NbTiZrHf HEA. Indexed peaks indicate a single-phase BCC crystal structure with a lattice parameter of 3.444 Å.

electropolishing to remove surface residual stresses. At least 120 nominally identical indentations were performed under each test condition to permit subsequent statistical analysis.

2.2 Results and discussion

X-ray diffraction patterns obtained from the current NbTiZrHf HEA are shown in Fig. 2.1b, in which diffraction peaks demonstrate a single-phase BCC structure. The lattice parameter was determined to be 3.444 Å. The lattice parameter can also be theoretically estimated from using the rule of mixture (i.e., Vegard's law [68]), $a_{mix} = \sum c_i a_i$, where c_i and a_i are atomic fraction and lattice parameter of the alloying element i , respectively. It is pointed out that Ti, Zr and Hf have a hexagonal close-packed (HCP) structure at room

temperature, but transform to BCC structure at high temperatures. Thus, lattice parameters of BCC-Ti, Zr and Hf at room temperature were estimated from the extrapolated values by using thermal expansion data measured at high temperatures [69]. With these lattice parameters of constituent metals ($a_{Ti}=3.276 \text{ \AA}$, $a_{Zr}=3.582 \text{ \AA}$, $a_{Hf}=3.559 \text{ \AA}$ and $a_{Nb}=3.301 \text{ \AA}$), a_{mix} (3.430 $\text{\AA}$) appears to agree well with the experimental value (3.444 $\text{\AA}$), indicating the rule-of-mixture calculation is actually a reasonable approximation in this particular HEA.

Typical load-displacement (P - h) curve is shown in Fig. 2.2a, which exhibits several discrete bursts of displacement, termed as “pop-ins”, of which the first one is normally regarded as the onset of plasticity. Prior to the first pop-in, the initial elastic portion of the load-displacement curve is well described (red curve in Fig. 2.2a) by the Hertzian elastic contact theory [70]: $P = (4/3)E_r\sqrt{Rh^3}$, where P is the applied indenting load, R is the tip radius of indenter, h is the indentation depth, and $E_r = [(1-\nu_i^2)/E_i + (1-\nu_s^2)/E_s]^{-1}$ is the reduced elastic modulus for a diamond indenter on HEA sample. In the reduced elastic modulus equation, $\nu_i = 0.07$ and $E_i = 1141 \text{ GPa}$ are the Poisson’s ratio and Young’s modulus of the diamond indenter, respectively, $\nu_s = 0.39$ [71] and E_s are the Poisson’s ratio and Young’s modulus of the HEA specimen, respectively. Statistic distribution of more than 480 indentation P - $h^{3/2}$ pairs at pop-ins is given in Fig. 2.2b. From the linearly fit (red line in Fig. 2.2b), the reduced modulus and Young’s modulus are readily deduced to be 83 and 76 GPa, respectively.

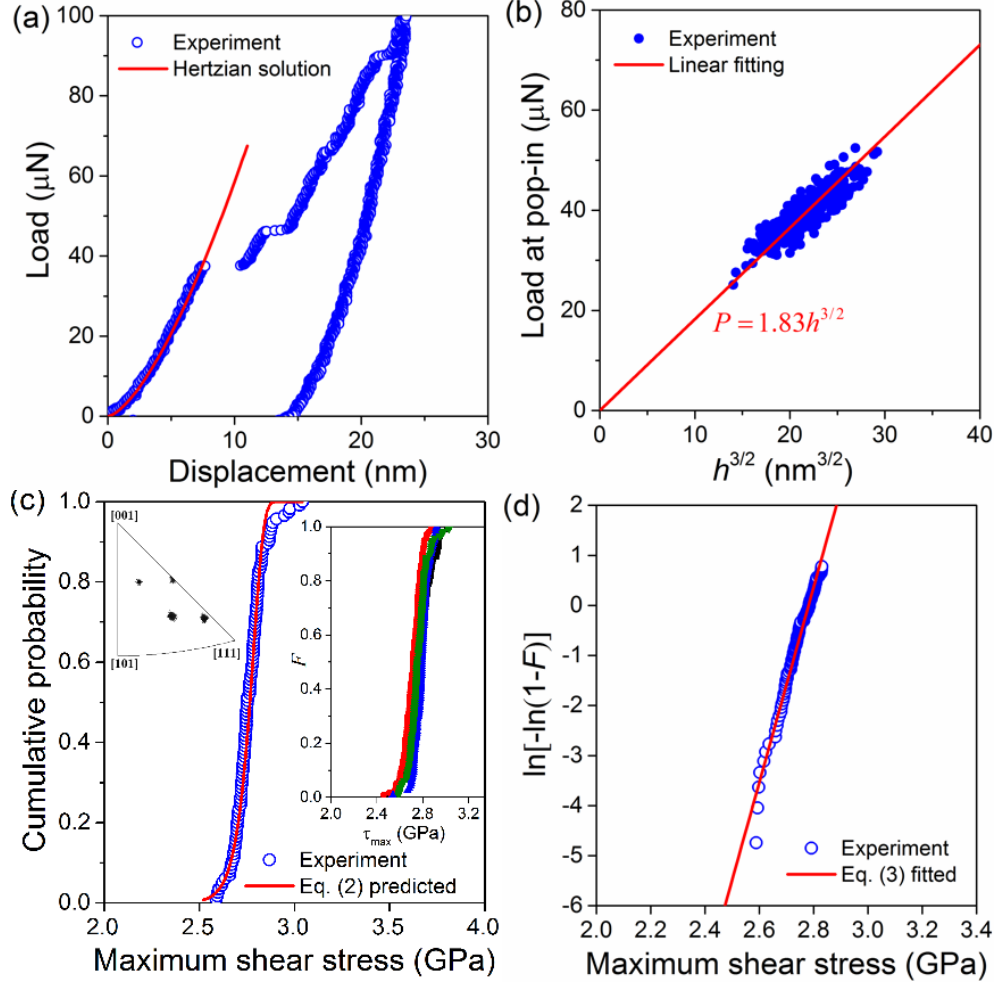


Fig. 2.2 (a) A representative load-displacement curve showing pop-in events; (b) statistics of 480 P - $h^{3/2}$ pairs at pop-ins; (c) cumulative probability of the first pop-in as a function of maximum shear stress, with the right-hand inset showing negligible crystallographic orientation dependence from 4 different grains and the upper left inset showing the corresponding crystal orientation; and (d) the relation between $\ln[-\ln(1-F)]$ and τ_{max} .

According to Hertz's contact theory [70], the maximum shear stress $\tau_{\max}$ beneath a spherical indenter occurs at a location of approximately 0.48 of the contact radius underneath the indenter tip with a value [23]

$$\tau_{\max} = \left(\frac{0.47}{\pi}\right) \left(\frac{4E_r}{3R}\right)^{2/3} P^{1/3} \quad (2.1)$$

Typical cumulative probability distribution against the maximum shear stress at the first pop-in, so-called nanoscale strength distribution (NSD), is shown in Fig. 2.2c. The maximum shear stress is noted to be in the range of 2.5-3.1 GPa, falling within the region of $G/11$ - $G/9$, where G is the shear modulus of NbTiZrHf-HEA (~ 27 GPa, estimated from the Young's modulus). The proximity to the theoretical strength ($\sim G/10$) indicates the onset of plasticity is triggered by a dislocation nucleation mechanism. To investigate the grain orientation effect, the cumulative probability plot for pop-in events from 4 different grains is shown in the right-hand inset of Fig 2.2c. The corresponding crystal orientation of these grains for indentation was shown in the upper left inset. At least 120 identical indentations were performed on each grain. The overlap of NSD curves from different grains suggests insignificant crystallographic orientation dependence for pop-in events in the present BCC-HEA. This insensitive grain orientation dependence is similar to that observed in a FCC-HEA [17].

It is generally recognized that the first nanoindentation pop-in is caused by a dislocation nucleation process [17, 22, 72-74]. The fact that the maximum shear stress required for pop-ins in the present BCC-HEA approaches the theoretical strength also supports this hypothesis. To shed lights on the exact nucleation process, let us evaluate the activation

volume employing a method proposed by Schuh and his co-workers [23, 24], which combines the transition-state theory [75] and Weibull-type statistics [76]. In the analysis, the dislocation nucleation is treated as a thermally activated, stress-assisted process, and the dislocation nucleation rate at any lattice site can be described through an Arrhenius equation $\dot{n} = \dot{n}_0 \cdot \exp(-\Delta\Pi/kT)$, where $\Delta\Pi$ is the stress-biased activation energy for dislocation nucleation ($\Delta\Pi = \varepsilon - \tau\nu^*$), $\dot{n}_0$ the attempt frequency per unit volume, ε the intrinsic nucleation energy barrier, ν^* the activation volume, k the Boltzmann's constant and T the absolute temperature. The local rate can be integrated over the indented volume underneath the indenter (V) to deduce the global nucleation rate ($\dot{N}$) at which pop-in would occur, that is, $\dot{N} = \dot{n}_0 \cdot \exp(-\frac{\varepsilon}{kT}) \cdot \iiint_V \exp(\tau\nu^*/kT) dV$, where V scales with the cube of contact radius $V \approx \pi a^3 = \pi(3PR/4E_r)$. Link this nucleation rate equation to Weibull statistics, the final cumulative probability is $F(t) = 1 - \exp\left(-\int_0^t \dot{N}(t) dt\right)$. With the relationship between load (or stress $\tau_{\max}$, which scales with $P^{1/3}$) and time, the cumulative probability is eventually expressed as (see Ref. [23] for details)

$$F(\tau_{\max}) = 1 - \exp\left[-\frac{9\pi R\eta}{4E_r\dot{P}\alpha^6} \cdot \gamma(\tau_{\max})\right] \quad (2.2)$$

where $\dot{P}$ is the loading rate, $\eta = \dot{N}_0 \cdot \exp(-\varepsilon/kT)$ is the nucleation rate without stress assistance, $\gamma(\tau_{\max})$ is a complex function of $\tau_{\max}$, $\alpha = (0.47/\pi)(4E_r/3R)^{2/3}(\nu^*/kT)$ is a collection of time-independent terms. The activation volume can be further obtained via

the equation of $\ln[-\ln(1-F)] = \alpha P^{1/3} + \beta$, where β is a much weaker function of the load as compared to the first term on the right-hand side [23]. Converting the load into stress in Eq. 2.1 and the parameter α , we get

$$\ln[-\ln(1-F)] = \frac{v^*}{kT} \tau_{\max} + \beta \quad (2.3)$$

It is readily seen that the activation volume can be extracted from Eq. 2.3, thus a plot of $\ln[-\ln(1-F)]$ versus τ is subsequently constructed, as shown in Fig. 2.2d. The activation volume, obtained from the slope of the fitted curve in the figure, is about $70 \text{ \AA}^3$, which corresponds to $1.7 a_0^3$, where a_0 is the lattice parameter of the alloy, or about 3Ω , where Ω is the atomic volume. The parameter β , associated with η , can be also obtained from the intercept of the solid red lines with $\tau = 0$ in Fig. 2d. Once we have all the parameters in Eq. 2.2, the predicted cumulative probability for the first pop-ins can be drawn as the solid red line in Fig. 2.2c. Despite of slight deviations at the two ends of the Heaviside-like curve, which may be attributed to the tip radius effect [77], Eq. 2.2 is quite accurate in describing the pop-in behavior.

There is yet another method to evaluate the activation volume, which involves the measurement of the strain rate sensitivity value, m . To obtain the m value, we conducted tests at different indentation rates. The effect of rate dependence on the onset of plasticity is shown in Fig. 2.3a. It is evident that the maximum shear stress required for the pop-in event increases with increasing loading rate in the present NbTiZrHf-HEA. This is consistent with the notion that, during a stress-assisted thermally activated nucleation

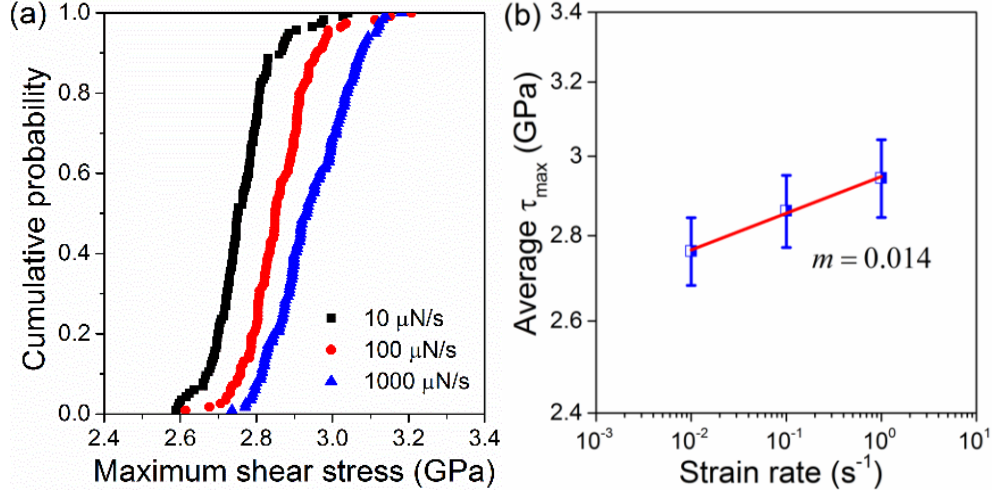


Fig. 2.3 (a) Plot of cumulative probability versus the maximum shear stress at various loading rates, and (b) double logarithmic plot of the average maximum shear stress as a function of the strain rate.

process [22-24], an increased time-at-load would result in a higher probability for a critical thermal fluctuation to occur. This phenomenon has been also observed in many metals, such as BCC-Ta [73], FCC-Pt [22, 23] and HCP-Mg [25]. The strain rate dependence of the present BCC-HEA, however, appears to be less prominent than that in the single-crystal FCC-Pt [22, 23].

The mean maximum shear stress versus strain rate plotted in a double logarithmic scale is given in Fig. 2.3b, where the strain rate sensitivity m is evaluated as 0.014. For a thermally activated process, the activation volume can be simply calculated using the equation $v^* = kT / \tau m$ [78]. Insert the current m value, the activation volume is computed as $2.4 a_0^3$, corresponding to $\sim 5 \Omega$, which is slightly larger than that estimated using the

former statistical method. The discrepancy by using the two methods is acceptable considering the fact that the rate data used in Fig. 2.3b is the loading rate not strain rate, even though they often linearly scale with each other [79, 80]. Furthermore, data variation in delicate nanoindentation measurements is always expected. Nevertheless, both methods yield a similar magnitude of v^* for the pop-in events and, specifically, it is greater than Ω .

Activation volume is a good indicator to reveal the atomic process for dislocation nucleation. Activation volume data for some BCC and FCC materials [17, 22, 26] are summarized on Table 2.1. It is noted that the activation volume for the conventional FCC and BCC metals is in the order of Ω , suggesting the migration of individual point-like defect (e.g., vacancy or impurity). In contrast, the activation volumes for both FCC-HEA (NiCoCrFeMn) [17] and the present BCC-HEA are approximately 3-5 Ω , indicating that dislocation nucleation in HEAs is relatively difficult, involving cooperative migration of several atoms.

Table 2.1 Summary of activation volume for the pop-in in some BCC and FCC materials.

Materials	FCC-Pt [22]	FCC-Ni [26]	BCC-Mo [26]	FCC-HEA [17]	BCC-HEA
Activation volume (Ω)	~0.5	~1	~1	~3	~3-5

In addition to having a slightly higher activation volume in current BCC-NbTiZrHf HEA as compared to FCC-NiCoCrFeMn HEA, it is of interest to compare the activation energy for dislocation nucleation between the two types of HEAs. Accumulative probability curves, thus the pop-in behavior, of the current BCC-HEA and previously studied FCC-HEA are directly compared in Fig. 2.4. In the figure, the shear stress in the x-axis is presented in a normalized form, since these two materials have significantly different values of shear modulus. It is apparent that the curve for the BCC-HEA is much steeper as compared to that for the FCC-HEA. According to continuum dislocation analysis [81, 82], the activation energy ΔU for dislocation nucleation can be calculated via the following equation $\Delta U = A(1 - \tau_{app} / \tau_{th})^n$ [83, 84], where τ_{app} is the applied shear stress, τ_{th} is the theoretical stress corresponding to the upper bound of the maximum shear stress, the exponent n (in the range of 1.5–4.5) and the pre-factor A (in the range of $(5-15)Gb^3$ with b being the Burgers vector) are fitting parameters [83-85]. For a first-order approximation, the cumulative probability for pop-in is given by,

$$F = 1 - q = 1 - \exp[-\dot{\gamma}_0 \cdot V \cdot \int_0^{P_{pop-in}} \exp(-\Delta U / kT) dP / \dot{P}] \quad [26, 84, 85],$$

where V in the equation is the indented volume and q is the survivability (i.e., the probability that no pop-in occurs), or

$$F = 1 - \exp \left[-\dot{\gamma}_0 \cdot V \cdot \frac{\tau_{th} \cdot kT}{nA(1 - \tau_{app} / \tau_{th})^{n-1} \cdot \dot{\tau}} \cdot \exp \left(-\frac{A(1 - \tau_{app} / \tau_{th})^n}{kT} \right) \right] \quad (2.4)$$

This equation can nicely fit the experimental curves for the BCC-HEA, as shown in Fig. 2.4. In this case, the fitted cumulative probability yields reasonable values of $n = 3.5$,

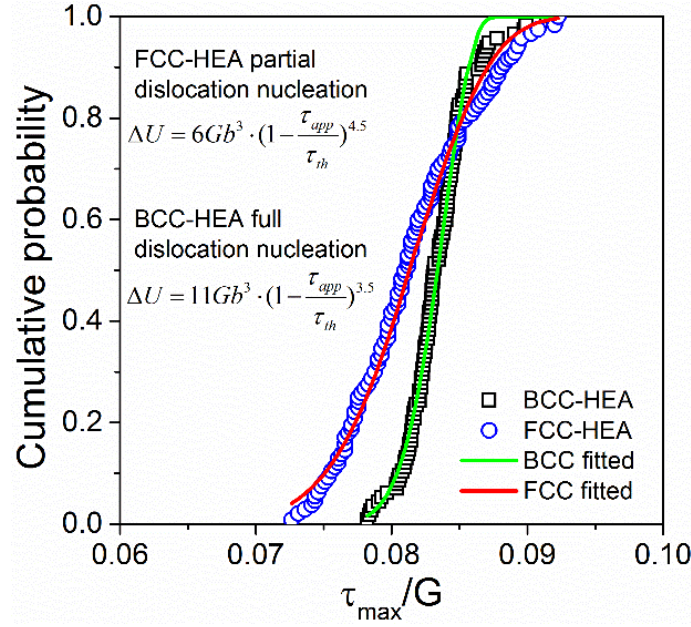


Fig. 2.4 Plot of cumulative probability of pop-in versus normalized shear stress for the current BCC-NbTiZrHf HEA and a FCC-NiCoCrFeMn HEA [17], and solid curves are fittings of Eq. 2.4.

$A \approx 11Gb^3$ with Burgers vector corresponding to the magnitude of $\langle 111 \rangle/2$ full dislocation. However, in the case of FCC-HEA, only using $\langle 11\bar{2} \rangle/6$ partial dislocation would yield reasonable values of $n = 4.5$, $A \approx 6Gb^3$. Fitting the cumulative probability curve with Burgers vector $\langle 110 \rangle/2$ would not yield reasonable values of n and A (specifically, $n = 14$ and $A \approx 3Gb^3$ are both beyond the reasonable ranges [83-85]). This suggests that dislocation nucleation in BCC-HEA is a full dislocation, whereas a partial dislocation is favored in FCC-HEA. Consequently, a steeper $f - \tau/G$ curve for the BCC-

HEA is a result of higher activation energy for full dislocation nucleation. In comparison, for the FCC-HEA, lower activation energy is required for partial dislocation nucleation. Similar observation has been reported before in conventional BCC-Mo and FCC-Ni metals [26].

2.3 Conclusions

In summary, we have conducted a series of instrumented nanoindentation tests to investigate dislocation nucleation in a single-phase BCC-NbTiZrHf HEA. The maximum shear stress required for dislocation nucleation in the alloy is about 1/10 of the shear modulus. Differed from conventional metals, the activation volume for dislocation nucleation in the present HEA is estimated to be ~3-5 atomic volumes, indicative of a process of cooperative migration of multiple atoms. The activation energy for pop-ins in the current BCC-HEA is also found to be much higher than that in the typical FCC-HEA, which is attributable to the fact that the nucleation of full dislocation is favored in BCC-HEAs, whereas nucleation of partial dislocation is energetically favored in FCC-HEAs.

Chapter 3. Effect of interstitial solutes on the incipient plasticity of NbTiZrHf HEAs

3.1 Methods

3.1.1 Experimental procedure

Ingots with nominal compositions of NbTiZrHf, (NbTiZrHf)₉₈O₂ and (NbTiZrHf)₉₈N₂ (at%) were prepared by arc-melting a mixture of the constituent pure metals (purity > 99.9 wt%), TiN (99.9 wt%) and TiO₂ (99.9 wt%) in an argon atmosphere purified by Ti-getter. The ingots were re-melted at least four times in high purity argon atmosphere to ensure chemical homogeneity before being drop-cast in a water-cooled copper mold. The as-cast ingots were then homogenized at 1290 °C for 24 h and cold rolled with 80% reduction in thickness. The rolled plates were additionally annealed at 1200 °C for 30 mins to remove the deformation substructure to obtain a recrystallized, equiaxed microstructure.

