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Nanomechanical studies of high-entropy alloys

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Abstract

In the past decade, nanomechanical techniques have become ubiquitous for mechanical measurement concurrently with the discovery of high-entropy alloys (HEAs). Different from large-scale testing, small-scale measurements offer quantitative details about mechanical behavior of materials at the micro/nano-scale, presenting new opportunities to probe fundamental nature of HEAs. This article will review the literature on using versatile nanomechanical tools for HEA studies, including nanoindentation, micro-compression, high-temperature deformation, fracture measurement, and in situ electron microscopy. With these approaches, many interesting phenomena and properties of HEAs have been unveiled, for example, properties about incipient plasticity, strain-rate sensitivity, creep, diffusion, size-dependent strength, and fracture, which are difficult, or impossible, to be measured in macroscopic experiments. Despite current literature only focusing on a few HEA compositions and several methods, as nanomechanics and HEAs are developing rapidly, a new avenue of research is to be exploited. The article concludes with perspectives about future directions in this field.

Keywords: nanoindentation; alloy; nanoscale; high-entropy alloys; micro-compression; size effects

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1. Introduction and overview

More than a century has passed since the initial scientific study on the mechanical behavior of materials.\textsuperscript{1,2} Still today, research on mechanical properties plays an essential role in materials science, especially for metallic materials. As the most widely used structural materials in the world, alloys contain complex structures (e.g., phases, grains, grain boundaries, dislocations, vacancies, and interstitials) across many length scales, extending from the macroscopic scale to the atomistic size, as illustrated in Fig. 1(a).

Over the past three decades, significant advances have been made in fundamentally understanding mechanical behavior of materials at the micrometer and nanometer scales, owing to the invention of instrumented nanoindentation.\textsuperscript{3,4} Particularly, in the past decade, the emerging techniques (e.g., focused ion beam (FIB), lithography, advanced atomic force microscopy (AFM), \textit{in situ} electron microscopy, and new sensors and actuators of nanoindenters) have led to a large variety of nanomechanical testing methods, including micro/nano-compression, micro-tension, micro-bending, high-temperature/cryogenic nanoindentation, high-strain-rate indentation, and \textit{in situ} electron microscopy (Fig. 1(b)), as reviewed in Refs.\textsuperscript{5-10} These techniques have generated a second wave of more sophisticated experiments and theories on small-scale plasticity: So far, over a thousand reports have been published on a large variety of materials, including regular metals,\textsuperscript{11} ordered intermetallics,\textsuperscript{12} ionic crystals,\textsuperscript{13} semiconductors,\textsuperscript{14} ceramics,\textsuperscript{15} quasicrystals,\textsuperscript{16} and metallic glasses,\textsuperscript{17} as summarized in the reviews\textsuperscript{5-7}. These techniques not only explore materials properties in the new regimes (i.e., size, temperature, and strain-rate) but also provide a database for the design of materials for new functionalities.\textsuperscript{18-20}

At almost the same time as the second wave of nanomechanics, the concept of high-entropy alloys (HEAs) was introduced by Yeh \textit{et al.}\textsuperscript{21} and Cantor \textit{et al.}\textsuperscript{22} in 2004, attracting significant attention in the materials community. HEAs are loosely defined as solid-solution alloys that made of five or more metallic elements with equimolar or near-equimolar ratios, wherein multiple principal elements tend to form single solid-solution-like phases. Typically, conventional alloys have one or two principal components, and their composition are restricted to the corners or edges of a phase diagram. In HEAs, it is difficult to distinguish which element is the principal one, i.e., solvent, and
which one is solute, their compositions are at the centers of their phase diagrams. It is generally believed that in
such HEAs the high configurational entropy assists to stabilize solid-solution phases at high temperatures,
preventing the formation of possible intermetallics, which is regarded as a thermodynamic mechanism.\textsuperscript{21, 23, 24} It is
also believed that the stability of HEAs can be attributed to suppressed long-range diffusion, which is due to a
kinetic mechanism.\textsuperscript{25, 26} As a broader definition, HEAs can contain multiple phases\textsuperscript{21, 22}, and their constitutional
elements are not necessarily equal atomic ratios (i.e., non-equiatomic but near the center of a phase diagram\textsuperscript{27}).
Many interesting and useful properties have been found in macroscopic mechanical testing of HEAs, such as high
strength levels at high temperatures,\textsuperscript{28} excellent fracture toughness at low temperatures,\textsuperscript{29} and outstanding strength-
ductility combination,\textsuperscript{30} as critically reviewed.\textsuperscript{31-35} The mechanical properties of HEAs at the micro- or nano-scale
have also attracted attention since about five years ago.