Phases and lattice parameter of each of the alloys were determined by synchrotron X-ray powder diffraction. Fine powders were ground from the annealed plates using an electric diamond grinding wheel saw. Synchrotron X-ray characterization was carried out at the 11-ID-B beamline with an X-ray wavelength of 0.2114 Å at the Advanced Photon Source at Argonne National Laboratory, USA. Microstructure and morphology of current alloys were characterized using a Zeiss Auriga scanning electron microscope (SEM) equipped with a Bruker QUANTAX electron backscatter diffraction (EBSD) system. Samples for EBSD examinations were prepared by initial mechanical polishing, followed

by electrochemical polishing in a mixed solution of 6% perchloric acid + 30% n-butyl alcohol + 64% methyl at 30 V at room temperature.

Instrumented nanoindentation experiments were conducted to investigate the pop-in behavior using a Berkovich diamond tip with an effective tip radius of ~ 270 nm in a Hysitron Triboindenter (Hysitron, Inc., USA) at room temperature. Indentations were performed at a constant load of 100 μN with a loading time of 10 s in load-controlled mode. Testes were made at a 5 μm interval to exclude possible overlap of the deformed zone produced by the adjacent indentations. Four grains were randomly selected and 121 nominally identical indentations on each grain were carried out to allow reliable statistical analysis of the pop-in behavior. To assess rate effect on pop-in behavior, various loading rates spanning two orders of magnitude (10-1000 $\mu\text{N/s}$) were applied. Additional nanoindentation hardness (deep indentation) tests were also performed at a high load of 8000 μN with various rates of 0.02, 0.1, 0.5, 2 s^{-1} . The test samples for nanoindentation were prepared by electrochemical polishing mentioned above.

3.1.2 Computational methodology

First-principles DFT calculations were conducted to obtain the energetics and electronic structures of the present HEAs. The calculations were performed using the projector-augmented wave (PAW) method [86] as implemented in the Vienna ab initio Simulation Package (VASP) [87]. Special quasi-random structures (SQSs) supercell with 36 atoms was used to model the TiZrHfNb HEA which served as the base reference alloy state. Such SQSs were constructed to make the cluster correlations approach the expected value in a

random atomic arrangement as closely as possible for a given structure size [88]. To investigate the effect of interstitial oxygen and nitrogen on the HEA, one interstitial atom of oxygen or nitrogen was inserted at the octahedral site. All calculations were performed with spin-polarization and initialized in a ferromagnetic spin state. A reciprocal space discretization of 25 k -points per $\text{\AA}^{-1}$ was applied, and the convergence criteria were set as 10^{-6} eV for electronic loops.

3.2 Results

3.2.1 Microstructure characterization

Synchrotron high energy X-ray powder diffraction patterns of the annealed base HEA as well as the interstitial-doped O-2 and N-2 HEAs are shown in Fig. 3.1a, which demonstrates a single BCC crystal structure without any secondary phase in these samples, also suggesting that the oxygen/nitrogen atoms are present as interstitials in the crystalline lattice. Based on the Rietveld method [89], the lattice parameters (a) of the base, O-2, and N-2 HEAs are determined to be 3.4357 $\text{\AA}$, 3.4376 $\text{\AA}$, and 3.4388 $\text{\AA}$, respectively; this is summarized in Fig. 3.1b and Table 3.1. It is evident that interstitial nitrogen and oxygen slightly increase the lattice parameter and the increment is larger for nitrogen than that for oxygen, which is probably associated with slightly larger atomic size of nitrogen.

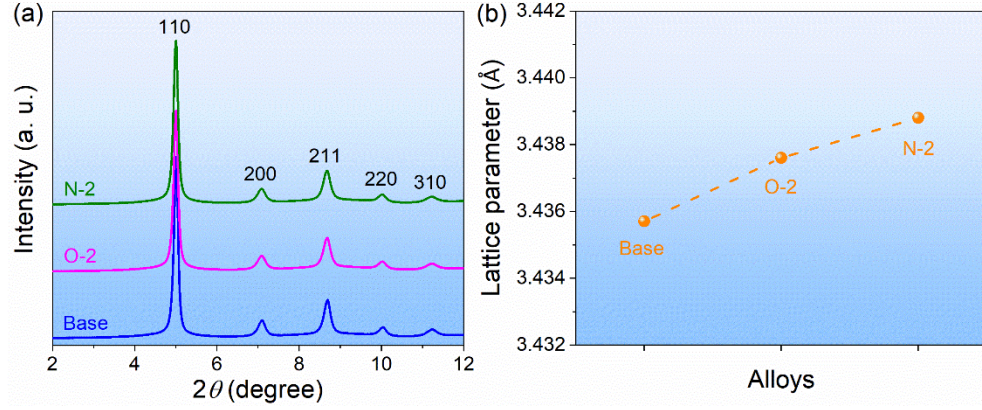


Fig. 3.1 (a) Synchrotron high energy X-ray powder diffraction patterns and (b) lattice parameters of the annealed equiatomic NbTiZrHf and interstitially doped HEAs.

Table 3.1 Summary of lattice constants (a), reduced moduli (E_r), Young's moduli (E), and shear moduli (G) of NbTiZrHf and the interstitial-doped HEAs.

Alloys	a (Å)	E_r (GPa)	E (GPa)	G (GPa)
Base HEA	3.4357	83.0	75.9	27.3
O-2 HEA	3.4376	88.1	80.9	29.1
N-2 HEA	3.4388	92.0	84.9	30.5

Grain morphology and the corresponding size distribution in the annealed NbTiZrHf and interstitial-doped alloys characterized by EBSD are shown in Fig. 3.2, which reveals that current alloys consist of equiaxed grains with sizes varying in a wide range from 30 to 350 μm . Whereas NbTiZrHf has an average grain size of $\sim 130 \mu\text{m}$, the O-2 HEA has a slightly larger average grain size of $\sim 160 \mu\text{m}$ and the N-2 exhibits somewhat finer grain size of $\sim 105 \mu\text{m}$. This indicates that the interstitial oxygen/nitrogen has only minor effect on recrystallization and grain growth during annealing.

3.2.2 The first pop-in and maximum shear stress

Typical load-displacement (P - h) curves at shallow indentation for the base, O-2, and N-2 HEAs are shown in Fig. 3.3. For clarity, each curve is displaced along the x-axis and only the loading portion is presented. It is evident that the P - h curves for all three alloys exhibit “pop-ins”, i.e., displacement bursts. The first pop-in, which is indicative of the onset of yielding or incipient plasticity, occurs typically at a depth of $\sim 10 \text{ nm}$. Prior to the first pop-in, the initial portion of the load-displacement curves is the elastic response, can be described by Hertzian contact theory [70]

$$P = \frac{4}{3} E_r R^{1/2} h^{3/2} \quad (3.1)$$

where P is the applied indenting load, R the tip radius of indenter ($\sim 270 \text{ nm}$), h the indentation depth, E_r the reduced elastic modulus for a diamond indenter on HEA samples:

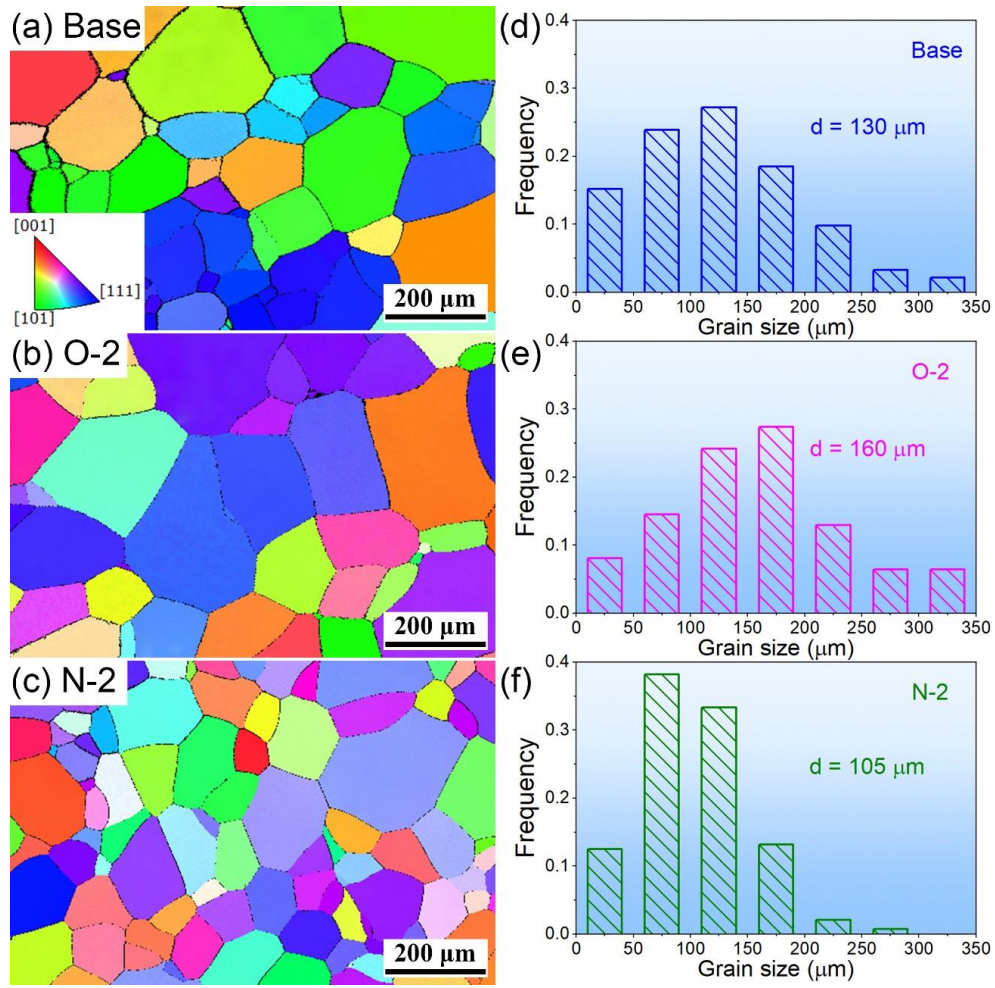


Fig. 3.2 (a-c) Electron back-scattering diffraction (EBSD) images, and (d-f) grain size distribution of the NbTiZrHf base, O-2, and N-2 HEAs, respectively.

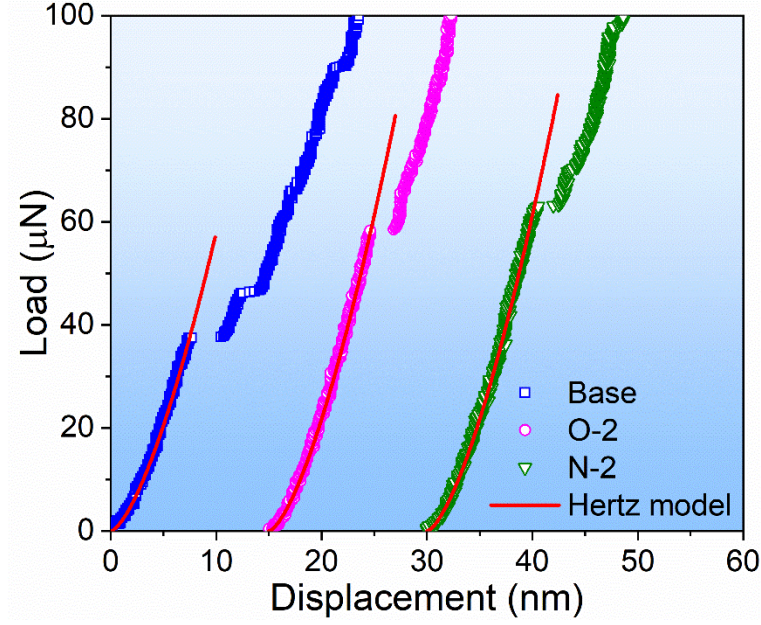


Fig. 3.3 Typical load-displacement curves at shallow indentation depth showing pop-in events of NbTiZrHf and interstitially doped HEAs.

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s} \quad (3.2)$$

where ν is Poisson's ratio, E is Young's modulus, and the subscripts i and s stand for properties of the diamond indenter and HEA samples. As shown in Fig. 3.3, the fitted red curves using the Hertz model agree well with the experimental results in the elastic region. It is noted that all P-h curves (2178 indentations in total) obtained in this study exhibit a clear pop-in, which appears to be affected by the presence of interstitial solutes. Specifically, as shown in Fig. 3.3, the critical load at the first pop-in in the interstitial-doped alloys are much higher than that in the interstitial-free base HEA, suggesting a solution

hardening effect. Further discussion regarding this solution hardening in the pop-in load is in Section 3.3.

The reduced modulus can be readily derived from loading portion of the P-h curve according to Eq. 3.1. Statistical data collection of $P-h^{3/2}$ pairs at the first pop-in from 484 indentations in four randomly selected grains are presented in Fig. 3.4. As seen in the figure, the pop-in loads for NbTiZrHf are in the range of 25-50 μN , but shift to much higher loads of 40-80 μN for O-2 HEA and 45-90 μN for N-2 HEA. The $P-h^{3/2}$ pairs can be well fitted by Eq. 3.1, as shown in Fig. 3.4, from which the reduced moduli (E_r) can be readily deduced as 83.0, 88.1, and 92.0 GPa for NbTiZrHf, O-2, and N-2 HEAs, respectively. Insert the elastic parameters for diamond indenter ($\nu_i = 0.07$ and $E_i = 1141$ GPa) and the HEA samples ($\nu_s = 0.39$ [71]) into Eq. 3.2, the Young's moduli (E) for the three materials are summarized in Table 3.1. Here, the Poisson's ratio of 0.39 for NbTiZrHf was measured using resonant ultrasound spectroscopy in a previous study [71] and the same value was used for the interstitial-doped alloys. Shear moduli (G) were estimated using $G = E / 2(1+\nu)$ and also included in Table 3.1. Evidently, the addition of oxygen or nitrogen to NbTiZrHf slightly increases the elastic moduli, and nitrogen has somewhat a larger effect than oxygen.

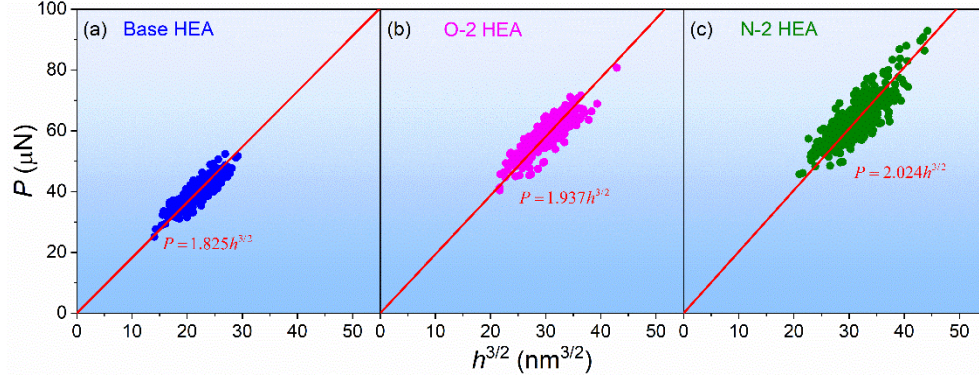


Fig. 3.4 Statistics of P - $h^{3/2}$ pairs at first pop-ins of NbTiZrHf and interstitial-doped HEAs.

The maximum shear stress τ_{max} at the first pop-in event can be estimated using Hertz's contact theory [70]:

$$\tau_{max} = \frac{0.47}{\pi} \left(\frac{4E_r}{3R} \right)^{2/3} P^{1/3} \quad (3.3)$$

where the maximum shear stress τ_{max} is located at a depth of approximately 0.48 of the contact radius underneath the indenter tip. To statistically describe the stochastic characteristic of the first pop-ins, the cumulative probability distributions as a function of maximum shear stress for the present three HEAs are summarized in Fig. 3.5a. These distributions, the so-called nanoscale strength distributions (NSD), give the spread of measured strength at which the maximum shear stress beneath the indenter that triggers the displacement bursts. It is readily observed that the cumulative probability curves for the interstitial-containing alloys shift towards higher stresses, and the shift is larger for the nitrogen-doped than that for oxygen-doped sample. Specifically, the τ_{max} for NbTiZrHf is in the range of 2.5-3.1 GPa, while it varies in the ranges of 3.0-3.5 GPa and 3.1-3.8 GPa

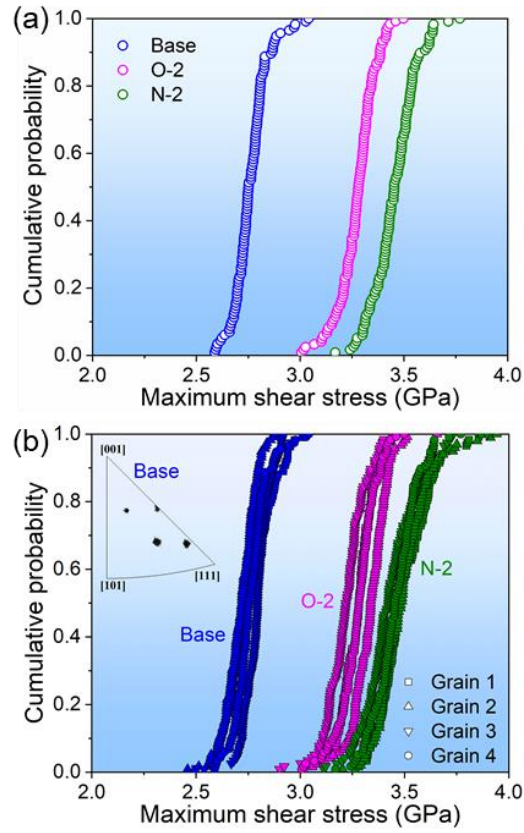


Fig. 3.5 (a) Cumulative probability of the first pop-in as a function of maximum shear stress of NbTiZrHf and interstitially doped HEAs. (b) A similar plot containing four randomly selected grains for each alloy, which shows insignificant grain orientation dependence.

for O-2 and N-2 samples, respectively. This reaffirms the hardening effect on incipient plasticity caused by interstitial doping. It is also noted that the maximum shear stresses are $(1/11-1/9)G$ for NbTiZrHf and $(1/10-1/8)G$ for the O-2 and N-2 samples, all approach the theoretical strength of $\sim G/10$, suggesting it is a result of dislocation nucleation. Further discussion of the effect of interstitial solutes on the initiation of plasticity will be presented in Section 3.3.

We also performed pop-in tests on four different grains to evaluate possible grain orientation effect and the results are given in Fig. 3.5b. Although the O-2 HEA shows a slightly larger orientation dependence, NSD curves for these four different grain orientations essentially overlap in all samples. It may therefore conclude that pop-in events in the present HEAs are insensitive to the crystallographic orientation.

3.2.3 Rate-dependent pop-in and activation volume

To evaluate the rate dependence of the dislocation nucleation process in the present interstitial-doped alloys, pop-in tests were performed at various loading rates, and measured results are displayed in Figs. 3.6a-3.6c for NbTiZrHf, O-2, and N-2 HEAs, respectively. The NSD curves for the interstitial-doped alloys are always located at higher maximum shear stress at any loading rate. Also, the maximum shear stress required to trigger the pop-in appears to increase with increasing loading rate for all three alloys, consistent with the stress-biased, thermally activated nucleation process [22, 23]. A higher loading rate allows less time to produce the pop-in event, thus lowers the probability to overcome the energy barrier by thermal fluctuations. Consequently, a higher shear stress is

needed to nucleate dislocations. Similar results have been reported in several metallic alloys, including FCC-NiCoCrFeMn HEA [17], BCC-Ti₆₀(AlCrVNb)₄₀ MEA [90], BCC-Ta [73], FCC-Pt [22], and HCP-Mg [25].

To understand the underpinned physics associated with the pop-in events, we conduct an analysis based on the transition-state theory combined with Weibull-type statistics proposed by Schuh et al. [22, 23]. In this analysis, the cumulative probability $F(P)$ is correlated with the indentation pop-in load P via the expression:

$$\ln[-\ln(1-F(P))] = \alpha P^{1/3} + \beta \quad (3.4)$$

where the parameter β is far more weakly dependent on P as compared to the first term to the right-hand side [23]. The parameter α is a collection of time-independent term, which can be correlated with the activation volume v^*

$$v_{pop-in}^* = \frac{\pi}{0.47} \left(\frac{3R}{4E_r} \right)^{2/3} kT \cdot \alpha \quad (3.5)$$

In other words, the activation volume can be extracted from the slope α in the $\ln[-\ln(1-F)]$ vs. $P^{1/3}$ plots (described in Eq. 3.4), as shown in Figs. 3.6d-3.6f for NbTiZrHf and interstitial-doped O-2 and N-2 HEAs, respectively. Following the above procedure, the average activation volumes are determined to be 67 Å³ (3.3 Ω or 2.5 b^3) for NbTiZrHf, 54 Å³ (2.7 Ω or 2.0 b^3) for O-2 HEA, and 48 Å³ (2.4 Ω or 1.8 b^3) for N-2 HEA. Here, the Ω is the atomic volume, and b is the Burger's vector. These activation volume values are tabulated in Table 3.2.

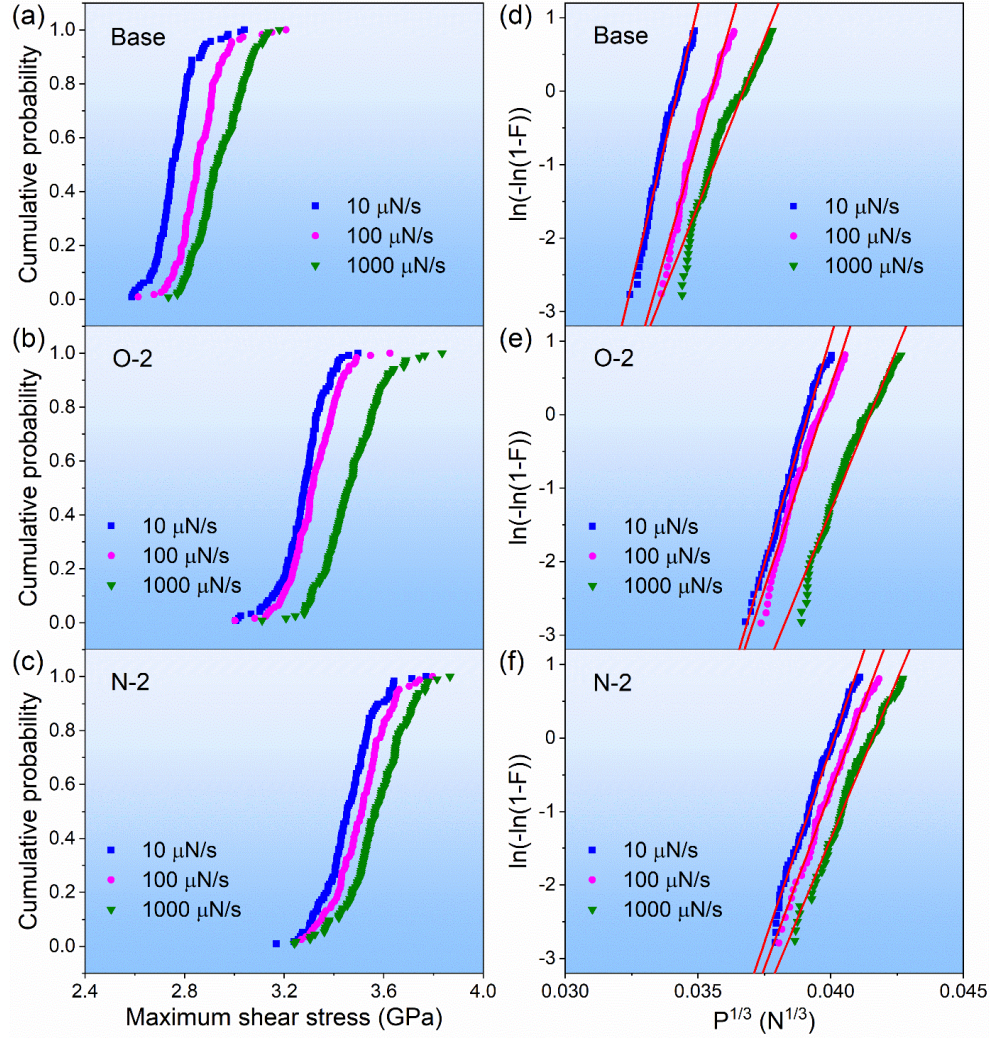


Fig. 3.6 (a-c) Nanoscale strength distributions (NSD) at various lading rates, and (d-f) the corresponding relation between $\ln[\ln(1-F)^{-1}]$ and $P^{1/3}$ of the NbTiZrHf base, O-2, and N-2 HEAs, respectively.

The activation volume is usually a good indicator to reveal the atomic process for dislocation nucleation [17, 22-25, 32, 91]. For easy discussion, we also include activation volumes reported for a variety of conventional metals/alloys and HEAs [17, 23, 25, 32, 90, 92-94] in Table 3.2. It is readily seen that the activation volume for well-annealed conventional pure metals and dilute alloys, irrespective of their crystal structures, is relatively small in the range of only 0.3-0.7 Ω , suggesting it is associated with the migration of individual point-like defect, such as vacancy and impurity. By contrast, the activation volume for well-annealed HEAs is much larger in the range of 2-4 Ω , indicating that dislocation nucleation in HEAs involves cooperative migration of multiple atoms. It is particularly noted in the table that the as-cast TiZrNbTa(Mo) HEAs and Ti₆₀(AlCrVNb)₄₀ MEA exhibit lower activation volumes than the fully annealed ones. It is probably due to the fact that as-cast materials usually contain a higher population of defects (e.g., vacancy or dislocations), thus easier to facilitate dislocation nucleation. Also noted in Table 3.2 is that interstitial-doping seems to have only a small effect on the activation volume. In fact, activation volume values are always at a magnitude of 2-3 Ω , indicating a similar process governing dislocation nucleation in the present three HEAs.

Table 3.2 Activation volume of dislocation nucleation characterized by nanoindentation pop-in tests in a variety of conventional metals/alloys and HEAs.

Materials	Material type	Processing	$v^*_{\text{pop-in}} (\Omega/b^3)$	References
Pt	FCC-pure metal	As-received	0.7/0.5	[23]
Ni	FCC-pure metal	Annealed	0.4/0.3	[92]
Cr	BCC-pure metal	Annealed	0.4/0.3	[93]
Mg	HCP-pure metal	Annealed	0.3-0.4/0.2-0.3	[25]
Mg-0.3 at.% X *	HCP-dilute alloys	Annealed	0.3-0.6/0.2-0.4	[25]
Ti ₆₀ (AlCrVNb) ₄₀	BCC-MEA	As-cast	0.9/0.7	[90]
TiZrNbTa	BCC-HEA	As-cast	1.6/1.2	[94]
TiZrNbTaMo	BCC-HEA	As-cast	1.7/1.3	[94]
NiCoCrFeMn	FCC-HEA	Annealed	2.9/2.0	[17]
(NiCoCrFeMn) _{100-x} H _x	FCC-HEA	Homogenized	2-4/1.4-2.8	[32]
NbTiZrHf	BCC-HEA	Annealed	3.3/2.5	Present work
(NbTiZrHf) ₉₈ O ₂	BCC-HEA	Annealed	2.7/2.0	Present work
(NbTiZrHf) ₉₈ N ₂	BCC-HEA	Annealed	2.4/1.8	Present work

* X = Al, Ca, Li, Y or Zn

3.2.4 Differentiating mechanisms between pop-in and hardness

It is intriguing to differentiate the kinetic processes between the indentation pop-in (yielding in a perfect crystal) and conventional yielding (onset of dislocation motion in ordinary crystals containing defects). In the former, the process is controlled by dislocation nucleation (e.g. dislocation loop formation), whilst the latter is controlled by the bypass of dislocation over obstacles. To separate them, we made efforts to examine the effect of interstitial solutes on hardness (deep indentation) and its rate-dependence to compare with that obtained from pop-in tests (shallow indentation). Representative load-displacement curves for NbTiZrHf and interstitially doped HEAs tested at deep indentation are given in Fig. 3.7a. At the fixed maximum load of 8 mN, NbTiZrHf exhibits the largest indentation depth ($\sim 300\text{nm}$), followed by O-2 and N-2 HEAs, showing considerable hardening effect due to the presence of interstitial oxygen and nitrogen ($\Delta H_O = 0.41\text{ GPa}$ and $\Delta H_N = 0.56\text{ GPa}$). Hardening during plastic deformation in metallic materials are generally associated with the interaction of dislocations with microstructural inhomogeneities, which lead to various mechanisms, such as solid-solution hardening, dislocation hardening, grain-boundary hardening, and precipitation hardening. In this study, all nanoindentation hardness tests were conducted within grain interiors (far away from grain boundaries) of well-annealed specimens, so grain-boundary hardening and dislocation hardening are excluded. Synchrotron high energy X-ray diffraction (Fig. 3.1) reveals the absence of secondary phase, thus also rules out precipitation hardening. Consequently, interstitial solid-solution hardening appears to be the only possible mechanism for hardness

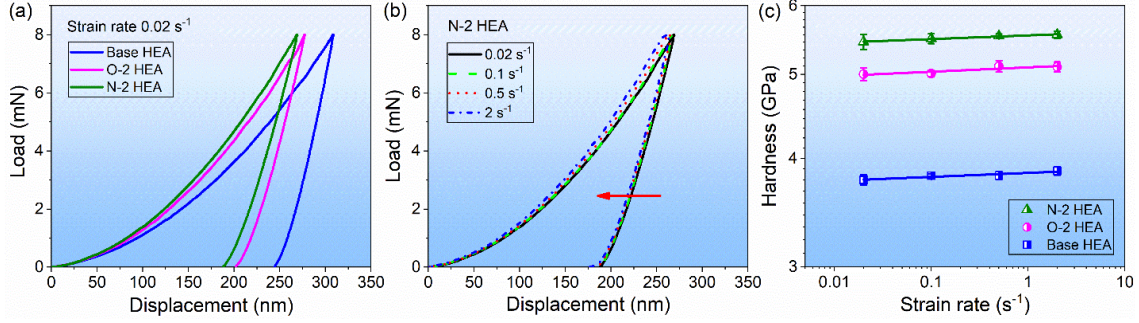


Fig. 3.7 (a) Representative load-displacement curves at deep indentation for present NbTiZrHf and interstitially doped HEAs at strain rates of 0.02 s⁻¹. (b) Load-displacement curves for N-2 HEA at various strain rate. The direction of red arrows represents the gradual increase in strain rate. (c) The double-log plot of nanoindentation hardness as a function of strain rate of present HEAs.

enhancement in the O-2 or N-2 alloys. Apply the classical interstitial solid-solution strengthening model by Fleischer [3, 95, 96], specifically, tetragonal distortion generated by interstitial solutes in BCC lattice which inhibits dislocation motion, the increment in hardness ΔH is estimated as

$$\Delta H = 3^{3/2} \frac{G \Delta \epsilon c^{1/2}}{3} \quad (3.6)$$

where G is shear modulus (Table 3.1), $\Delta \epsilon$ denotes the difference between the longitudinal and transverse strain of the tetragonal distortion, and c (2% for both O-2 and N-2 HEAs) is the atomic concentration of interstitial atoms. By inserting appropriate parameters, $\Delta \epsilon$ are calculated to be 0.17 and 0.22 for O-2 and N-2 HEAs, respectively. These $\Delta \epsilon$ values

are, in fact, comparable to that reported in other materials containing tetragonal distortions at room temperature [3, 95-97], suggesting the occurrence of traditional interstitial solid-solution hardening.

To further investigate the rate dependence of hardness, load-displacement curves at various loading rates for the N-2 HEA are shown in Fig. 3.7b, in which the direction of arrows marks increasing strain rate. The indentation depth is noted to slightly decrease as the strain rate increases in the N-2 HEA specimens, indicative of increase in hardness. Curves obtained from NbTiZrHf and O-2 HEAs also follow a similar trend, but are not included here for brevity. Hardness of the three alloys as a function of strain rate is further plotted in a double-logarithmic graph in Fig. 3.7c, from which the strain rate sensitivity m is directly obtained from the slope. For a thermally activated deformation process, the strain rate sensitivity is linked to activation volume v^* via [98, 99]

$$v_{hardness}^* = \frac{3\sqrt{3}kT}{mH} \quad (3.7)$$

where H is the hardness from nanoindentation tests, k and T have the same meaning as previously mentioned. The activation volumes for the present three HEAs are found to fall in the range of $\sim 30-45 b^3$, as listed in Table 3.3. These values are in the typical range of $10-100 b^3$, indicating that deformation during hardness tests is probably similar to thermally activated kink-pair mechanism in coarse-grained BCC metals and alloys [100]. However, the activation volume obtained for pop-in is only approximately $2-3 b^3$, over one order of magnitude smaller than that obtained from the hardness tests. This distinct difference reveals that the mechanism for indentation pop-in, which is associated with the

dislocation nucleation in a small, defect-free region is indeed quite different from that for hardness measurement, which involves interactions of moving dislocations with crystalline defects in a relatively large deformation volume. We may, therefore, conclude that strength enhancement during pop-in in the interstitial-doped samples is not attributed to the classical interstitial solid-solution strengthening mechanism; other mechanism prevails.

Table 3.3 Activation volumes obtained from pop-in and hardness tests for NbTiZrHf and interstitial-doped solid-solution HEAs.

Alloys	$v^*_{pop-in} (\text{\AA}^3 / \Omega / b^3)$	$v^*_{hardness} (\text{\AA}^3 / \Omega / b^3)$
Base HEA	67/3.3/2.5	1200/59.1/45.5
O-2 HEA	54/2.7/2.0	830/40.9/31.5
N-2 HEA	48/2.4/1.8	900/44.4/34.2

3.3 Discussion

Several mechanisms have been proposed to describe the effect of interstitials on the pop-in stress [32, 34, 101, 102]. For example, the critical load at which the pop-in occurred during nanoindentation was found to be much higher in the ultralow carbon steel than that in interstitial free steel [34]. It was argued that the interstitial carbon atoms could lower the dislocation mobility and shorten the length of Frank-Read source for dislocation multiplication, so that a higher shear stress is needed to activate the Frank-Read source according to $\tau_{cr} = Gb/l_{cr}$, where τ_{cr} and l_{cr} are the critical shear stress and spacing of Frank-Read source, respectively. In other words, the model suggests pop-in is caused by a sudden multiplication of mobile dislocations. In our pop-in study, indentation depth was shallow (~ 10 nm), thus only a small volume of material was probed (estimated to be $V \sim \pi a_c^3$ [23], where $a_c = \sqrt{Rh} \sim 50$ nm is the contact radius). Our previous TEM images taken from annealed NbTiZrHf also revealed the absence of dislocation prior to plastic deformation [14]. Also, based on the fact the dislocation density is typically about 10^6 - 10^8 cm⁻² for well-annealed metals and alloys [102, 103], the dislocation spacing would be about 1-10 μ m, which is far greater than the dimension of the stressed zone underneath the indenter (~ 50 nm). In such case, probability that the stressed zone underneath the fine indenter tip contains pre-existing dislocation would be extremely low. Therefore, we may comfortably conclude that the pop-in stress is determined by dislocation nucleation, and dislocation multiplication from Frank-Read sources is obviously not pertinent to our case.

It is noted that the Frank-Read sources scenario is also difficult to reconcile recent observation that the presence of hydrogen in FCC NiCoCrFeMn HEA significantly lowered the critical shear stress for the onset of yielding [32]. In this case, it was argued that hydrogen could induce the formation of stable hydrogen-vacancy complexes and increase vacancy concentration to promote the heterogeneous dislocation nucleation [104, 105]. Since the oxygen or nitrogen addition can also form their respective interstitial-vacancy complexes due to vacancy trapping [106-109], in a similar fashion, a reduced critical shear stress at pop-in might also occur in our interstitials-containing HEAs. However, this expectation is contrary to our results of higher pop-in loads/stresses. In fact, another recent atomistic molecular dynamics (MD) simulation study showed that hydrogen actually had no direct effect on dislocation nucleation during nanoindentation in Ni and Pd metals [101]. Therefore, it appears that there is no universal agreement on the effect of interstitials on the pop-in stress during nanoindentation. To clarify the exact role of interstitial oxygen/nitrogen on the pop-in stress in the current HEAs, we subsequently carry out the following DFT calculations.

Two types of slip systems are considered in the DFT calculations of ideal shear strength, i.e., the $\{110\}\langle 111 \rangle$ and $\{112\}\langle 111 \rangle$ shear deformations, as shown in Fig. 3.8. Affine shear deformation $[110]$ is applied so that all the atoms in the simulation cell are deformed along the shear direction. The coordinate system of supercells is constructed with basis vectors of $\langle 1\bar{1}0 \rangle$, $\langle 111 \rangle$ and $\langle 11\bar{2} \rangle$, with $\langle 111 \rangle$ pointing in the slip direction.

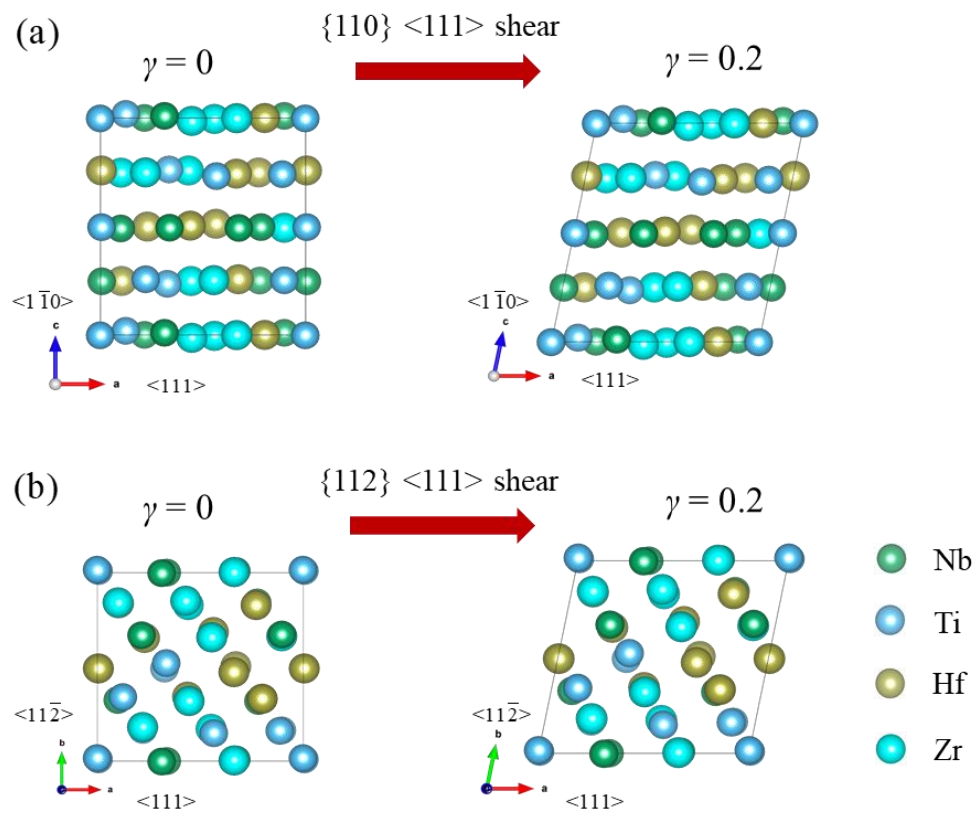


Fig. 3.8 Structures used for calculating the energy and stress of present HEAs under (a) $\{110\}\langle 111 \rangle$ and (b) $\{112\}\langle 111 \rangle$ shear deformations.

The calculated energy as a function of shear strain for the $\{110\}\langle 111\rangle$ and $\{112\}\langle 111\rangle$ shears in the present NbTiZrHf and interstitially doped HEAs is shown in Figs. 3.9a and 3.9b. The energy shows a sinusoidal-like evolution with the strain, and interstitials oxygen/nitrogen increase the energy ($N-2 > O-2 > \text{base HEAs}$) for both slip systems. The corresponding shear stress τ can be obtained by differentiating the energy curves with respect to the strain γ , given by

$$\tau = \frac{1}{V} \frac{\partial U}{\partial \gamma} \quad (3.8)$$

where U and V are the energy and volume at a given strain, respectively. The maximum in the shear stress-strain curve is the ideal shear strength that a perfect crystal becomes unstable when this stress is exceeded [111, 112]. The shear stress-strain curves under both shear deformations are displayed in Figs. 3.9c and 3.9d. It can be readily observed that shear stresses generally follow $N-2 > O-2 > \text{base HEAs}$, except the strain range 0.4-0.6 for the slip system $\{112\}\langle 111\rangle$. It is worth noting that both energy and shear stress for the present HEAs under the $\{110\}\langle 111\rangle$ shear deformation are much lower than those under $\{112\}\langle 111\rangle$ shear, indicating the $\{110\}\langle 111\rangle$ shear is the easy shear path, thus the dominating slip system.

The above DFT calculations clearly reveal that interstitial oxygen/nitrogen improve both energy and ideal shear strength of the NbTiZrHf HEA, and nitrogen doping produces a slightly larger effect than oxygen doping. This is consistent with the nanoindentation result, namely, pop-in loads/stresses are, in an ascending order, NbTiZrHf < O-2 < N-2 HEAs (Figs. 3.3 and 3.5).