Regular metals and metallic glasses present two extreme classes of materials regarding chemical and structural
complexity – the number of constituted elements, structure order, and periodicity (Fig. 1(c)). HEAs could be
regarded as one of the intermediate states between single-element regular metals and multi-element disordered
metallic glasses. Despite simple average structures of HEAs – face-centered cubic (fcc),\textsuperscript{22} body-centered cubic
(bcc),\textsuperscript{36} and hexagonal closest packed (hcp),\textsuperscript{37} they present many complexities at small length scales: local lattice
distortion,\textsuperscript{38} nanoscale clusters,\textsuperscript{39} grain-boundary segregation,\textsuperscript{40} and nanoscale phase separation\textsuperscript{41}. The overall
mechanical performance of the bulk HEAs considerably depends on these structures at the micrometer and even
nanometer scales, where nanomechanical tools will be essentially useful. A large number of new HEAs were
developed at the same time the invention of many advanced nanomechanical methods in the last decade,
consequently, when nanomechanics “meets” HEAs, the number of literature on this topic has been dramatically
increased over the past five years. Up to date, about 50 papers have been published, a few examples shown in Table
1. To the author’s knowledge, so far, there has been no review article focusing nanomechanical studies of HEAs,
and many fundamental aspects of mechanical behavior at small scales remain unresolved for HEAs – much in
contrast to regular alloys and metallic glasses. Hence, it is time to review recent findings and highlight the state of
the art on this topic.
In this article, we will focus our attention on a few well-known HEAs, fcc FeCoCrMnNi (also known as the Cantor alloy) and bcc refractory NbMoTaW. This entire review is organized by techniques – nanoindentation (Section 2), micro-compression (Section 3), and fracture testing (Section 4). Many properties of HEAs will be discussed: incipient plasticity, grain-boundary strengthening, strain-rate sensitivity, creep behavior, wear/friction properties, size dependence of plasticity, the temperature dependence of strength, and fracture toughness. In closing (Section 5), this article will summarize the findings in HEAs based on nanomechanical methods, and raise unanswered questions, and point out new opportunities in this field.

2. Nanoindentation of HEAs

2.1. Incipient plasticity and dislocation nucleation in HEAs

Nanoindentation was initially used to study incipient plasticity in HEAs for understanding their dislocation nucleation mechanism. Similar experiments have been intensively applied for analyzing the onset of plasticity in regular metals and metallic glasses, as reviewed in Refs. During the indentation process, a diamond tip, which is typically a Berkovich tip with an effective tip radius of ~100-500 nm (inevitably blunt), contact a sample from its surface, generating a load \((P)\)-displacement \((h)\) curve. Incipient plasticity occurs at the very earliest stages of mechanical deformation when the transition from elasticity to plasticity happens in a tiny volume of deformation. In an indentation experiment, such incipient plasticity is often revealed by a discontinuity in the \(P-h\) curve, often called a “pop-in” event. Thus, the onset of plastic deformation, or yield point, during nanoindentation can be identified. In a typical load-controlled experiment, it shows a plateau of load – without a steady increase of load, as shown in Fig. 2(a). Such “pop-in” phenomena are believed to be associated with the dislocation nucleation underneath the sample surface or initial shear banding in metallic glasses. The activation energy and activation volume for the dislocation nucleation can be calculated and used to interpret the underlying mechanisms during the process.
Using this methodology, Zhu et al.\textsuperscript{42} studied the onset of plasticity in the single-phase fcc FeCoCrMnNi HEA. Fig. 2(a) shows typical load-displacement curves with “pop-ins” during the indentation. This observed pop-in phenomenon is not associated with oxide cracking at the surface but the intrinsic behavior of the HEA. The maximum shear stress of the HEA at the pop-in was calculated to be 5.2-6.8 GPa, within 1/15 - 1/10 of the shear modulus. More in-depth information related to the intrinsic behavior was revealed by changing loading rates and deformation temperatures. Fig. 2(b) shows a series of indentations using different loading rates (25–2500 µN/S) at room temperature, presenting load-rate dependence of pop-in stress. Using an analytical method proposed by Mason \textit{et al.}\textsuperscript{52}, the cumulative probability, \( F(P) \), is correlated with the indentation pop-in load, \( P \), as

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

(1)

Where \( \alpha \) and \( \beta \) are fitting parameters. The activation volume \( V \) can be calculated, as follows:

\[
V = \frac{\pi}{0.47} \left( \frac{3R}{4E_r} \right)^{2/3} KT \cdot \alpha
\]  

(2)

Where \( R \) is the tip radius of the indenter, \( E_r \) the reduced modulus of the indenter-sample combination, \( K \) Boltzmann constant, and \( T \) temperature. Thus, the activation volume \( V \) can be calculated, accordingly. Moreover, as temperature increases, the pop-in load decreases and the average load at pop-in drops nearly one-third from 22 to 150 °C, indicating that the pop-in event is a thermally activated process (Figs. 2(c)-(d)). Such rate- and temperature dependence of pop-in loads in the HEA is comparable to those in pure fcc metals.\textsuperscript{50, 51} As reported, typical activation volumes for pop-in in fcc metals are \( \sim 1 \) \( \Omega \) (where \( \Omega \) is the atomic volume, see Table 2). Interestingly, the activation energy and volume for the onset of plasticity are \( 1.72 \pm 0.35 \) eV and \( 34 \pm 7 \)\( \text{Å}^3 \) (\( \sim 3\Omega \)), respectively. To interpret the higher activation energy and volume in the HEAs than that of fcc metals, Zhu \textit{et al.}\textsuperscript{42} suggested that a vacancy or vacancy-like mediated heterogeneous dislocation nucleation was associated with the onset of plasticity in the HEAs, which is different from the conventional one-to-one atom–vacancy exchange in typical fcc metals.
Using the similar method, the same research group also studied the incipient plasticity of a bcc TiZrHfNb HEA.\textsuperscript{43} They found that the activation volume for the pop-ins in this bcc HEA is \( \sim3-5 \) atomic volumes (Table 2). The higher activation volume in the bcc-HEA than that in fcc-HEAs suggests that the former one deforms with full dislocation nucleation while the latter one starts with partial dislocation nucleation. Although a few other groups also investigated the incipient plasticity and measured mechanical properties of HEAs using a nanoindenter,\textsuperscript{44-47} no theoretical model and atomistic simulation, unfortunately, has been provided to support their hypotheses. So far, the dislocation nucleation in HEAs at the atomic level is still not well known.