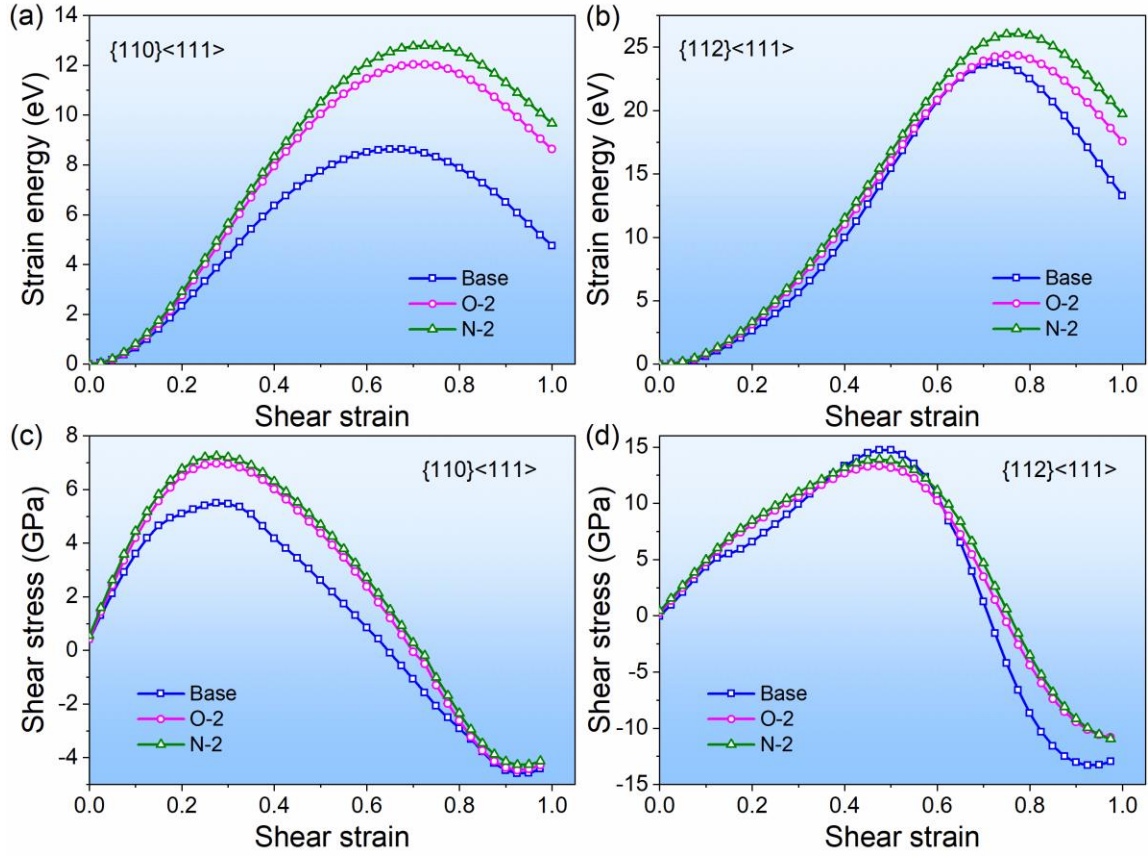


Fig. 3.9 Strain energy as a function of shear strain under (a) $\{110\}\langle 111 \rangle$ and (b) $\{112\}\langle 111 \rangle$ shear deformations for NbTiZrHf and interstitially doped HEAs. The corresponding shear stress as a function of shear strain under (c) $\{110\}\langle 111 \rangle$ and (d) $\{112\}\langle 111 \rangle$ shear deformations.

To further understand the origin of enhanced energy and ideal shear strength in oxygen/nitrogen doped HEAs, we analyze the local charge transfer between oxygen/nitrogen and metallic atoms in the first neighboring coordination shell. As the bader charge reflects the number of electrons localized near a certain atomic core [53, 54], it can serve as a convenient tool to analyze the charge transfer among atoms. The calculated bader charge of the local structure is tabulated in Table 3.4. For each of the chemical species, the number of valence electrons considered in DFT calculations are denoted as “total e-included”. The calculated bader charge of all corresponding atoms for current three HEA systems are listed for comparison. It is readily observed that the bader charges of all metallic atoms for O-2 and N-2 HEAs are lowered when compared with that for the base HEA. On the other hand, oxygen or nitrogen atom attracts significant electrons from their local environment, which yields larger bader charge than their respective neutral state. Specifically, the bader charges of oxygen and nitrogen atoms increase by $1.49 e^-$ and $1.94 e^-$ for O-2 and N-2 HEAs, respectively. In other words, interstitials draw more charges from their six nearest neighbored metallic atoms in N-2 HEA than that in O-2 HEA. The charge transfer between oxygen/nitrogen and nearby metallic atoms is anticipated to transform the original metal-metal bond to ionic-like metal-oxygen or metal-nitrogen bonds, which results in enhanced cohesion. Such interstitial-metal matrix interaction is readily visualized in the plot of charge density isosurface in Fig. 3.10.

Table 3.4 Calculated bader charge for oxygen/nitrogen atom and its first neighboring coordination shell. The total valence electrons considered in the DFT calculations are denoted as “total e- included”.

System	Hf1	Hf2	Zr1	Zr2	Ti1	Nb1	O	N
Total e ⁻ included	10.0	10.0	12.0	12.0	10.0	11.0	6.0	5.0
Base	9.78	9.88	11.95	11.96	9.66	11.68	N/A	N/A
O-2	9.44	9.58	11.93	11.48	9.63	11.34	7.49	N/A
N-2	9.35	9.45	11.76	11.39	9.47	11.19	N/A	6.94

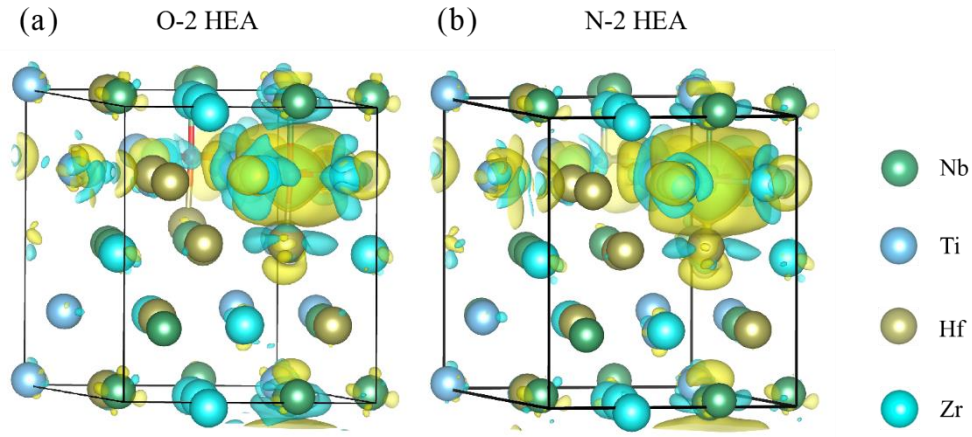


Fig. 3. 10 Calculated 3D charge density for (a) oxygen and (b) nitrogen nearest neighboring atoms.

As a result of enhanced cohesion, when applying shear deformation, higher energy and stress are required to break the metal-oxygen or metal-nitrogen bond in comparison with that in the interstitial-free alloy, as displayed in Fig. 3.9. Also, a larger charge transfer in the N-2 HEA as compared to that in O-2 HEA results in higher energy and ideal shear strength. These calculations are all in line with the results obtained from nanoindentation pop-in experiments. We can also estimate the number of the ionic-like metal-oxygen or metal nitrogen complexes ($N_{\text{metal-O/N}}$) within the indented volume as

$$N_{\text{metal-O/N}} = \frac{\pi a_c^3 (\text{stressed volume})}{a^3 (\text{volume/unit cell})} \cdot 2 (\text{atoms/unit cell}) \cdot 2\% (\text{O/N concentration}) \quad (3.9)$$

where a_c and a have the same meaning and values as previously mentioned, $2(\pi a_c^3/a^3)$ includes all atom sites in the stressed volume, and a uniform distribution of oxygen/nitrogen atoms is assumed. In our case, $N_{\text{metal-O/N}}$ is estimated to be of the order of 10^5 in the stressed volume. Obviously, such a large amount of ionic-like metal-oxygen or metal-nitrogen complexes in the indented volume is expected to induce a notable effect on the dislocation nucleation in the present interstitially doped HEAs.

In summary, our DFT calculations reveal that improved pop-in stress in the current interstitial oxygen/nitrogen-containing HEAs is not attributed to the modification of dislocation nucleation process, but rather associated with charge transfer between interstitials and their surrounding metallic atoms, which results in ionic-like metal-oxygen or metal-nitrogen bonds with enhanced cohesion.

3.4 Conclusions

In this chapter, I conducted a series of instrumented nanoindentation tests, in combination with quantitative statistical analysis and density functional theory (DFT) calculations, to investigate the effect of interstitial oxygen and nitrogen on incipient plasticity and dislocation nucleation in well-annealed BCC-NbTiZrHf HEAs. Several key results and observations are summarized as follows.

1. The presence of interstitial oxygen and nitrogen atoms could both increase the pop-in load/stress at which dislocations are nucleated, and nitrogen has a slightly stronger hardening effect.
2. The maximum shear stress required to trigger dislocation nucleation is $\sim 1/11$ - $1/8$ of the shear modulus, approaching the theoretical strength, and appears to be relatively insensitive to grain orientation. The observed indentation-induced incipient plasticity is predominantly mediated by $\{110\}\langle 111 \rangle$ slip system in the currently studied HEAs.
3. The onset of yielding exhibits significant rate-dependence - a higher loading rate yields a higher pop-in load/stress. The activation volumes for dislocation nucleation (i.e., pop-in) in the present three HEAs are estimated to be ~ 1.8 - $2.5 b^3$, corresponding to 2-3 atomic volumes, indicating the nucleation process involves cooperative migration of multiple constituent atoms.
4. In comparison, the activation volumes obtained from deep indentation during hardness test are much larger at ~ 30 - $45 b^3$, implying a different mechanism. Specifically, hardness increase caused by interstitial oxygen or nitrogen addition is a result of the traditional solid-

solution strengthening, i.e., dislocation moving through crystalline lattice distorted by the interstitials.

5. The first-principles calculations reveal that the interstitial (oxygen/nitrogen) and its surrounding neighboring metals form ionic-like complexes. These metal-interstitial complexes improve lattice cohesion due to significant charge transfer between the interstitial and the neighboring metals, which is responsible for the observed increase in the critical shear stress required for dislocation nucleation in the interstitially doped HEAs.

Chapter 4. Tribological behavior of a BCC NbTiZrHf HEA studied using nanoscratch technique

4.1 Experimental

The equiatomic quaternary NbTiZrHf used in this study was prepared by arc-melting using pure metals (purity higher than 99.9 wt.%) in a high-purity argon atmosphere. To ensure chemical homogeneity, the ingot was re-melted at least four times before drop-casting into a water-cooled copper mold. The as-cast ingot was subsequently homogenized at 1290 °C for 24 h, followed by cold rolling with 80% reduction in thickness. The rolled plate was further annealed at 1200 °C for 30 mins to remove deformation substructure to obtain a recrystallized, equiaxed microstructure.

Crystal structure and lattice parameter of the HEA were measured using X-ray diffraction (XRD) with Cu-K α radiation. A scanning electron microscope (SEM) equipped with back-scattered electron (BSE) detector and energy dispersive X-ray spectrometry (EDX) was used to examine the microstructure and determine the chemical compositions. Orientations of grains were identified using electron back-scattered diffraction (EBSD) in a Zeiss Auriga SEM. The hardness was measured using Hysitron Triboindenter (Hysitron, Inc., USA) with a Berkovich indenter at a peak load of 8000 μ N and loading time of 5s under load-controlled mode. At least 64 indents were performed to obtain the average value. Samples for SEM/EDX and EBSD characterization, indentation, and scratch tests were all prepared by initial mechanical polishing, followed by electropolishing.

Nanoscratch tests were carried out at room temperature ($\sim 22\text{ }^{\circ}\text{C}$) employing also a Hysitron Triboindenter equipped with a 2D transducer which was attached with a normal force/displacement sensor and two lateral force/displacement sensors. A 90 degrees' cono-spherical diamond tip with an effective radius $\sim 600\text{ nm}$ was used for scratching. Scratch tests were conducted in either ramping load or constant load mode. In the case of ramping load scratching, applied normal force was linearly increased from $0\text{ }\mu\text{N}$ to $1000\text{ }\mu\text{N}$; whereas for the constant load tests, normal forces in the range of $10\text{--}1000\text{ }\mu\text{N}$ were applied (15 different normal loads were used in total). Both scratch modes were carried out at a scratch speed of $0.5\text{ }\mu\text{m/s}$ over a scratch distance of $8\text{ }\mu\text{m}$. To prevent possible overlap of the deformed zone induced by adjacent scratches, tests were conducted at a $20\text{-}\mu\text{m}$ separation distance. At least three scratches were performed at each testing condition to ensure reproducibility. To investigate scratch rate effect, scratch tests were also conducted at speeds of $0.01, 0.1, 1\text{ }\mu\text{m/s}$. The roughness of the initial surface and surface profile of the scratched specimens were characterized using scanning probe microscopy (SPM) integrated in the Hysitron Triboindenter. A sharp cube corner diamond tip with an effective radius of $\sim 80\text{ nm}$ was used for the SPM imaging in order to get a high resolution. The wear volume, which is the volume removed by the indenter below the original surface, was measured from the topography profile, and the wear rate (wear volume divided by scratch distance) was calculated. The morphologies of scratched surfaces were observed via SEM as well. The dislocation structure underneath the scratched surface was characterized using a Zeiss Libra 200 MC transmission electron microscopy (TEM) and the cross-sectional foil

of the scratch track region produced with a force of 1000 μN was prepared by the focused ion beam (FIB) lift-out technique. In the present study, pure Nb and Nb-based Nb-5.4Hf-2Ti alloy (commercially known as C103 alloy) were also tested in order to compare their nanotribological properties with that of the current BCC-HEA.

4.2 Results

4.2.1 Microstructure and hardness

X-ray diffraction pattern of the current NbTiZrHf HEA is shown in Fig. 4.1a, which demonstrates a single-phase BCC structure. The lattice parameter was determined to be 3.444 Å, close to the predicted value of 3.430 Å according to the rule of mixture [91]. The microstructure of the alloy (Fig. 4.1b) consists of equiaxed grains with sizes varying from 100 to 300 μm after recrystallization. Orientations of grains were also examined by EBSD, wherein a large grain with $[3\bar{1}0]$ orientation (as circled in red) was selected for nanoscratch tests to minimize the possible effect of grain boundary or orientation. The BSE image (Fig. 4.1c) shows three adjacent grains. Alloying elements are uniformly distributed in the microstructure - no elemental segregations or additional phase was observed - within the resolution limit of EDX analysis, as shown in Fig. 4.1d. In fact, the measured chemical composition (inset of Fig. 4.1c) is close to the nominally equiatomic composition. A high resolution TEM (HRTEM) image (Fig. 4.2a) was taken along the zone axis of $[111]$. The selected area electron diffraction (SAED) pattern in the upper right inset confirms the HEA is single-phase. A lattice constant of 3.445 Å is in good agreement with the XRD result.

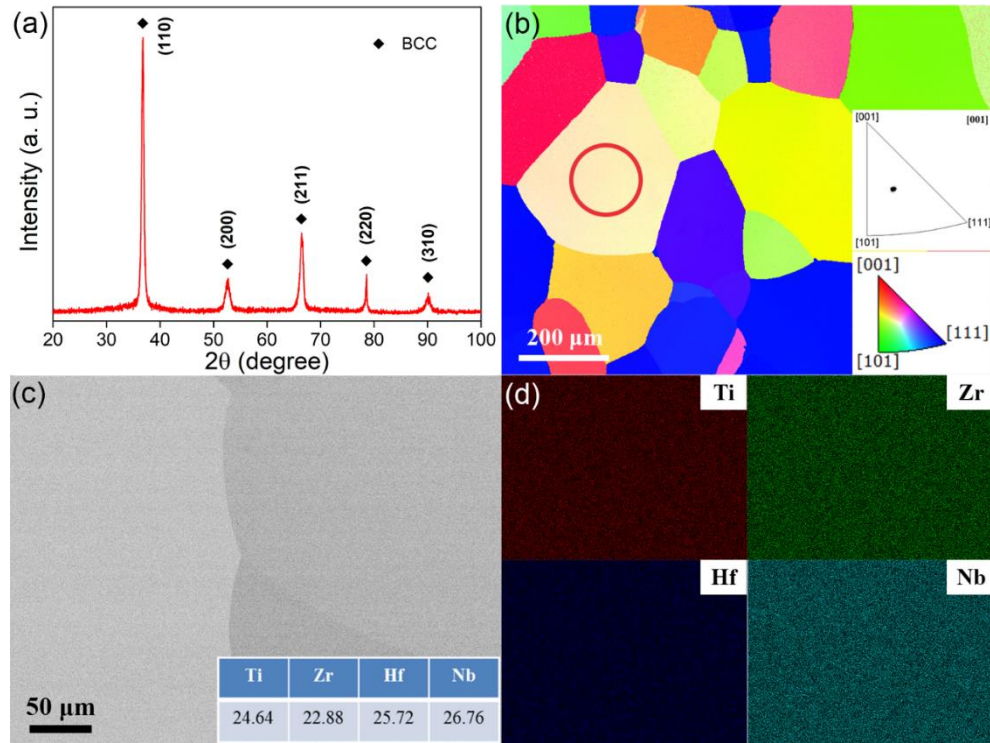


Fig. 4.1 (a) XRD pattern of NbTiZrHf HEA indicating a single-phase BCC structure. (b) EBSD image, in which the selected grain for nanoscratch tests was circled. The orientation of the selected grain is indicated in the inverse pole figure in the inset. (c) A representative of SEM/BSE image, with inset showing the measured chemical compositions in at.%. (d) The corresponding EDX mappings of the four constituent elements.

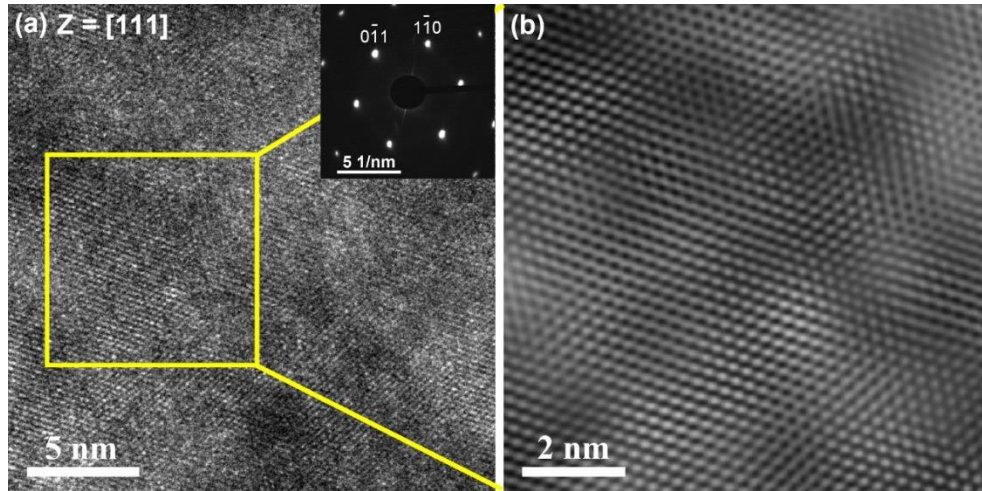


Fig. 4.2 (a) A typical HRTEM image of the NbTiZrHf HEA along [111] zone axis, with the upper right inset showing the SAED pattern. (b) The IFFT image corresponding to the area of the yellow square in (a).

The local lattice distortion is also observed in the inverse fast Fourier transform (IFFT) image (Fig. 4.2b), which is one of the key features of HEAs.

Typical load-displacement curves for pure Nb, C103 and HEAs are plotted together in Fig. 4.3. The HEA has the highest hardness value, followed by C103 and Nb, and these values are listed in Table 4.1. C103 alloy has a higher hardness than that of Nb due to substitutional solid-solution strengthening by Ti and Hf solute atoms. In the case of HEA, however, the strengthening has been attributed to the intrinsic strength (or lattice friction stress) of multicomponent, concentrated alloys [46, 47]. Solid-solution strengthening has also been invoked to rationalize the high strength in equiatomic alloys [113]. Both theories conclude NbTiZrHf HEA has a higher strength than C103 and Nb.

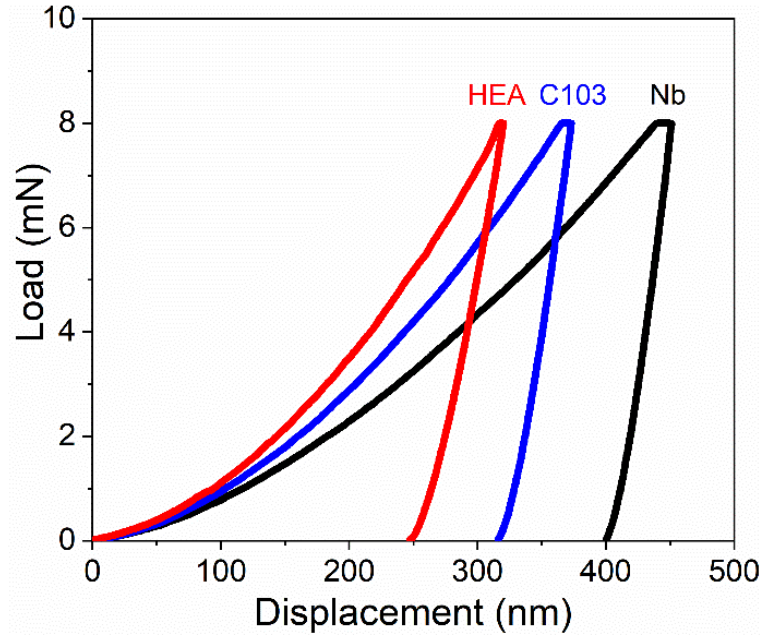


Fig. 4.3 Representative load-displacement curves for pure Nb, C103, and NbTiZrHf HEAs.

Table 4.1 Summary of hardness, COF and wear resistance measured by indentation and scratch tests.