2.2. Single crystalline (sx) HEAs vs. nanocrystalline (nc) HEAs

Nanomechanical techniques can be used to quantitatively compare mechanical properties between sx-HEAs and nc-HEAs. HEAs with ultrafine grains or nanoscale grains have been prepared using many different methods, for example, mechanical alloying, high-pressure torsion (HPT), and magnetron sputtering.\textsuperscript{53} Using nanoindentation, Lee and his co-workers studied an as-cast coarse-grained FeCoCrMnNi HEA and a nanocrystalline one made by HPT.\textsuperscript{54-56} After two turns of HPT, the grain size of the as-cast HEA (\( \sim40 \) µm) was refined to \( \sim40 \) nm (Figs. 3(a) and (b)). The hardness is increased with decreasing grain size, fitting the Hall-Petch relationship well (Fig. 3(c)).\textsuperscript{54} Using various nanoindenter tips, Lee \textit{et al.}\textsuperscript{56} also systematically studied the annealing effect on the strength of the nc-HEAs after annealing at 450 °C for 1 hour and 10 hours (Samples: HPT+1A and HPT+10A, Fig. 3(d)). Interestingly, they found that the nanohardness of nc-HEAs was increased after heat treatment, showing an “annealing-induced hardening” phenomenon (Fig. 3(d)). Fig. 3(d) also shows considerable “strain softening” effect in nc-HEAs – flow stress decreases with flow strain, but this trend was not observed in coarse-grained (cg) HEAs. As evidenced by TEM analysis, the “annealing-induced hardening” effect is attributed to the formation of nanoscale intermetallic phases, such as NiMn-, FeCo-, and Cr-rich phases (Figs. 3(e) and (f)). These authors also showed the hardness of annealed HEAs decreases with increasing indentation depth. Such pronounced “strain softening” could be because indentation deformation may assist dissolution of the precipitates. However, no detailed theoretical model and further evidence were provided to support this assumption.
In addition to regular force-displacement measurement, nanoindentation strain-rate jump testing is a powerful approach to investigate thermally activated deformation behavior, particularly over a broad temperature range. By measuring strain-rate sensitivity (SRS) and activation volume ($V$), the deformation mechanism can be fundamentally understood. In nanoindentation, the strain rates vary from $1 \times 10^{-4}/s$ to $1 \times 10^{-1}/s$, and the temperature is from room temperature to $~600 \, ^\circ C$ and SRS can be measured by the relation of flow stress, $\sigma$, as a function of strain rate, $\dot{\varepsilon}$, by:

$$SRS = \frac{\partial \ln \sigma}{\partial \ln \dot{\varepsilon}} \quad (3)$$

The SRS is related to the apparent activation volume ($V$), as:

$$V = \sqrt{\frac{3 K_B T}{SRS \sigma}} \quad (4)$$

In the experiment, the measurement of $V$ is essential, because $V$ is related to the area swept by the dislocation during the thermally activated event. In general, it is believed that a tiny $V$ ($\sim 0.1-1 \, b^3$) corresponds to a diffusion-controlled deformation, where $b$ is the Burgers vector; a small one ($\sim 10-100 \, b^3$) can be related to the Peierls mechanism; a large one ($100-1000 \, b^3$) can be associated with dislocation solute interactions, and a very large one ($\sim 1000 \, b^3$) is the forest mechanism.

Quantitative details on the nature of plasticity of sx-HEAs and nc-HEAs have recently been studied through the use of the strain-rate jump test in a high-temperature nanoindenter. Maier-Kiener et al. revealed the thermal-mechanical behavior of the fcc FeCoCrMnNi HEA from room temperature to 400 °C. Two microstructure states were compared: one is a <100>-oriented grain from a coarse-grained specimen and the other is nanocrystalline one (grain size $\sim 50$ nm) made by HPT. They found a few interesting phenomena. First, both the sx-HEA and nc-HEA exhibit zig-zag scattered plastic flows, which could be associated with dynamic strain aging or dislocation interaction with obstacles (Figs. 4(a) and (b)). Second, the SRS in the sx-HEA decreases significantly above 150 °C,
from 0.018 to 0.002; the $V$ of the sx-HEA increases linearly from ~40·$b^3$ at room temperature to 530·$b^3$ at 300 °C (Figs. 4(c) and (d)). Compared with the room-temperature $V$ of typical fcc metals (~1000·$b^3$), the $V$ value of sx-HEA is relatively low, suggesting the sx-HEA is deformed in a thermally activated process at room temperature, so the critical temperature for the temperature-independent flow in the fcc HEAs is well above room temperature. Third, the SRS in the nc-HEA stays nearly consistent from room temperature to about 200 °C and increases almost linearly above 200 °C, suggesting the change of deformation mechanism. As shown in Fig. 4 (d), the $V$ of the nc-HEA shows three temperature-dependent regimes: increasing at 25-100 °C (similar trend as the sx-HEA), remaining constant at ~100-300 °C, and decreasing above 300 °C. This phenomenon suggests there is a competition between dislocation mechanism (bulk behavior) and diffusion or grain-boundary sliding mechanism (nanocrystalline behavior). The latter one becomes a controlling mechanism for the plastic deformation above ~300 °C. These researchers also suggested the formation of precipitates during the high-temperature indentation process, but this is to be confirmed by additional investigation.

The strain-rate jump results of such fcc HEA, are different from a bcc NbMoTaW HEA, as discussed in the next session. It is mainly because in the bcc HEAs one thermally activated double kink mechanism is believed to be primarily responsible for dislocation motion. Although this work does not show this fcc HEA is very different from other fcc metals or alloys, the strain-rate jump test provides a unique method to probe the thermal-mechanical behavior of a large variety of HEAs. A systematical indentation study on different HEAs over large temperature and strain-rate ranges would be interesting to reveal the fundamental difference between HEAs and other alloys.

2.3. Creep behavior of HEAs

Using an instrumented nanoindenter, a few groups focused on studying creep behavior of HEAs. Lee et al. compared creep properties of coarse-grained (cg) and nanocrystalline (nc) FeCoCrMnNi HEAs using different indenter tips. The authors indicated that the spherical nanoindentation creep tests produced more reliable creep data than the sharp indentation tests. Figs. 5(a)-(c) plot the creep strain rates as functions of holding time. Both creep displacement and strain rates of HEAs were increased with applied loads at the onset of creep. The creep stress
exponent, $n$, was estimated as ~3 for cg HEA and ~1 for nc HEA, indicating the nc-HEA creeps faster than the cg-HEA, which could be associated with grain-boundary diffusion in the nc-HEAs. More interestingly, the creep strain rates of the fcc nc-HEA are significantly lower than that of fcc nc Ni (within a factor of ~4). As suggested by the authors, the nc HEA exhibits much higher creep resistance than conventional fcc nc metals because of the sluggish diffusion in HEAs.

A few other groups also investigated the creep behavior in various HEAs. Ma et al.\textsuperscript{64} compared the creep behavior of fcc and bcc nc-HEA thin films. They indicated that creep strains of the fcc CoCrFeNiCu HEA film were increased by increasing a holding load or loading rate, while a bcc CoCrFeNiCuAl\textsubscript{2.5} HEA thin film exhibited a consistent creep flow. Zhang et al.\textsuperscript{65} also found that the creep mechanism is dependent on indentation loads: at high indentation loads (> 500 µN). The dominant creep mechanism could be dislocation slip, while at low loads (< 500 µN), self-diffusion along the indenter/specimen interface and the free surface of the specimen may play an important role. Wang et al.\textsuperscript{63} evaluated the initial creep behavior in CoFeNi multiple-component alloy systems. They revealed a crossover behavior, showing the change of the slopes in the double logarithmic plot of initial displacement as a function of time at initial creep stage. They suggested that the different deformation mechanisms are associated with such a crossover: Before the crossover point, separated dislocations entanglement lead to work hardening; after the dislocation cell formation, the work hardening effect is saturated, and the residual dislocations migrate into the domain boundary of the dislocation cell, showing a viscous behavior.