Sample	Hardness (GPa)	Steady-state COF	Wear resistance (10^{10} Pa)
Nb	1.69 ± 0.06	~ 0.27	4.02
C103	2.55 ± 0.15	~ 0.24	5.46
NbTiZrHf	3.68 ± 0.06	~ 0.16	7.81

SEM images of the scratched surface under ramping load mode are shown in Figs. 4.4a and 4.4b. The scratched groove becomes wider and deeper as the applied normal force continuously increases from 0 to 1000 μN . No scratch trace is detected in the initial portion (white arrow in Fig. 4.4a), indicative of a purely elastic deformation at low applied force. On the other hand, under constant load mode at a fixed load (for example, 500 and 1000 μN in Figs. 4.4c-4.4f), scratched traces are clearly revealed in the entire scratched process and the width and depth of scratched grooves remain essentially unchanged. In fact, we carried out a series of constant load scratches in the range of 10-1000 μN and found that when the applied normal force $F_n < 150 \mu\text{N}$, no scratch mark could be traced, which was consistent with the results observed during ramping load mode at low applied force (Fig. 4.4a). It is known that abrasive wear can generally occur by three different mechanisms: plowing, wedge formation and microcutting [40, 114, 115]. In this current case, scratched morphologies from both ramping and constant load modes exhibit remarkably smooth grooves without the presence of either microcracks or chips/debris. Material pile-up along groove edges is also shown in SEM images, suggesting that ductile plowing is the dominant abrasive wear mechanism. This result is in good accord with the fact that the present HEA is ductile with a high tensile elongation of $\sim 15\%$ [116]. Enlarged SEM images (Figs. 4.4b, 4.4d and 4.4f) show that parallel slip bands are formed from the edges of the scratched trace, but the material pile-up along the two sides of the scratched trace is not exactly symmetrical. The nonsymmetrical pile-up has often been observed during scratching and, it was probably due to slight misalignment between the tip and the sample surface [36].

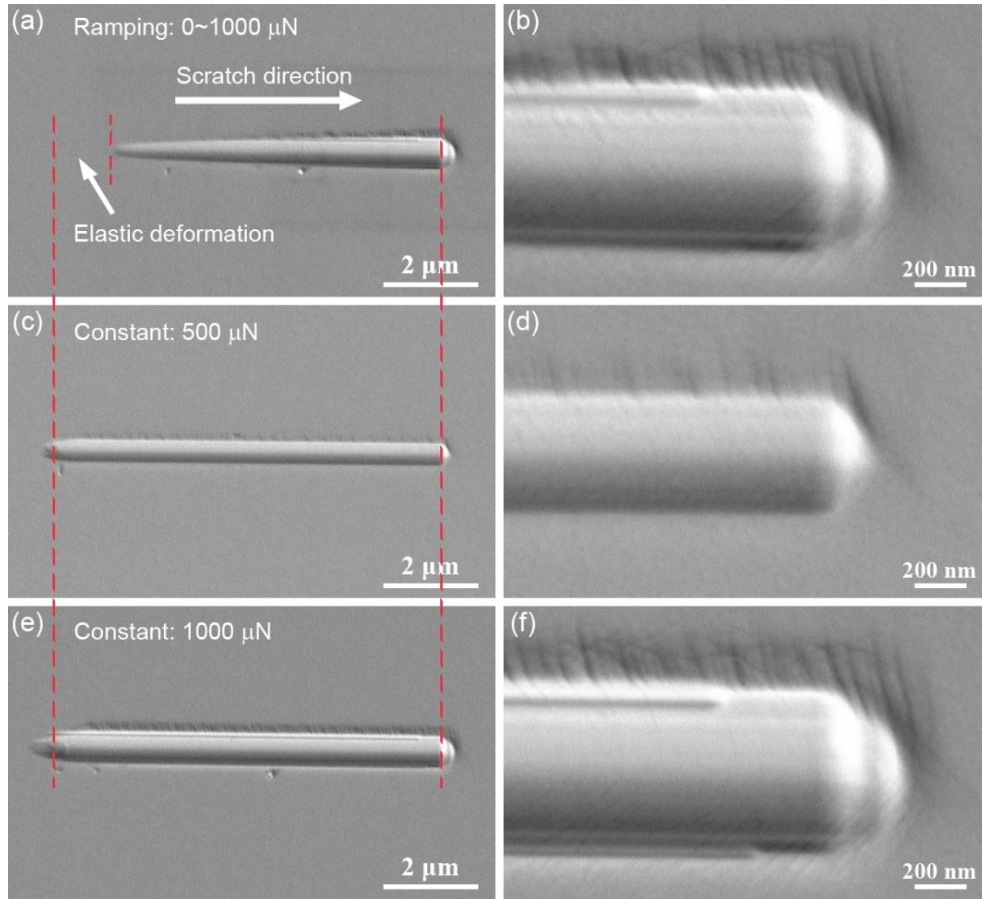


Fig. 4.4 SEM images of scratched morphologies of the HEA under (a, b) ramping load mode from 0 to 1000 μN , (c, d) constant load mode at 500 μN , and (e, f) constant load mode at 1000 μN . (b), (d) and (f) are the enlarged images of the end parts of scratched tracks in (a), (c) and (e), respectively.

To examine subsurface microstructural changes in scratched HEA, TEM lamella was cut from the cross-sectional wear track using FIB lift-out technique. As shown in Fig. 4.5a and 4.5b, the bright field TEM images taken from two different diffraction vectors clearly reveal the presence of dislocations but without deformation twinning, suggesting that the plastic deformation during nanoscratching is dislocation controlled. At least two different dislocation patterns were visible under the two diffraction vectors, indicating multiple slip systems were activated. To further examine the dislocation features, HRTEM (Fig. 4.5c) was also employed at the deformed region. The IFFT image (Fig. 4.5d) apparently shows severely distorted lattice and high density of dislocations due to plastic deformation during nanoscratching. Several different $1/2 \langle 111 \rangle$ types of dislocations determined from the Burgers circuits confirm the multiple slip systems accommodating the plastic deformation during nanoscratch tests. The dislocation density, measured by statistically analyzing the dislocation number from 16 images with the size of Fig. 4.5d, is estimated to be $\sim 3 \times 10^{16} \text{ m}^{-2}$, which is in the same range as that in a cold-worked metal. In comparison, the dislocations in the starting fully annealed sample are not observed in Fig. 4.2b, indicative of much lower dislocation density (in the order of 10^{12} m^{-2} for fully annealed metals [103]).

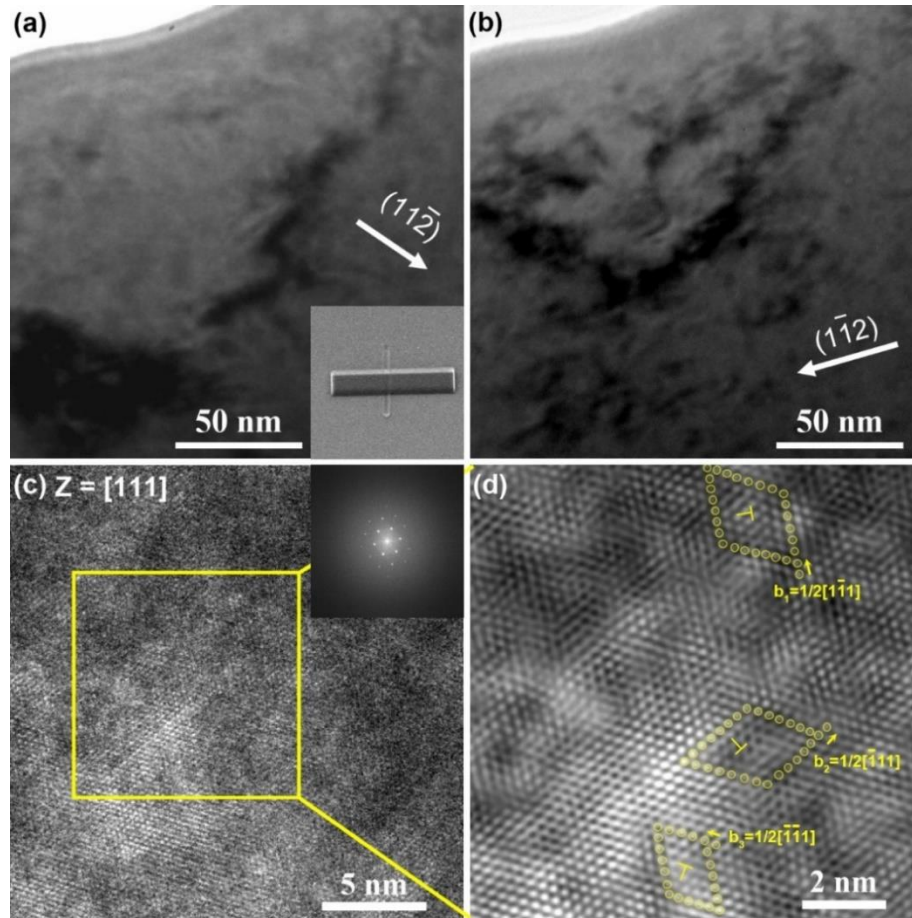


Fig. 4.5 Bright field TEM images of the cross-sectional scratched track region using different diffraction vectors of (a) $g_1 = (11\bar{2})$ and (b) $g_2 = (1\bar{1}2)$ showing the dislocation structure. The lower right inset in (a) shows the location where the TEM lamella was taken. (c) The HRTEM image along zone axis of $[111]$, with upper right inset showing the FFT pattern. (d) The IFFT image, corresponding to the area of the yellow square in (c), shows severely distorted lattice and high density of dislocations with Burgers vectors of $1/2 \langle 111 \rangle$.

4.2.2 Friction behavior during nanoscratching

The results from scratch test at loads ramping from 0 to 1000 μN are summarized in Fig. 4.6. Scratch depth vs. lateral displacement graph is presented in Fig. 4.6a, showing surface profiles before (blue), during (red), and after (green) the scratch test. For easy discussion, the normal force is also included in the figure (black line). The pre-scratch and post-scratch profiles were produced at an extremely low applied normal force of 2 μN to minimize artifacts. A slight fluctuation of the pre-scratch curve suggests that the initial surface of the test sample is relatively smooth. During scratching, the penetration depth increases monotonically with increasing normal force and eventually reaches a maximum value of ~ 70 nm, as shown in Fig. 4.6a. Although the imposed normal force is linearly increased with the scratch distance, the penetration depth does not follow the linear relationship. The depth difference between the pre- and post-scratch is simply a result of elastic recovery of the scratched surface. It is noted that the initial portion of the post-scratch curve is fully recovered when the normal force is less than ~ 180 μN (green curve and black arrows in Fig. 4.6a), indicative of a purely elastic deformation, consistent with the SEM image of scratched surface shown in Fig. 4.4a.

It is of interest to note that the critical load of ~ 180 μN for the elastic-plastic transition is, in fact, much lower than that measured from the static nanoindentation. Specifically, the onset of plasticity under static nanoindentation occurs at an average applied load of ~ 500 μN , as shown in Fig. 4.7a. The discrepancy can be explained by the Hamilton analytical model for subsurface stresses beneath a sliding spherical contact [117]. In an indentation

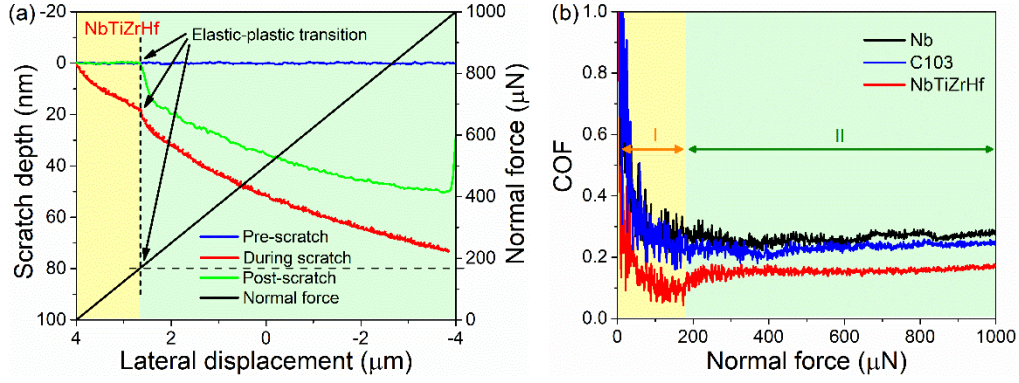


Fig. 4.6 (a) Surface profiles of the HEA, and (b) COF as a function of normal force of Nb, C103 and HEAs under ramping load mode. Regimes I and II respectively correspond to elastic and plastic dominated deformations.

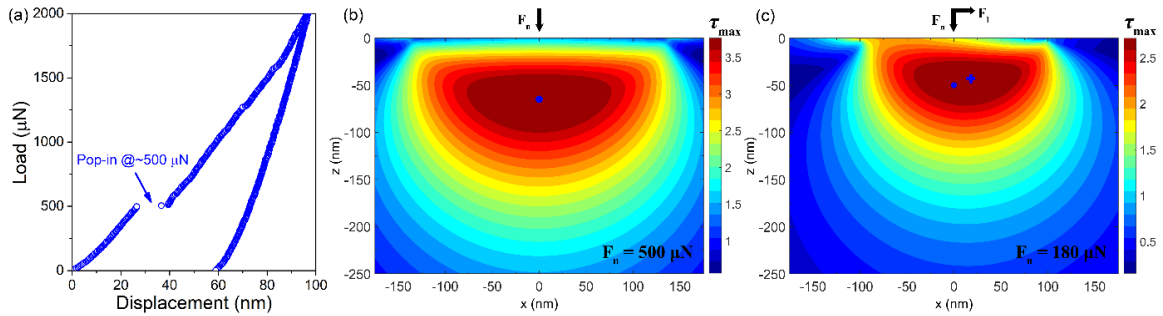


Fig. 4.7 (a) A representative load-displacement curve showing pop-in event in nanoindentation test of the HEA. The distribution of maximum shear stress calculated based on elastic contact theory in the cases of (b) nanoindentation and (c) nanoscratch. The blue circles denote the positions of highest stress under only normal force applied, and the blue plus symbol corresponds to the one under normal loading plus sliding.

test with only a normal force applied, as shown in Fig. 4.7b, the distribution of maximum shear stress ($\tau_{\max}$) below the contact is axially symmetric as the tip-sample contact reduces to the well-known Hertzian model for sphere on plate contact. The critical shear stress for the onset of plasticity is located beneath the contact surface at a depth of $\sim 1/2$ of the indenter-sample contact radius (blue circle in Fig. 4.7b). As a tangential force is applied during scratching, however, the stress field becomes asymmetric, as shown in Fig. 4.7c. The introduction of friction has several effects. It adds a compressive stress to the front edge and intensifies the tensile stress at the rear edge of the contact region; the maximum subsurface shear stress is increased and the original position of the maximum stress (blue circle in Fig. 4.7c) shifts in the scratching direction and rises closer to the surface (blue plus symbol in Fig. 4.7c). As a consequence, yielding will occur at lower loads.

The coefficient of friction (COF), α , against applied normal force for the NbTiZrHf sample tested under the ramping load mode is shown in Fig. 4.6b; for comparison, results from the pure Nb and C103 alloy are also included in the figure. Here, the COF is simply defined as the ratio of the lateral force over normal force during the scratch. It is readily seen that COFs for all three samples exhibit two distinct regimes, consistent with the results in Figs. 4.4a and 4.6a. When the normal force is low, the deformation is purely elastic and, in this regime (Regime I), the COF decreases rapidly as the normal force increases until about 180 μN . By contrast, at a high normal force, plowing deformation begins to dominate and, in this regime (Regime II), COFs of all three samples reach their respective steady-state values. In this regime, whereas Nb and C103 alloy have comparable COF values of

~0.27 and ~0.24, respectively, the current HEA has a much lower value of ~0.16 (Table 4.1). The low COF value in the HEA is, in fact, comparable to those of many harder amorphous alloys [37]. As the steady state does not begin until the load is around 220 μN , while the critical load for the elastic-plastic transition is only about 180 μN , the overall COF curve appears to have an “undershoot” in the elastic regime (Fig. 4.6b).

To allow better analysis of the friction behavior, nanoscratch tests were also carried out at constant loads ranging from 10 to 1000 μN . For brevity, only one of the tests with a normal load of 500 μN is presented. The depth profile of the scratch track (Fig. 4.8a) shows that both the penetration depth (~50 nm) and residual depth (~30 nm) remain essentially constant. The measured COF also exhibits a steady-state value of ~0.16 through the entire scratch process (Fig. 4.8b), except for the initial part when the indenter tip was trying to settle down. It is particularly noted that the depth profiles from all scratch tests are smooth without any sharp discontinuity, indicating no microcrack formation; this is consistent with the SEM images (Fig. 4.4) in which no chip or fractured debris was detected. Gauthier et al. [118, 119] have shown that the deformation strain during scratching with a spherical tip is $\varepsilon = 0.2a / R$, where $a = \sqrt{2hR - h^2}$ is the contact radius, R the tip radius and h the penetration depth. Based on the equation, the maximum strain in the current nanoscratch tests is estimated to be 9%, less than the tensile elongation of 15% [116], which further confirms that the deformation mechanism is ductile plowing.

Variations of the penetration depth, residual depth, and COF of the NbTiZrHf HEA at various applied normal forces under constant-load scratch are summarized in Fig. 4.8c and

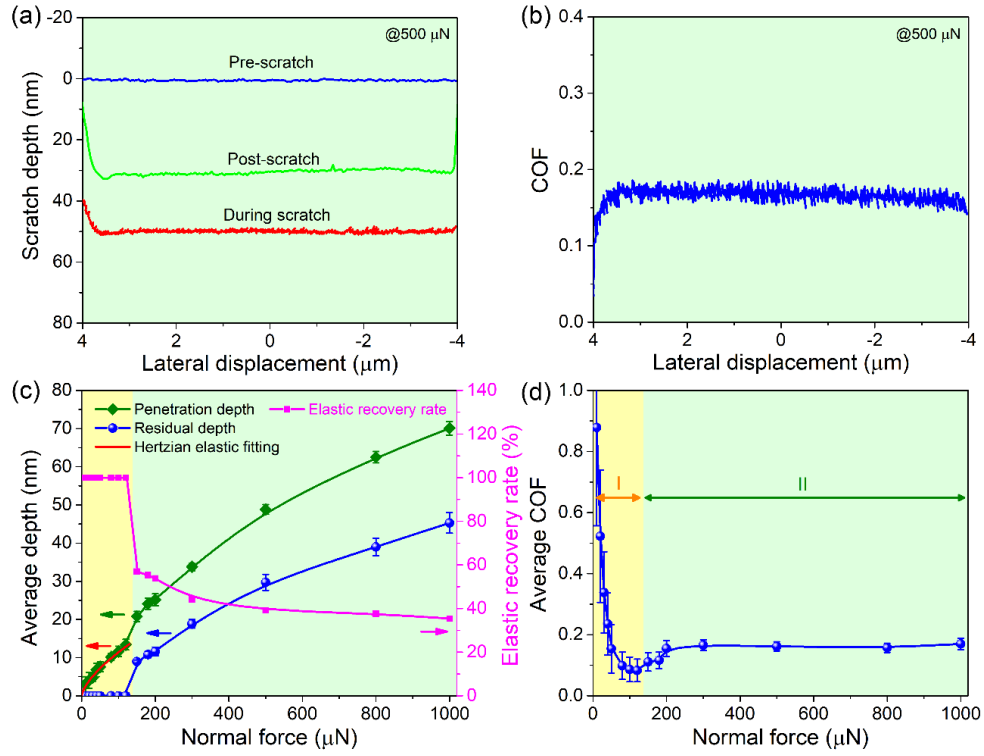


Fig. 4.8 (a) Surface profiles and (b) COF as a function of lateral displacement of the HEA under constant load mode at normal force of 500 μN . Variations of (c) penetration depth, residual depth and elastic recovery rate, and (d) COF as a function of normal forces of the HEA under constant load mode.

4.8d. The results obviously exhibit both the elastic and plastic regimes, similar to that observed under ramping-load scratch. The penetration depth in the elastic portion (Regime I) can be simply described by the Hertzian elastic contact equation (red curve in Fig. 4.8c):

$$F_n = (4/3)E_r\sqrt{Rh^3} [70], \text{ or}$$

$$h = \left(\frac{3}{4E_r\sqrt{R}}\right)^{2/3} \cdot F_n^{2/3} \quad (4.1)$$

where $E_r = [(1-\nu_i^2)/E_i + (1-\nu_s^2)/E_s]^{-1}$ is the reduced elastic modulus for a diamond indenter on the HEA, which is 83.0 GPa [91]. In the reduced elastic modulus equation, E_i , ν_i , E_s , ν_s represent the elastic moduli and Poisson's ratios of diamond tip and the HEA, respectively. In Regime II, both the penetration and residual depths monotonically increase with the normal force. The elastic-plastic transition takes place at a normal force of about 120-150 μN , which is close but slightly lower than the critical load under the ramping load mode ($\sim 180 \mu\text{N}$). The difference between penetration depth and residual depth is attributed to the elastic recovery, which can be evaluated by the elastic recovery rate (δ), defined as $\delta = (h - h_r)/h$ [39, 41], where h_r is the residual depth. The variation of elastic recovery rate with normal force is also included in Fig. 4.8c (pink curve). In Regime I, the recovery rate is 100%, as expected. As the normal force exceeds the elastic range, the recovery rate immediately drops to $\sim 60\%$ and, then, gradually decreases to a steady-state value of $\sim 40\%$. Average COF as a function of the normal forces for the HEA is shown in Fig. 4.8d, which exhibits, again, two regimes. Detailed discussion on the COF will be presented in Section 4.3.