As suggested by many studies, HEAs may exhibit distinct diffusion behavior compared to conventional alloys. Unfortunately, sluggish diffusion as one of the four primary HEA hypotheses has not been sufficiently proved,\textsuperscript{33} it was only demonstrated in one study\textsuperscript{26}. A better understanding of diffusion in both cg- and nc-HEAs is essential to understand the creep behavior in HEAs and the design of creep-resistant HEAs.

2.4. Friction and wear of HEAs
Wear-resistant properties of HEAs have also attracted considerable attention in the HEA community. Most previous studies were based on macroscopic wear/friction experiments, such as pin-on-disc and ball-on-disc. Studies of tribology and related mechanisms of HEAs at micro/nanoscale have rarely been reported. Using a nanoscratch method in an instrumented nanoindenter, Ye et al. studied wear and friction behavior of a bcc TiZrHfNb HEA under both ramping and constant load modes (Figs. 6(a)-(f)). The wear behavior of the HEA is comparable to conventional alloys, following the Archard’s equation for dry wear and with wear rates proportional to the applied load. The friction behavior of the HEA is much more complicated: In the elastic regime, the coefficient of friction (COF) decreased rapidly with increasing the normal load, while in the plastic regime, as indicated by dislocations in underneath the deformation zone (Figs. 6(g) and (h)), the COF became constant, indicating different friction mechanisms. However, what induced such transition is not very clear. Overall, such an HEA exhibits improved wear resistance and a lower COF as compared to its traditional alloy counterparts (pure Nb and Nb-based C103 alloys) (Fig. 6(i)), implying the HEA may have the potential for tribological applications. Unfortunately, so far, only very few studies have been reported on friction and wear of HEAs at small scales. Many questions are still unanswered: what is the fundamental difference of wear/friction between HEAs and conventional alloys? What is the wear and friction behavior over a large temperature and load ranges? What is the wear-corrosion behavior in HEAs?

3. Micro-compression and size effects in HEAs

In the last decade, there has been a significant advance in applying FIB technique and micro-compression methodology to study mechanical properties of micro/nano-pillars with the dimension from several microns down to ~100 nanometers. In 2004, Uchic and his co-workers first reported the plastic behavior of micrometer-scale cylinder metal pillars under uniaxial compression. The micro-pillars were produced using the FIB milling technique, and the compression was employed in a nanoindentation system with a flat-punch tip. At the submicrometer scales, the yield strength of materials can attain a significant fraction of their theoretical strength. It has been widely found that the yield or flow strength ($\sigma$) of the pillar can be strongly increased when its dimension ($D$) is decreased, exhibiting a “smaller-is-stronger” phenomenon (see reviews). This relation has commonly been
expressed by a relationship of $\sigma \propto D^m$, where $m$ is called size-effect exponent. Fcc metals (e.g., Ni, Au, Al, and Cu) exhibit a pronounced and constant size dependence of plasticity with $m$ in the range between -0.6 and -0.8. Bcc metals (e.g., Nb, Mo, V, Ta, and W) show a much more complicated size-related behavior with various $m$ values ranging from -0.2 to -0.9, reported by Schneider et al. and Kim et al. So far, two prominent mechanisms have been proposed to explain these size-related phenomena: single-arm source (SAS) or source-dominated model developed by Rao et al. and dislocation starvation theory proposed by Greer and Nix. It is believed that the latter mechanism plays an important role only when the pillar at or below the submicrometer.

HEAs, which were also first reported in 2004, are solid solutions with a simple fcc or bcc structure (only a few with hcp structures). Two questions thus arise: What are the strength of these HEA pillars at micron and submicron scales, compared with their bulk forms? And what is the size effects of fcc and bcc HEAs, compared with those of pure fcc and bcc metals? Using the micro-compression method, several research groups have investigated these questions.