4.2.3 Wear behavior during nanoscratching

The topography of scratched track of the HEA after being tested at constant load of 500 μN is shown in Fig. 4.9a. The dark region is the scratched groove and the bright region is material pile-ups caused by the scratch. Groove and pile-up patterns can be better observed in the 3D view (Fig. 4.9b). Noted that the units for the X- and Y-axes are in μm , but the Z-axis is in nm. Cross-section profile of the groove is shown in Fig. 4.9c, in which data measured from pure Nb and C103 alloy are also included for comparison. It is evident that the scratched groove in the HEA is narrower and shallower than that in pure Nb and C103, indicating that the material has the best wear resistance. The wear resistance was quantitatively evaluated by measuring the volume of materials that was removed by scratching. The wear volume (or material removed) can be directly measured from the scratch depth and cross-sectional profiles, and the results under different scratch conditions for the HEA are summarized in Fig. 4.10a. The wear volume is noted to linearly increase with the scratch distance at a fixed normal force. It also increases with the increasing normal force. Both pure Nb and C103 samples also exhibit similar trend, but with a larger wear volume. According to the Archard equation for dry wear, the wear volume, V , during scratching is given by [48, 114]

$$V = \frac{KF_n}{H} x \quad (4.2)$$

where K is the wear coefficient, F_n the normal force, H the hardness, x the scratch distance. Simply recasting Eq. 4.2, the wear rate, defined as the volume removed per unit scratch distance, is written as

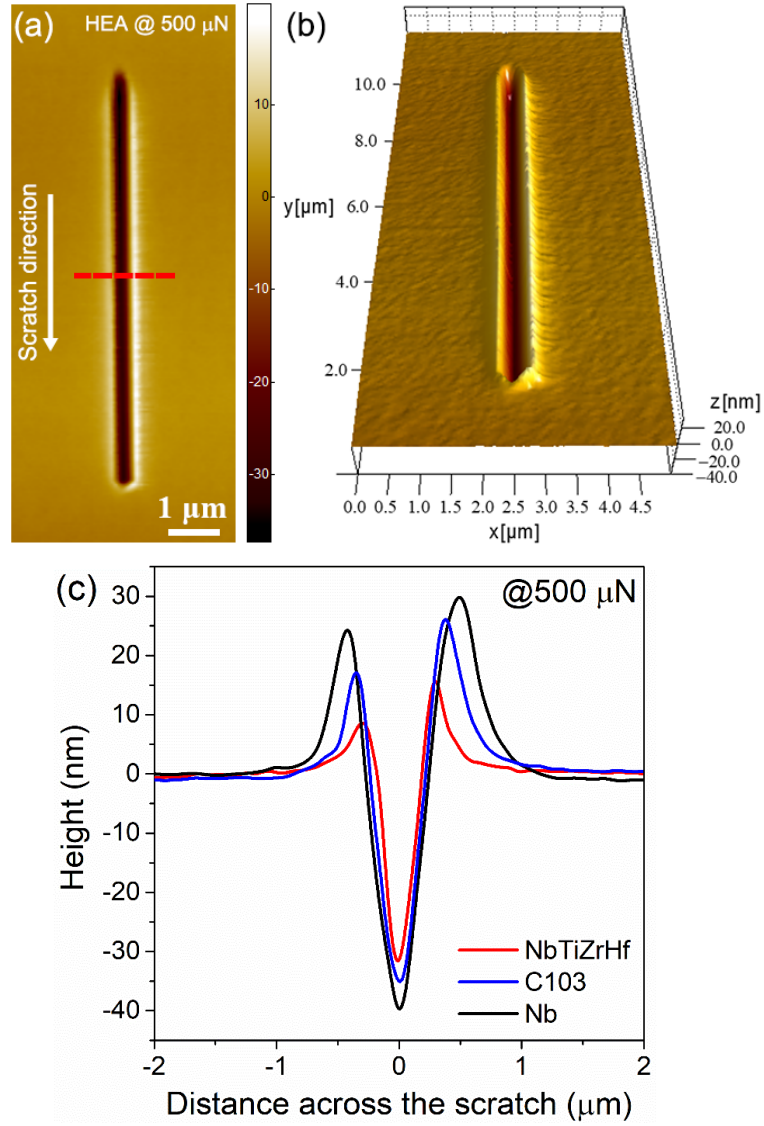


Fig. 4.9 (a) A representative SPM image showing the topography of scratch track of the HEA under constant load testing at 500 μN , (b) the corresponding 3D view, and (c) cross-section profiles as indicated with red dash line in (a) as well as those of pure Nb and C103 alloy.

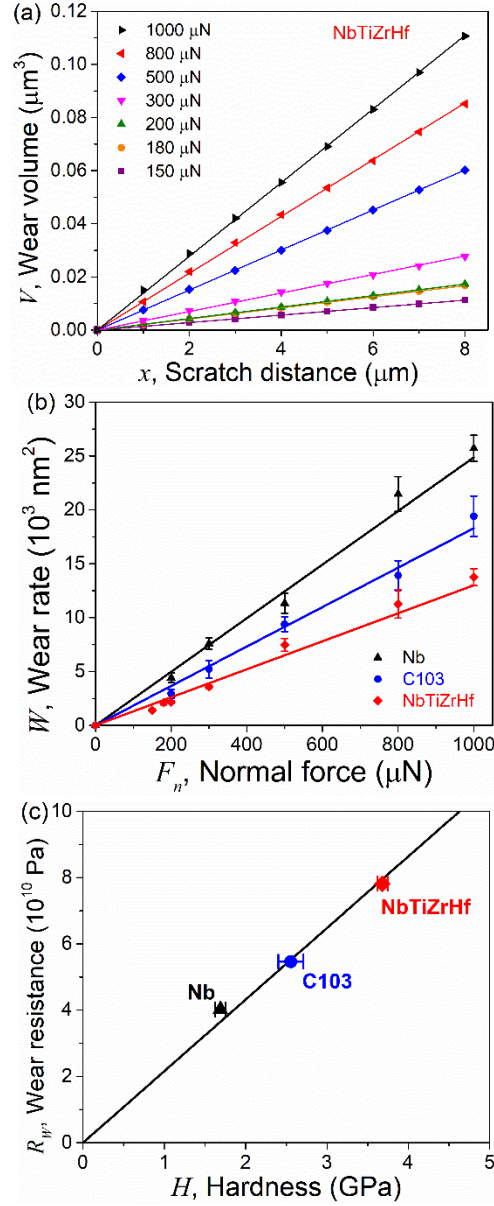


Fig. 4.10 (a) Volume removed (or wear volume) against scratch distance under various normal loads in NbTiZrHf HEA. (b) Wear rate vs. normal force and (c) wear resistance coefficient vs. hardness for pure Nb, C103 and NbTiZrHf HEAs.

$$W = \frac{V}{x} = \frac{K}{H} F_n \quad (4.3)$$

where W the wear rate. In other words, the wear rate is simply the slope of the curve in Fig. 4.10a. In this form, the wear resistance coefficient, $R_w = H / K$ [37, 120, 121], can be readily obtained from the reciprocal of the slope in the W - F_n graph shown in Fig. 4.10b. The HEA evidently has the lowest slope, thus is the most wear resistant alloy. Specifically, the wear resistance coefficients are 4.02, 5.46 and 7.81×10^{10} Pa for pure Nb, C103 and HEAs, respectively. These wear resistance coefficients plotted as a function of material hardness is shown in Fig. 4.10c. The linear correlation between wear resistance coefficient and hardness affirms the relation for dry abrasive wear (Eq. 4.3), namely, the harder HEA has higher wear resistance. It is somewhat expected since a similar ductile plowing wear is prevalent in these three different samples.

4.2.4 Effect of scratch rate

To evaluate the scratch rate effect, scratch tests under ramping load mode were conducted at scratch speeds of 0.01, 0.1, 0.5 and 1 $\mu\text{m/s}$, and the resulting scratch depth profiles are displayed in Fig. 4.11a. It appears that the scratch speed has a negligible effect on the scratch depth, suggesting that the wear resistance is independent of scratch speed. The independence between scratch depth and scratch rate was also previously reported in several metallic glasses [37, 122]. Variations of COF are also compared at different scratch speeds, as shown in Fig. 4.11b, in which COF curves almost overlap with each other. Consequently, it may be concluded that the friction and wear behavior of the current HEA

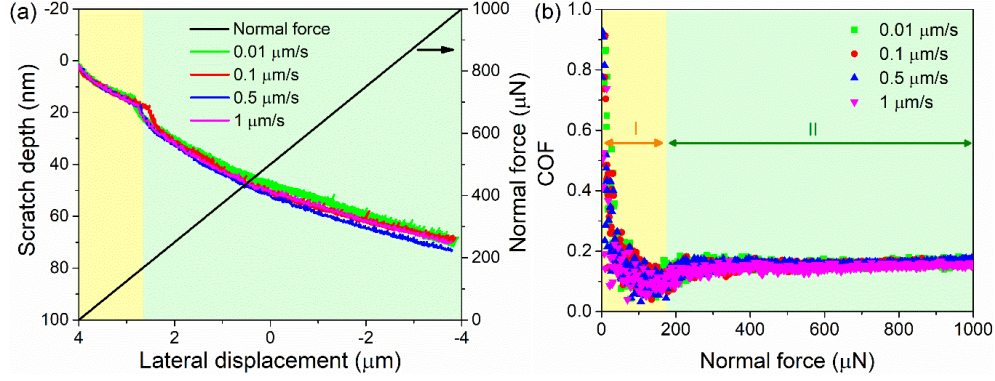


Fig. 4.11 (a) Scratch depth vs. scratch distance and (b) COF vs. normal force of the HEA at various scratch speeds under ramping load mode.

is insensitive to scratch rate, at least within the scratch speeds of 0.01-1 μm/s.

We also made special effort to estimate the possible temperature rise resulting from frictional heating during scratching. Archard's approach [123] was adopted to calculate the maximum attainable flash temperature during scratching. To perform the calculation, we first estimate the Peclet number, $L = va / 2D$ [123, 124], where the v is the scratch speed, a the contact radius, $D = \kappa / \rho C$ the thermal diffusivity, κ thermal conductivity, ρ the density and C the specific heat capacity. Peclet number determines the heat transfer regime, specifically, when $L < 0.1$ it is in the quasi-stationary regime, in which frictional heat has sufficient time to be dissipated to the surrounding [123, 124]. The parameters [125, 126] used for the calculation of flash temperature is summarized in Table 4.2. It is noted that since some parameters (κ , ρ , and C) are not available for the present HEA, the rule-of-mixture is used for the estimation. The Peclet number is estimated to be only 10^{-10} - 10^{-8} in

Table 4.2 Summary of parameters of NbTiZrHf-HEA used for the calculation of temperature rise.

κ [125] * (W/m·K)	ρ [125] * (Kg/m ³)	C [126] * (J/Kg·K)	D (10 ⁻⁵ m ² /s)	a (nm)	α	P_m (GPa)	F_n (μN)	ν (μm/s)
30.5	8381	301.75	1.23	281	0.16	3.68	0-1000	0.01-1

* based on the rule of mixture

the current experiments, which is much smaller than 0.1 for the quasi-stationary thermal regime. Therefore, the maximum possible flash temperature spike is [123]

$$\Delta T_{flash} = 0.25 \frac{\alpha \pi p_m}{\rho C} \frac{F_n^{1/2} \nu}{2D(\pi p_m)^{1/2}} \quad (4.4)$$

where ΔT_{flash} is the temperature rise, α is the COF and the p_m is the flow pressure or hardness of the HEA, other parameters have the same meaning as previously mentioned. It is calculated to be only 2.3×10^{-8} - 10^{-6} K, which obviously would have a negligible effect on the friction and wear behavior.

4.3 Discussion

Friction and wear are two important considerations during metal contacts in engineering operations. A low friction coefficient and wear rate are generally desirable for tribological applications. The present results indicate that NbTiZrHf-HEA exhibits a lower COF and higher wear resistance than its conventional counterparts, e.g., pure Nb and Nb-based C103

alloy. Dry wear of these samples can be well described by the Archard equation, and the higher hardness/strength of the HEA contributes to its better wear resistance. The lower COF in the HEA is particularly intriguing as it is directly pertinent to engineering applications. However, friction behavior of the alloy appears to be slightly complicated as the COF generally exhibits two distinct regimes. In the following, we discuss the possible origins of the two regimes and the apparently low value of COF.

In the current study, a 90° cono-spherical diamond tip with an effective radius ~ 600 nm was used for scratch tests, whose geometry can be described by a sphere with radius R and a cone with half-angle θ , as schematically illustrated in Fig. 4.12a. The transition from the spherical to conical shape of this tip takes place at a critical contact radius $a_{cr} = R \cos \theta$, below which the tip can be treated as a sphere. Since the contact radius is linked to the penetration depth via $a = \sqrt{2hR - h^2}$, the critical penetration depth for the transition from the spherical to conical shape is obtained as $h^{cr} = R(1 - \sin \theta) = 176$ nm for the diamond indenter. As the maximum penetration depth in the current experiments is only ~ 70 nm, it is reasonable to assume a simple spherical tip during the scratch tests.

Bowden and Tabor [127] proposed that friction was resulted from two components: an adhesion force necessary to shear the contacting junction, and a plowing force accompanied by plastic deformation of soft material imposed by a hard asperity. As shown in Fig. 4.12b, forces parallel to the interface (red arrows) due to shearing are the adhesion

when a hard spherical tip impresses into a specimen, we have $a = (3F_n R / 4E_r)^{1/3}$. Since the contact area between the tip and specimen is given by $A_c = \pi a^2$, we readily get

$$A_c = \pi \cdot \left(\frac{3F_n R}{4E_r} \right)^{2/3} \quad (4.6)$$

Bowden and Tabor [127] also suggested that the adhesive friction force required to shear a contacting interface is given by [127-129]:

$$F_{ad} = \tau_s \cdot A_c \quad (4.7)$$

where τ_s is the interfacial shear strength which is a material-related constant associated with the fundamental properties of the interface. Combine Eqs. 4.6 and 4.7, the adhesive friction force becomes

$$F_{ad} = \tau_s \cdot \pi \cdot \left(\frac{3R}{4E_r} \right)^{2/3} \cdot F_n^{2/3} \quad (4.8)$$

This equation indicates that the adhesive friction force should be proportional to the applied normal load raised to a two-third power. It is confirmed in Fig. 4.13a, in which the slope of the logarithmic friction force vs. the logarithmic normal force graph in the elastic regime is indeed 0.667. The friction coefficient can be straightforwardly deduced from Eq. 4.8

$$\alpha_{ad} = \frac{F_{fric}}{F_n} = \tau_s \cdot \pi \cdot \left(\frac{3R}{4E_r} \right)^{2/3} \cdot F_n^{-1/3} \quad (4.9)$$

This equation indicates that α_{ad} decreases when the applied normal force increases in Regime I, which agrees with the experimental results (Figs. 4.6b and 4.8d). It is noted that the interfacial shear strength for the current HEA is not available, so it is treated as a fitting

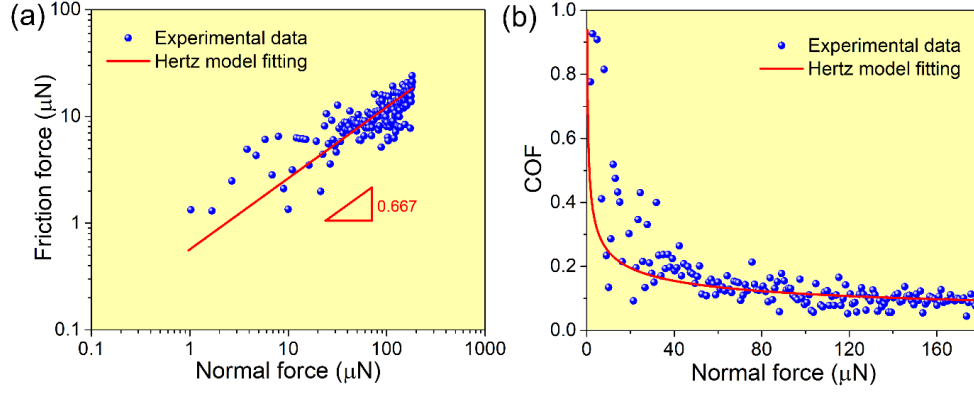


Fig. 4.13 Modeling of (a) friction force and (b) COF as a function of normal force via Hertz contact theory of the HEA in elastic regime.

parameter in Eq. 4.9. In fact, with $\tau_s = 0.6 \text{ GPa}$, the friction coefficient as a function of the normal force in the elastic regime can be well fitted using Eq. 4.9 (red curve in Fig. 4.13b). Friction coefficients of Nb and C103 samples can be also fitted by Eq. 4.9 following the same procedures, which are not shown here for brevity. The large data variation at ultralow normal forces ($< \sim 20 \text{ μN}$) in Figs. 4.13a and 4.13b, is probably attributable to the machine noise at the resolution limitation or other factors (e.g., uncertain capillary force due to the presence of water moisture in the surrounding environment).

When the normal force is higher than the critical value ($\sim 180 \text{ μN}$), plastic deformation or plowing mechanism begins to take over. Friction coefficients for Nb, C103 and HEAs approach asymptotically to respective constant values of about 0.27, 0.24 and 0.16 (Fig. 4.6b). As mentioned before, COF consists of two contributions, i.e., adhesion and plowing. The plowing COF, α_{pl} , is primarily determined by the areal ratio of A_l / A_n [127, 130],

where A_t and A_n are the projections of the tip-sample contact area in the lateral and normal directions, respectively. Goddard and Wilman [130] suggested that, in the case of using a spherical tip to scratch a smooth surface under the condition of plastic contact without elastic recovery, $\alpha_{pl} = (2 / \pi a^2) \cdot [R^2 \sin^{-1}(a / R) - a\sqrt{R^2 - a^2}]$. However, since the elastic recovery rate can be as high as ~40-60% in the plastic regime in our tests (Fig. 4.8c), elastic recovery at the rear part of the scratch track should not be ignored, as schematically illustrated in Fig. 4.12b (yellow curve). In fact, it has been demonstrated that the effect of elastic recovery of the worn material in the rear end on α_{pl} , sometimes, could be quite significant [131-133]. Lafaye et al. [131, 132] subsequently made special effort to incorporate elastic recovery into Goddard and Wilman's model to calculate the effective projected areas A_t and A_n , and their results are summarized as

$$\begin{aligned}\alpha_{pl} &= \frac{2}{a^2} \cdot \frac{\beta^2 \cdot \sin^{-1}(a \cos \omega / \beta) - \sqrt{R^2 - a^2} \cdot a \cos \omega}{\pi + 2\omega + \sin 2\omega} \\ a &= \sqrt{2hR - h^2} \\ \omega &= \sin^{-1} \sqrt{2H(R - h) / aE_r} \\ \beta &= \sqrt{R^2 - a^2 \sin^2 \omega}\end{aligned}\tag{4.10}$$

where a is the contact radius, ω is the rear angle [133] accounting for the elastic recovery (Fig. 4.12b), β is considered as a fictive radius of the spherical tip. Insert the data for hardness (H), tip radius (R), reduced modulus (E_r) and penetration depth (h) into Eq. 4.10, α_{pl} can be calculated. It is noted that the scratch depth h , which depends on the applied normal force (Fig. 4.8c), is implicitly embedded in the above equation for α_{pl} . Both h and

the normal force are readily measured from a nanoscratch test. Subsequently, α_{pl} plotted as a function of the normal force is shown in Fig. 4.14a. The figure reveals that α_{pl} increases monotonically with the normal force for all three samples and, apparently, the HEA has a lower α_{pl} as compared to those of pure Nb and C103 alloy at any given normal force. The low α_{pl} in the HEA is explained as follows.

First, it is noted in Fig. 4.14b that a shallower scratch depth generally leads to a lower α_{pl} . For the HEA, which has a higher hardness, the penetration depth during scratch is shallower at a fixed normal force, thus contributes to a lower α_{pl} . Second, according to Eq. 4.10, a higher rear angle ω (or more elastic recovery) also results in a lower α_{pl} value during nanoscratching; this is shown in Fig. 4.14c. Since the HEA is the hardest and has the largest rear angle among the three samples at any given normal force (Fig. 4.14d), it is intuitively expected to have the lowest α_{pl} . In essence, the combination of higher hardness and larger elastic recovery results in a lower α_{pl} in the HEA, as compared to that in Nb and C103 alloy.