3.1. Micro-compression of fcc HEA pillars

The largest body of literature on micro-compression of HEAs is focused on the fcc FeCrCoMnNi HEA. However, the reported size-effect exponents by several groups are not very consistent. Raghavan et al. compressed single-crystal FeCrCoMnNi micropillars (cylinder shape, 1-10 µm in diameter) along [113 5] orientation (Fig. 6(a)). They observed a planar slip on the (1-11)[110] slip system, with the highest Schmid factor of 0.48. The size dependence of yield strength follows a power-law relation with a log-log exponent of -0.32, which is a considerably lower size effect than that of pure fcc metals ($m \sim -0.6$). They suggested that their lower size effect than that pure fcc metals was attributed to a high bulk-to-theoretical strength ratio in the HEA. In a similar study, Zhang et al. reported a size-effect exponent of -0.46 in such fcc HEA, also showing a lower size effect than typical fcc metals.

Okamoto et al. investigated the size effect of the same fcc FeCrCoMnNi HEA by compressing rectangular micropillars (diameters of ~1-8 µm) along the loading orientations of [126] and [123] (Fig. 7(b)). They found that the slip systems were also \{111\}<\{101\>, but the size-effect exponents were about -0.63 (independent of orientation),
which was comparable to that of typical fcc metal micropillars. In another fcc HEA (Al_{0.7}CoCrFeNi), Giwa et al.\textsuperscript{80} studied the size effect of the fcc phase and showed a size-effect exponent of -0.66, which is also equivalent to most of the fcc metals. (Fig. 7(c)).

It is interesting to find that different groups have reported various size effects even in the same fcc HEA. As reported in pure metals and other solids, the size effect is not only dependent of its crystal structure but also relies on many other factors, such as defect density and how the sample prepared.\textsuperscript{85,86} The difference of the size effects observed in the fcc HEAs might be attributed to many other factors such as FIB preparation, initial dislocation density, local point defect density, microstructure, and pillar shapes. So far, only two HEAs have been reported for micro-compression, and future work is needed to make a substantial conclusion. Also, the reported FIB-milled HEA pillars are limited to \textasciitilde{}500 nm in diameter, and what the deformation mechanism and mechanical strength of an HEA pillar with an even smaller dimension (< 100 nm) are still unknown.

3.2. Micro-compression of bcc HEA pillars: single-crystalline (sx) and nanocrystalline (nc)

Using the micro-compression method, the author of this review and his coworkers studied bcc HEA micro-pillars and their size effects for the first time, on both sx-HEA pillars\textsuperscript{87} and nc-HEA pillars\textsuperscript{88}. Sx-NbMoTaW HEA pillars (diameters of \textasciitilde{}250 nm – 2 \textmu{}m) were compressed along two orientations ([001] and [316]). These bcc HEA pillars can reach high strength levels of \textasciitilde{}4 GPa, which is \textasciitilde{}3 times higher than that of the bulk HEA (Fig. 8). The bcc-HEA pillars exhibit higher strengths than any of pure bcc Nb, Mo, Ta and W pillars\textsuperscript{72-75}, in both absolute and normalized values. Also, the bcc-HEA pillars also show relatively low compressive size effects, with size-effect exponents ($m$) of about -0.3 (Fig. 8(d)). The higher strength levels and lower size dependence for the HEA could be attributed to the increased lattice resistance caused by localized distortion at atomic length scales, as observed in high-resolution TEM and detected by XRD.\textsuperscript{87} In addition, Giwa et al.\textsuperscript{80} also studied the size effect in a bcc (A2+B2) phase in an Al_{0.7}CoCrFeNi HEA. They discovered that the bcc phase also presented a “smaller is stronger” size effect with the exponent of \textasciitilde{}0.28 between strength and pillar diameter, which is also lower than all size dependence reported for pure bcc metals.
For pure bcc metal pillars, Schneider and his co-workers noticed that various m values in bcc metals could be correlated with different critical temperatures (T_c), above which flow stress becomes insensitive to test temperature, and equivalently residual Peierls potentials: the higher T_c, the lower size dependence. The popular interpretation of this correlation is that different non-planar dislocation cores in bcc metals play essential roles in the mobility of screw dislocations. Both the simulation and experiment suggest that bcc and fcc metal pillars differ in the controlling mechanisms of the size effect. The lower size dependence of the strength of bcc HEAs compared to pure bcc metals could be attributed to the severe lattice distortions in the HEA, which results in a significantly higher Peierls potential than for each of the constituents.