For the contribution from adhesion friction, on the other hand, it is particularly noted that the Hertz analysis in Eq. 4.9 only applies to the elastic contact. To evaluate the adhesion contribution in Regime II, we extrapolate the adhesion component by recasting Eq. 4.5 into $\alpha_{ad} = \alpha_{app} - \alpha_{pl}$. Then, α_{ad} can be obtained and it is plotted in Fig. 4.15; α_{ad} decreases with increasing normal force for all samples. α_{ad} for Nb and C103 alloy almost

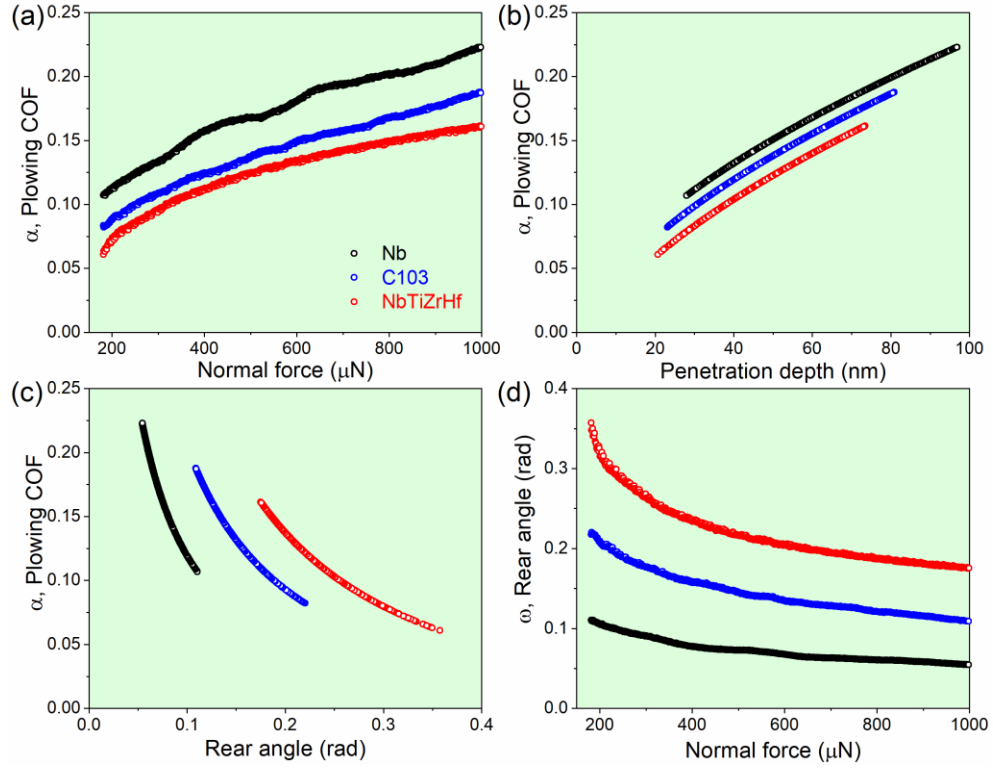


Fig. 4.14 Calculated plowing COF as a function of (a) normal force, (b) penetration depth, and (c) rear angle; (d) rear angle as a function of normal force for Nb, C103 and HEAs in plastic dominated regime.

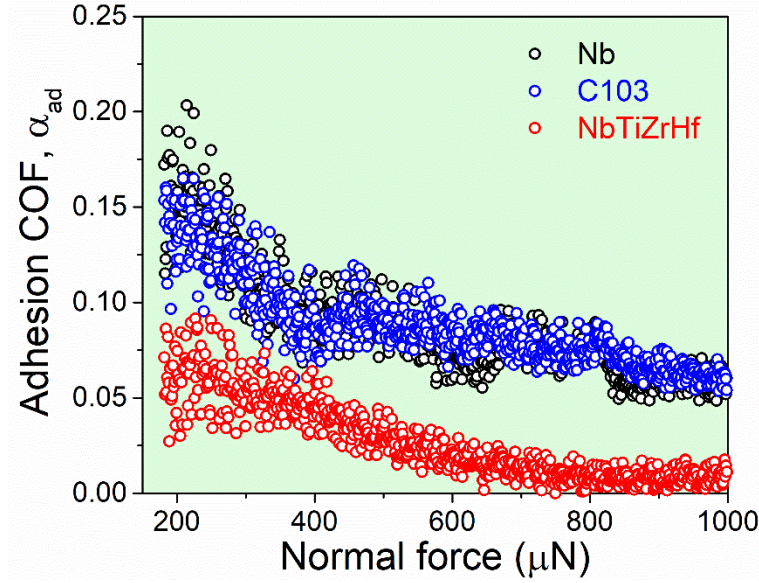


Fig. 4.15 Calculated adhesion COF as a function of the normal force for Nb, C103 and HEAs in the plasticity-dominated regime.

overlap with each other, similar to that in the elastic regime where adhesion dominates (Regime I in Fig. 4.6b). More importantly, α_{ad} for the HEA is much lower than that for Nb and C103. It is pointed out that all constituent elements in the current Nb, Nb-5.4Hf-2Ti and NbTiZrHf-HEA samples are strong carbide formers. From a chemical point of view, good adhesion between diamond (carbon) and all these samples is expected. Therefore, it is unclear why the HEA exhibits the lowest α_{ad} . However, since in the plastic range (Regime II) the contribution from plowing is much greater than that from adhesion, that is, $\alpha_{pl} > \alpha_{ad}$, the understanding of α_{ad} is probably not crucial.

4.4 Conclusions

In this study, nanoscratch experiments have been conducted on an equiatomic BCC-NbTiZrHf HEA under both ramping and constant load modes to investigate its friction and wear behavior. Friction behavior of the alloy can be divided into two distinct regimes – elastic and plastic. In the elastic regime, the coefficient of friction (COF) decreases rapidly when the normal load increases and is inversely proportional to one-third power of the normal load, which can be rationalized using the Hertz contact theory. By contrast, the COF is essentially constant (~ 0.16) in the plastic regime. The wear rate (or material removed) of the NbTiZrHf HEA is proportional to the applied load and the wear resistance scales linearly with the hardness of the alloy; these are consistent with the Archard's equation for dry wear. Both wear and friction are seemingly insensitive to the scratch rate, and the estimated temperature rise caused by local frictional heating even at the fastest scratch speed is insignificant. In comparison with the pure Nb and C103 (Nb-5.4Hf-2Ti), NbTiZrHf HEA exhibits improved wear resistance, apparently resulting from a higher hardness/strength. The NbTiZrHf HEA also has a relatively low COF as compared to Nb and C103, which may be attributable to small plowing and adhesion friction coefficients. The good combination of low COF and high wear resistance suggests that the current HEA may have potential for tribological applications.

Chapter 5. Elastic properties of a BCC NbTiZrHf HEA

5.1. Methods

5.1.1 Experimental procedure

Elastic constants were measured using resonant ultrasound spectroscopy (RUS). A rectangular parallelepiped sample was corner mounted between two transducers as schematically illustrated in Fig. 5.1. Utilizing the mechanical resonances of a material, RUS uses sample dimensions and resonances to fit the experimentally collected resonances to a calculated spectrum based on estimated elastic moduli, using an iteratively inverse fitting process [134]. The elastic constants C_{ij} were determined from ~ 40 resonances with frequency ranging from 200 to 1000 kHz. A typical RUS resonance spectrum obtained from the current NbTiZrHf HEA is shown in Fig. 5.1, in which the inset shows an example of Lorentz fitting of a single resonance peak. In the absence of texture, elastic isotropy was assumed in the polycrystalline specimen. The density of the annealed alloy was measured using a Denver Instrument SI-234 device.

5.1.2 Computational methodology

Kohn-Sham density functional theory [135, 136] simulations were performed to calculate the elastic constants of the alloy using Vienna *Ab initio* Simulation Package (VASP) [87, 137], in which the projector-augmented wave (PAW) method [138] was employed. The exchange-correlation functional in the framework of Perdew-Burke-

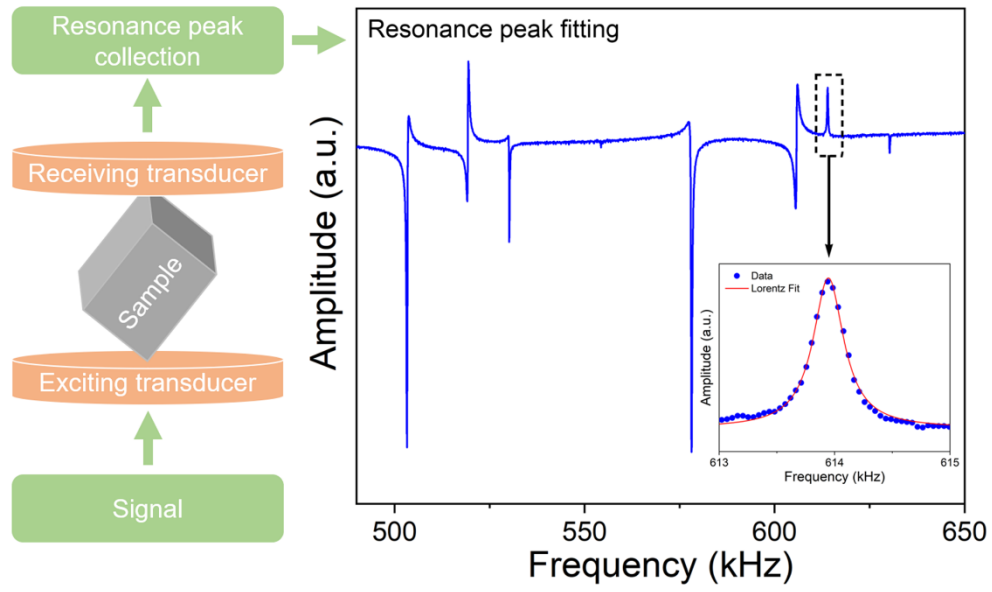


Fig. 5.1 Schematic diagram for RUS measurement setup and a typical RUS resonance spectrum (in-phase signal amplitude vs. frequency) of NbTiZrHf HEA with an inset showing the Lorentz fitting of a selected peak.

Ernzerhof (PBE) [139] was used. Special quasi-random structures (SQSs) [88] were generated via the mcsqs [140] program in the Alloy-Theoretic Automated Toolkit (ATAT) [141, 142], and were utilized in the calculations in order to achieve statistically better results due to the vast configuration space of the alloys. Specifically, 3 SQSs of $4 \times 4 \times 4$ supercell size in the unit of conventional BCC unit cell were tested (Fig. 5.2). For each configuration, its lattice parameter was optimized before the elastic constant calculation while allowing the ionic relaxation till the Hellmann-Feynman force is smaller than 0.01 eV/Å on each atom. The average lattice constant of the 3 SQSs was found to be 3.428 Å, which agrees well with our previous experimental result of 3.444 Å [91]. The elastic constants were then derived from the relaxed structures by calculating the stress-strain relationship through a finite difference approach with a displacement size of 0.1 Å [143, 144]. The results obtained for each SQS (compiled in Table 5.1) exhibit lower symmetry than the theoretical cubic ones due to the limited supercell size; hence we take the arithmetic average among the supposedly equivalent terms for C_{11} , C_{12} , and C_{44} , respectively. The calculated properties were further averaged among the 3 SQSs and summarized in Table 5.2. Our results indicate that the modulus calculations are robust against different SQSs with the relative standard deviations being 1.2%, 1.6%, and 7.6% for C_{11} , C_{12} , and C_{44} , respectively. For all the simulations, the energy cut-off for plane-wave basis was set as 500 eV while the Brillouin zone was sampled by a $2 \times 2 \times 2$ mesh. Electronic convergence criterion was set to be 10^{-5} eV.

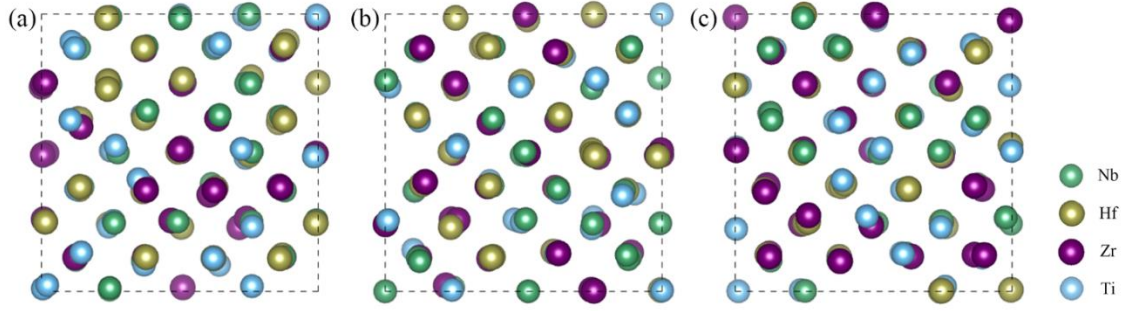


Fig. 5.2 Side view of the atomistic configurations of the three SQSs used to model NbTiZrHf HEA.

Table 5.1 Non-zero elastic constants (in GPa) of the 3 SQSs.

SQS No.	C_{11}	C_{22}	C_{33}	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
1	135.7	136.1	133.2	99.5	102.6	99.8	31.1	25.3	32
2	138.1	132.6	134.8	98.6	98.4	103.1	31.5	32	31
3	135.6	135.5	134.8	100.3	100.4	100.9	28.7	32.2	28.5

5.2 Results and discussion

The three single-crystal elastic constants C_{11} , C_{12} and C_{44} of the present NbTiZrHf HEA calculated from DFT and the two polycrystalline moduli determined from RUS are listed in Table 5.2. It is noted that for polycrystals with only two independent elastic constants, C_{12} is constrained by the equation $C_{44} = (C_{11} - C_{12}) / 2$. The calculated single-crystal elastic constants are noted to satisfy the Born dynamical stability criteria for cubic systems [64, 145], namely, $C_{11} + 2C_{12} > 0$, $C_{11} > |C_{12}|$ and $C_{44} > 0$. Thus, the current NbTiZrHf HEA is expected to be mechanically stable.

Use the single-crystal elastic constants, the polycrystalline elastic properties (specifically, bulk modulus B , shear modulus G , Young's modulus E , and Poisson's ratio ν) can be estimated according to Voigt-Reuss-Hill (VRH) averaging approximations [146]. The shear modulus can be subsequently obtained from

$$G = \frac{(G_V + G_R)}{2} \quad (5.1)$$

where G_V and G_R are Voigt and Reuss shear moduli, respectively, representing the upper and lower limit of the polycrystalline moduli, given by

$$G_V = \frac{(C_{11} - C_{12}) + 3C_{44}}{5} \text{ and } G_R = \frac{5(C_{11} - C_{12})C_{44}}{3(C_{11} - C_{12}) + 4C_{44}} \quad (5.2)$$

B , E and ν are calculated from the following equations

$$B = \frac{C_{11} + 2C_{12}}{3} \quad (5.3)$$

Table 5.2 Comparison of elastic constants and polycrystalline moduli of NbTiZrHf HEA between RUS measurements and DFT calculations. The percentage differences between DFT calculations and RUS measurements are shown in the parenthesis.

Methods	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	CP (GPa)	A_z	E (GPa)	G (GPa)	B (GPa)	ν	B/G
RUS	139.2	89.0	25.1	63.9	\	69.7	25.1	105.7	0.390	4.2
DFT	135.1	100.4	30.2	70.2	1.74	67.7 (-3%)	24.2 (-4%)	112.0 (6%)	0.399 (2%)	4.6

$$E = \frac{9BG}{3B + G} \quad (5.4)$$

$$\nu = \frac{3B - 2G}{6B + 2G} \quad (5.5)$$

The polycrystalline moduli (B , G , E and ν) of the current NbTiZrHf HEA deduced from Eqs. 5.1-5.5 by inserting RUS measurements and DFT calculations are summarized in Table 5.2. It is clearly seen that DFT and RUS results display excellent consistency within 6% difference for all polycrystalline moduli.

The above elastic properties also allow us to predict the brittle/ductile characteristic of a material in light of Pugh's ratio (B/G) [147], Poisson's ratio ν , and Cauchy pressure ($CP = C_{12} - C_{44}$) [148]. In principle, bulk modulus B reflects the bonding strength between atoms and the resistance to cleavage, whereas the shear modulus G describes the resistance against dislocation movement. A high Pugh's ratio with $B/G > 1.75$ generally implies a

ductile material ($B/G < 1.75$ indicates brittle behavior) [147]. For polycrystals, the Poisson's ratio ν is actually connected to the B/G ratio by recasting Eq. 5.5 as $\nu = (3B/G - 2)/(6B/G + 2)$, which yields a critical value of 0.26 for the brittle/ductile transition. It is clearly seen from Table 5.2 that B/G values range from 4.2 to 4.6 and the Poisson's ratio $\nu \sim 0.39$, determined by RUS experiments and DFT calculations, both predict ductile nature of the present HEA. In addition, Cauchy pressure (CP), which relates to the angular character of atomic bonding, is often indicative of ductility and, in fact, a negative CP corresponds to covalent bond accompanied with brittle behavior, and a positive CP stands for more metallic character and tendency toward ductility [148]. The present NbTiZrHf HEA exhibits a large positive CP value (Table 5.2), suggesting it is a ductile alloy. In summary, all relevant elastic parameters indicate that the present HEA would be ductile with a high room-temperature tensile ductility, which is consistent with the experimental observation (ductility $\sim 15\%$) [116].

Elastic anisotropy can affect various mechanical behavior, such as micro-cracking and the incipient plasticity in materials [149, 150]. It is, therefore, pertinent to evaluate the elastic anisotropy of the current HEA. Elastic anisotropy is usually described by the Zener anisotropy ratio, $A_z = 2C_{44} / (C_{11} - C_{12})$, in which $A_z = 1$ corresponds to elastic isotropy and any departure from unity indicates the degree of elastic anisotropy [65, 145]. In Table 5.2, it can be observed that our DFT calculation predicts $A_z = 1.74$. It is noted, however, only isotopically polycrystalline samples are available for the RUS measurements, which prohibits us from directly verifying the above calculations. In order to further visualize the

anisotropic characteristics, the three-dimensional (3D) distributions of Young's modulus E , shear modulus G , bulk modulus B and Poisson's ratio ν based on our DFT results are plotted in Fig. 5.3. Equations used for evaluating the elastic properties in any arbitrary crystallographic direction $[hkl]$ for cubic systems are given as [145, 151, 152]

$$1/E = S_{11} - 2(S_{11} - S_{12} - S_{44}/2)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2) \quad (5.6)$$

$$1/G = S_{44} + 4(S_{11} - S_{12} - S_{44}/2)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2) \quad (5.7)$$

$$1/B = 3(S_{11} + 2S_{12}) \quad (5.8)$$

$$\nu = -\frac{S_{12} + (S_{11} - S_{12} - S_{44}/2)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)}{S_{11} - 2(S_{11} - S_{12} - S_{44}/2)(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)} \quad (5.9)$$

where $S_{11} = (C_{11} + C_{12})/[(C_{11} - C_{12})(C_{11} + 2C_{12})]$, $S_{12} = -C_{12}/[(C_{11} - C_{12})(C_{11} + 2C_{12})]$ and $S_{44} = 1/C_{44}$ are elastic compliances, and l_1, l_2, l_3 are the direction cosines. In Fig. 5.3, it is observed that Young's modulus, shear modulus, and Poisson's ratio exhibit orientation-dependence and thus anisotropy, whilst the bulk modulus is a perfect sphere since it is always isotropic for the cubic system. It is noted that, whereas E has its highest (lowest) value along $\langle 111 \rangle$ ($\langle 100 \rangle$) directions with a descending order of $E_{111} > E_{110} > E_{100}$, G and ν show a completely opposite trend. The orientation dependence of elastic modulus can be also described as a function of θ , where θ denotes the angle between the $\langle 100 \rangle$ direction and a certain crystal direction on the $\{110\}$ planes. Some crystal directions corresponding to θ angles are marked on the top axis of Fig. 5.4a. For the present NbTiZrHf HEA, since Nb is the only constituent element with a BCC structure, we plot the Young's moduli of the two materials together in Fig. 5.4a for easy comparison (elastic constants of Nb are

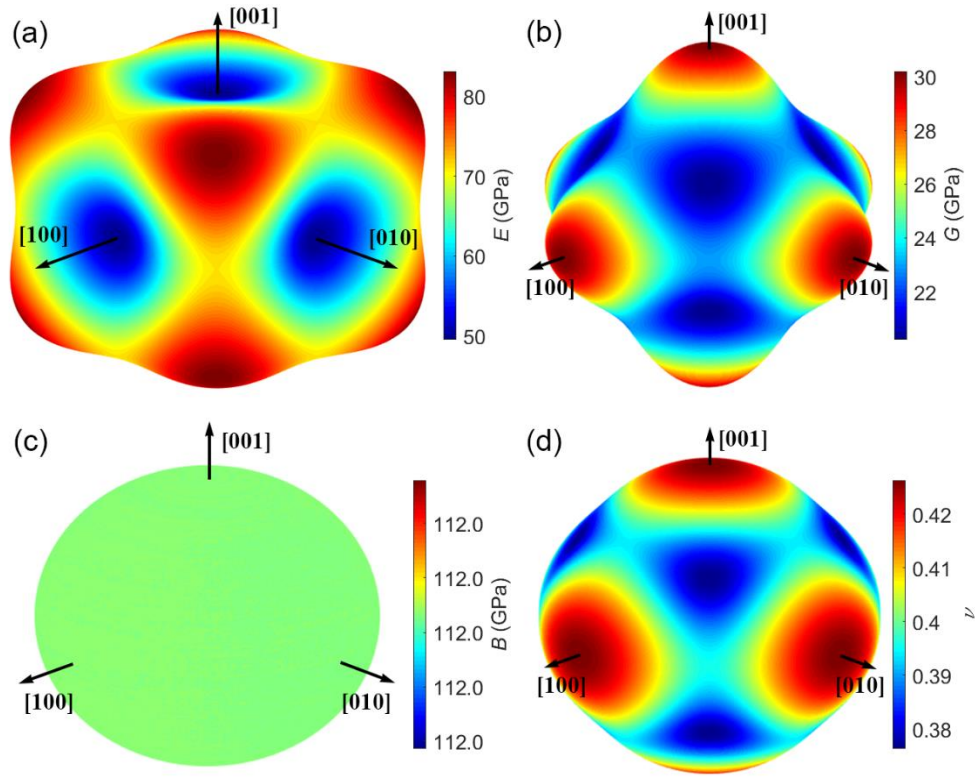


Fig. 5.3 3D visualizations of (a) Young's modulus, (b) shear modulus, (c) bulk modulus, and (d) Poisson's ratio of NbTiZrHf HEA.

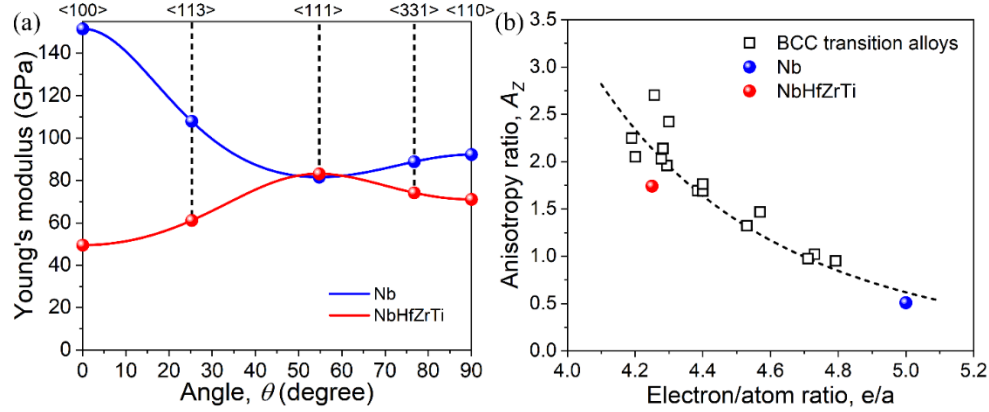


Fig. 5.4 (a) Young's modulus as a function of crystal direction in the (110) plane showing orientation dependence for pure Nb and NbTiZrHf HEA. (b) Relationship between Zener anisotropy ratio and electron/atom (e/a) ratio for pure Nb, NbTiZrHf HEA, and BCC transition alloys from literature (Ti-Nb [153-156], Ti-Cr [157], and Ti-V [158-160] alloys). The dash curve in (b) is drawn to show the trend.

from Ref. [161]). It is particularly noted that Nb displays an opposite trend against NbTiZrHf, namely, Nb has its highest (lowest) value along <100> (<111>) directions with a descending order of $E_{100} > E_{110} > E_{111}$. Moreover, it is readily seen from Fig. 5.4a that Young's moduli along <100> direction highly differ between pure Nb and the current NbTiZrHf HEA, i.e., 151.5 vs 49.5 GPa. which can be rationalized as follows. Combined with Zener anisotropy ratio, Eq. 5.6 for Young's modulus in an arbitrary direction can be recast as $1/E = S_{11} - (A_z - 1)S_{44}(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2)$. If the Zener anisotropy ratio $A_z < 1$, i.e., $(A_z - 1)$ is negative, Young's modulus would have its maximum value in the <100> direction and minimum value in the <111> direction; by contrast, if the Zener anisotropy

ratio $A_Z > 1$, i.e., $(A_Z - 1)$ is positive, Young's modulus would be a minimum in the $\langle 100 \rangle$ and maximum in the $\langle 111 \rangle$ direction. The present NbTiZrHf HEA and pure Nb have a Zener ratio of $A_Z^{HEA} = 1.74 > 1$ and $A_Z^{Nb} = 0.51 < 1$, respectively, resulting in an opposite trend and largest difference in Young's moduli along the $\langle 100 \rangle$ direction. The opposite anisotropy can be verified on the basis of electron configurations. It is generally recognized that the average valence electrons per atom (e/a ratio) in the free atom configuration is a dominant factor in controlling the elastic properties (e.g., elastic anisotropy) of BCC transition metals and alloys [156, 157, 160]. The Zener anisotropy ratio for pure Nb and the current NbTiZrHf HEA as a function of e/a ratio is plotted in Fig. 5.4b, in which values for some BCC transition alloys from literature [153-160] are also included for comparison. It is clearly observed that the Zener anisotropy ratio decreases with the increase of e/a ratio, and particularly an e/a ratio of ~ 4.7 would predict an elastic anisotropy of $A_Z = 1$. The present HEA and pure Nb have their e/a ratios of 4.25 and 5, resulting in $A_Z^{HEA} > 1$ and $A_Z^{Nb} < 1$, respectively. It should be noted that the relationship between anisotropy factor and e/a ratio can, in principle, provide a useful guideline to manipulate the elastic anisotropy via compositional adjustment to produce an elastically isotropic HEA [62].

Debye temperature (Θ_D) is one of the fundamental solid-state dynamic parameters that can be deduced from the experimentally/theoretically determined elastic constants, and the standard equation is [162]

$$\Theta_D = \frac{h}{k_B} \left(\frac{3}{4\pi V_a} \right)^{1/3} v_m \quad (5.10)$$

where h is Planck's constant, k_B is Boltzmann's constant, $V_a = a^3 / 2$ is the atomic volume for a BCC crystal and is determined from our previous XRD results [14, 91]. The v_m in the above equation is the average wave velocity in the polycrystalline material, given by

$$v_m = \left[\frac{1}{3} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \right]^{-1/3} \quad (5.11)$$

where $v_L = \sqrt{(B + 4G/3)/\rho}$ and $v_T = \sqrt{G/\rho}$ are respectively the longitudinal and transverse sound velocity, and ρ is density. The resulting parameters and calculated Debye temperature Θ_D are summarized in Table 5.3. It is readily seen in the table that our theoretical DFT calculations and experimental RUS measurements agree quite well ($\sim$ within 2%) for the longitudinal, transverse and mean sound velocity, and the Debye temperature. It is also noted that the estimated Debye temperatures ($\Theta_D^{RUS} = 214\text{ K}$ and $\Theta_D^{DFT} = 210\text{ K}$) are slightly lower than that for the corresponding constituent elements Zr (291K), Hf (252K) and Nb (275K), but much lower than that for Ti (420K) [125]. From the viewpoint of thermodynamics [162], the Debye temperature of an alloy is expected to be lower than its constituents due to the local strain generated by a mismatch of atomic sizes; this is in agreement with our calculations.

Table 5.3 Summary of relevant parameters of NbTiZrHf HEA used for the calculation of Debye temperature. The percentage differences between DFT calculations and RUS measurements are shown in the parenthesis.

Methods	G (GPa)	B (GPa)	ρ (g/cm ³)	V_a (Å ³)	U_L (m/s)	U_T (m/s)	U_m (m/s)	Θ_D (K)
RUS	25.1	105.7	8.32	20.42	4090	1737	1964	214
DFT	24.2	112.0	8.32	20.42	4164	1706	1930	210
	(-4%)	(6%)			(2%)	(-2%)	(-2%)	(-2%)

Rule-of-mixtures (ROM) has been successfully applied to predict the elastic moduli of multi-component alloy systems, in particular, metallic glasses (or amorphous alloys) [163]. Since HEAs are also multi-component, ROM is expected to be applicable to HEAs. In fact, Tian et al. [61] recently conducted DFT calculations and compared the results with the ROM predictions. They found elastic constants obtained from the two methods agreed reasonably well. However, in another study [65], results showed that, whereas bulk and shear moduli seemed to be in good agreement, Young's modulus appeared to deviate significantly from the ROM prediction. Consequently, in the current study, we also carried out the ROM analysis and compared with experiments as follows.

According to ROM, the elastic moduli, M (E , G or B), of HEAs can be estimated using equations: [163]

$$M = \frac{\sum c_i V_i M_i}{\sum c_i V_i} \quad (5.12)$$

or

$$M^{-1} = \frac{\sum c_i V_i M_i^{-1}}{\sum c_i V_i} \quad (5.13)$$

where c_i , V_i and M_i are respectively atomic fraction, molar volume and moduli of constituent elements [147, 164] (summarized in Table 5.4). Noted that Eqs. 5.12 and 5.13 represent the upper and lower bound values, respectively. To give a broader perspective, in addition to the experimentally measured elastic moduli (E , G and B) of the current alloy, available literature data for other equiatomic single-phase, solid-solution alloys [12, 66, 67, 165-170] are all listed in Table 5.5. For easy comparison, ROM predictions using both Eqs. 5.12 and 5.13 are included in Table 5.5, and plotted in Fig. 5.5. It is apparent that ROM based on the lower-bound prediction, Eq. 5.13 ($R^2 = 0.91$ in Fig. 5.5b), fits slightly better ($M_{ROM} = M_{Exp.}$) than that based on the upper-bound prediction, Eq. 5.12 ($R^2 = 0.84$ in Fig. 5.5a). Data variation from the predictions is evident, especially for the BCC-structured NbMoTaWTi and NbMoTaWTiV, in which the constituent elements have significantly different moduli (Table 5.4). Nevertheless, results in Fig. 5.5 suggest that ROM (Eq. 5.13) is a practical tool to estimate the elastic moduli of a HEA with either single-phase FCC or BCC structure. However, it is necessary to point out that, despite the usefulness of such a simplistic method, certain factors like chemical interactions among constituent elements and lattice distortion in HEAs are ignored, although they may play a secondary role on elastic moduli.

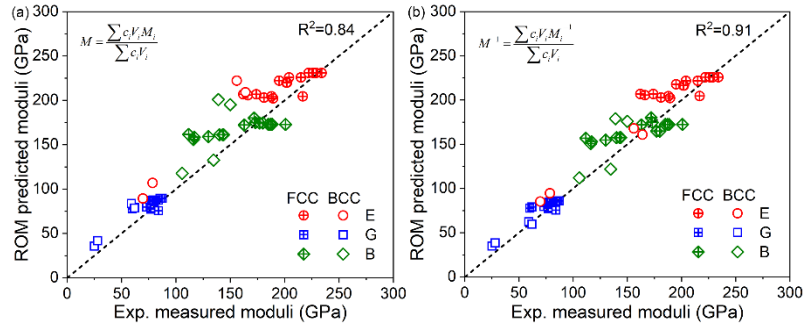


Fig. 5.5 Comparison of polycrystalline moduli (E , G and B) of HEAs between ROM predictions and available experimental data. (a) upper-bound predictions and (b) lower-bound predictions.

Table 5.4 Material parameters [147, 164] used for the rule-of-mixtures (ROM) calculations of equiatomic solid-solution alloys.

Elements	E (GPa)	G (GPa)	B (GPa)	V (cm ³)
Ti	116	44	110	10.64
V	128	47	160	8.32
Cr	279	115	160	7.23
Mn	198	80.8	120	7.35
Fe	211	82	170	7.09
Co	209	75	180	6.67
Ni	200	76	180	6.59
Zr	68	33	91	14.02
Nb	105	38	170	10.83
Mo	329	120	230	9.38
Hf	78	30	110	13.44
Ta	186	69	200	10.85
W	411	161	310	9.47

Table 5.5 Summary of elastic moduli (E , G and B) in a unit of GPa from available experimental measurements using ultrasound methods and ROM predictions. Suffixes u and l denote upper and lower bound predictions using Eqs. 5.12 and 5.13, respectively.

Alloys	$E_{\text{exp.}}$	E_u	E_l	$G_{\text{exp.}}$	G_u	G_l	$B_{\text{exp.}}$	B_u	B_l
NbTiZrHf ^a	69.7	89.4	85.3	25.1	35.7	34.9	105.7	117.8	112.0
NbTaHfZrTi [66] ^b	78.5	106.9	94.6	28	41.7	38.4	134.6	132.7	121.8
NbMoTaWTi [67] ^a	156	222.2	167.9	59	83.6	62.3	139	200.8	178.9
NbMoTaWTiV [67] ^a	164	209.0	160.9	62	78.5	59.6	150	195.1	176
NiCoCrFeMn [165] ^a	201.6	219.9	216.3	80	86.1	84	140.0	161.2	157.5
NiCoCrFeMn [166] ^a	202	219.9	216.3	80	86.1	84	143	161.2	157.5
NiCoCrFeMn [167] ^a	202.2	219.9	216.3	80.2	86.1	84	143.8	161.2	157.5
NiCoFeCr [165] ^a	215.0	225.7	221.7	84	87.5	84.9	162.9	172.2	171.8
NiCoFeCr [168] ^b	204	225.7	221.7	79	87.5	84.9	163	172.2	171.8
NiCoFeMn [165] ^a	187.9	204.5	204.3	77	78.6	78.4	111.8	161.5	156.8
NiCoCrMn [165] ^a	195.0	222.1	217.7	78	87.2	84.5	130.0	159.0	154.6
NiCoFe [165] ^a	162.0	206.8	206.7	60	77.8	77.6	180.0	174.4	164.8
NiCoFe [169] ^b	174	206.8	206.7	60	77.8	77.6	177	174.4	164.8
NiCoCr [165] ^a	226.2	230.8	225.7	87	89.4	85.9	188.5	172.9	172.4
NiCoCr [170] ^a	222	230.8	225.7	85.4	89.4	85.9	185	172.9	172.4
NiCoCr [12] ^a	229	230.8	225.7	87.4	89.4	85.9	200.9	172.9	172.4
NiCoCr [169] ^b	234	230.8	225.7	87	89.4	85.9	187	172.9	172.4
NiFeMn [165] ^a	181.0	203.0	202.8	73	79.7	79.6	116.1	155.7	150.7
NiCoMn [165] ^a	189.4	202.2	202.1	77	77.4	77.3	116.9	158.6	152.8
NiCo [165] ^a	216.7	204.5	204.4	84	75.5	75.5	172.0	180.0	180
NiFe [165] ^a	166.2	205.7	205.5	62	79.1	79	173.1	174.8	174.7

^a Resonant ultrasound spectroscopy (RUS)

^b Ultrasonic pulse-echo technique

5.3 Conclusions

In this study, elastic constants of the single-phase BCC-NbTiZrHf HEA are experimentally measured using resonant ultrasonic spectroscopy (RUS) and also theoretically calculated using the DFT method. Elastic moduli, such as Young's modulus (69.7/67.7 GPa), shear modulus (25.1/24.2 GPa), bulk modulus (105.7/112 GPa) and the Poisson's ratio (0.39/0.40), and the Debye temperature (214/210 K) for polycrystalline aggregates are obtained from the measured and calculated elastic constants. It was found that our RUS experiments and DFT calculations are in excellent agreement (within 6%). The current BCC-NbTiZrHf HEA exhibits a large Pugh's ratio (4.2/4.6), high Poisson's ratio (0.39/0.4), and a positive Cauchy pressure. These elastic properties all affirm that the alloy is ductile, which is actually consistent with reported result [116]. The elastic anisotropy of the alloy is characterized by the Zener ratio (1.74) and 3D visualizations of moduli. Additionally, we have evaluated the applicability of the rule-of-mixtures method to predict the moduli and found that the lower-bond approach is an appropriate way to estimate the elastic moduli of single-phase HEAs with decent precision.

Chapter 6. Concluding remarks

In conclusion, the objective of this dissertation work is to provide a fundamental understanding of the mechanical behavior of BCC HEAs, especially at small scales. To achieve this goal, both nanoindentation and nanoscratch tests were performed on the BCC HEAs and/or their conventional counterparts. The summary of this thesis work is as follows.

(1) A series of instrumented nanoindentation tests were conducted to investigate dislocation nucleation in a single-phase BCC-NbTiZrHf HEA. The maximum shear stress required for dislocation nucleation in the alloy is about 1/10 of the shear modulus. Differed from conventional metals, the activation volume for dislocation nucleation in the present HEA is estimated to be ~3-5 atomic volumes, indicative of a process of cooperative migration of multiple atoms. The activation energy for pop-ins in the current BCC-HEA is also found to be much higher than that in the typical FCC-HEA, which is attributable to the fact that the nucleation of full dislocation is favored in BCC-HEAs, whereas nucleation of partial dislocation is energetically favored in FCC-HEAs.

(2) I have conducted a series of instrumented nanoindentation tests, in combination with quantitative statistical analysis and density functional theory (DFT) calculations, to investigate the effect of interstitial oxygen and nitrogen on incipient plasticity and dislocation nucleation in well-annealed BCC-NbTiZrHf HEAs. The presence of interstitial oxygen and nitrogen atoms could both increase the pop-in load/stress at which dislocations

are nucleated, and nitrogen has a slightly stronger hardening effect. The maximum shear stress required to trigger dislocation nucleation is $\sim 1/11$ - $1/8$ of the shear modulus, approaching the theoretical strength, and appears to be relatively insensitive to grain orientation. The observed indentation-induced incipient plasticity is predominantly mediated by $\{110\}\langle 111\rangle$ slip system in the currently studied HEAs. The onset of yielding exhibits significant rate-dependence - a higher loading rate yields a higher pop-in load/stress. The activation volumes for dislocation nucleation (i.e., pop-in) in the present three HEAs are estimated to be ~ 1.8 - $2.5\ b^3$, corresponding to 2-3 atomic volumes, indicating the nucleation process involves cooperative migration of multiple constituent atoms. In comparison, the activation volumes obtained from deep indentation during hardness test are much larger at ~ 30 - $45\ b^3$, implying a different mechanism. Specifically, hardness increase caused by interstitial oxygen or nitrogen addition is a result of the traditional solid-solution strengthening, i.e., dislocation moving through crystalline lattice distorted by the interstitials. The first-principles calculations reveal that the interstitial (oxygen/nitrogen) and its surrounding neighboring metals form ionic-like complexes. These metal-interstitial complexes improve lattice cohesion due to significant charge transfer between the interstitial and the neighboring metals, which is responsible for the observed increase in the critical shear stress required for dislocation nucleation in the interstitially doped HEAs.

(3) Nanoscratch experiments have been conducted on an equiatomic BCC-NbTiZrHf HEA under both ramping and constant load modes to investigate its friction and wear

behavior. Friction behavior of the alloy can be divided into two distinct regimes – elastic and plastic. In the elastic regime, the coefficient of friction (COF) decreases rapidly when the normal load increases and is inversely proportional to one-third power of the normal load, which can be rationalized using the Hertz contact theory. By contrast, the COF is essentially constant (~ 0.16) in the plastic regime. The wear rate (or material removed) of the NbTiZrHf HEA is proportional to the applied load and the wear resistance scales linearly with the hardness of the alloy; these are consistent with the Archard's equation for dry wear. Both wear and friction are seemingly insensitive to the scratch rate, and the estimated temperature rise caused by local frictional heating even at the fastest scratch speed is insignificant. In comparison with the pure Nb and C103 (Nb-5.4Hf-2Ti), NbTiZrHf exhibits improved wear resistance, apparently resulting from a higher hardness/strength. The NbTiZrHf alloy also has a relatively low COF as compared to Nb and C103, which may be attributable to small plowing and adhesion friction coefficients. The good combination of low COF and high wear resistance suggests that the current HEA may have potential for tribological applications.

(4) Elastic constants of the single-phase BCC-NbTiZrHf HEA are experimentally measured using resonant ultrasonic spectroscopy (RUS) and also theoretically calculated using the DFT method. Elastic moduli, such as Young's modulus (69.7/67.7 GPa), shear modulus (25.1/24.2 GPa), bulk modulus (105.7/112 GPa) and the Poisson's ratio (0.39/0.40), and the Debye temperature (214/210 K) for polycrystalline aggregates are obtained from the measured and calculated elastic constants. It was found that our RUS

experiments and DFT calculations are in excellent agreement (within 6%). The current BCC-NbTiZrHf HEA exhibits a large Pugh's ratio (4.2/4.6), high Poisson's ratio (0.39/0.4), and a positive Cauchy pressure. These elastic properties all affirm that the alloy is ductile, which is actually consistent with reported result [116]. The elastic anisotropy of the alloy is characterized by the Zener ratio (1.74) and 3D visualizations of moduli. Additionally, we have evaluated the applicability of the rule-of-mixtures method to predict the moduli and found that the lower-bound approach is an appropriate way to estimate the elastic moduli of single-phase HEAs with decent precision.

Chapter 7. Future perspectives

Based on the research results and my experiences throughout my PhD study, the following possible future topics are suggested.

(1) The initiation of plasticity and dislocation nucleation of BCC NbTiZrHf HEAs were investigated using nanoindentation technique. However, I mainly focused on the mechanical responses at room temperature. Since the NbTiZrHf refractory HEAs are potential for high temperature applications, it is of significance to investigate the incipient plasticity at elevated temperatures and to provide the basic deformation information at high temperatures. Obviously, the role the interstitial oxygen or nitrogen atoms on the initiation of plasticity at elevated temperatures is also worthy of exploration.

(2) Chapter 4 in this thesis has systematically presented the friction and wear behavior and aimed to uncover the related fundamental mechanism. The results showed the wear performance could be improved for a material with higher hardness and higher elastic recovery (associated with strength/modulus ratio) if the sliding wear correspond to a ductile plowing mechanism. Based on this finding, design of HEAs with excellent tribological properties may be a practical topic for the future technological applications.

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