The first report about nc-HEA micro-pillars examined FIB-milled pillars prepared from bcc NbMoTaW HEA thin films by the co-sputtering technique. Such nc-HEA pillars exhibit extraordinarily high yield strengths of approximately 10 GPa – among the highest reported strengths in micro-/nano-pillar compression (even stronger than nc-W pillars) and one order of magnitude higher than that of its bulk form. As shown in Figs. 8(e)-(j), the smallest HEA pillars (~70-100 nm in diameter) exhibit high yield strengths of ~8-10 GPa, with a low size-effect exponent of ~0.2. Such ultra-high strength in the nc-HEA pillars is contributed by the combination of substantial solid-solution hardening effect in HEAs, sample-size effect (source-controlled strengthening) and grain-boundary strengthening.

3.3. Micro-compression of nanocrystalline (nc) HEAs: room temperature vs. high temperature

Based on high-temperature indentation, the mechanical properties of sx-HEA and nc-HEA pillars can be compared over a broad temperature range. In general, nanocrystalline metals exhibit high strengths at ambient conditions, yet their strengths substantially decrease with increasing temperature. Surprisingly, bcc NbMoTaW nc-HEA pillars retain an extraordinarily high yield strength over 5 GPa up to 600 °C – one order of magnitude higher than that of its coarse-grained form, and five times higher than that of its single-crystalline counterpart, as shown in Fig. 9.
The strain-rate jump method was also applied to determine the strain-rate sensitivity (SRS) and activation volume \( (V) \). At 600 °C, the activation volume of the sc-HEA pillars is \( \sim 175 \, b^3 \), implying that sx-HEAs are deformed by the Peierls mechanism at 600 °C, which is comparable to the deformation of fcc metals\(^91\); At 600 °C, the \( V \) of the nc-HEAs slightly increases to \( \sim 50 \, b^3 \) at 600 °C, suggesting the deformation of nc-HEAs could be still dominated by the kink-pair mechanism rather than the grain-boundary mediated mechanism. Such nanostructured HEAs reveal strengthening figures of merit – normalized strength by the shear modulus above 1/50 and strength-to-density ratios above 0.4 MJ/kg, which are substantially higher than any previously reported values for nanocrystalline metals in the same homologous temperature range (Figs. 9(k) and (j)).

Using the similar calculation method in the last section, the activation volumes for the sx- and nc-HEAs are calculated to be \( \sim 10 \, b^3 \) at room temperature. This value is identical to that reported from bulk tensile measurements on W, in which thermally activated double kink mechanism is believed to be responsible for the motion of screw dislocations\(^92\). With increasing temperature, the \( V \) of the sx-HEA pillars increases to an average value of \( \sim 175 \, b^3 \) at 600 °C, implying that sx-HEAs are deformed by, or partially by, the Peierls mechanism at 600 °C, which is comparable to the deformation of fcc metals\(^91\). The \( V \) of the nc-HEAs slightly increases to \( \sim 50 \, b^3 \) at 600 °C, suggesting the deformation of nc-HEAs could be still dominated by the kink-pair mechanism rather than the grain-boundary mediated mechanism. These \( V \) values for bcc HEAs are different from that of previous studies on fcc HEA pillars, in which activation volumes increase with increasing test temperature, suggesting an enhanced grain-boundary mediated deformation\(^93\).

4. **In situ** fracture tests of HEAs at small scales

Using *in situ* SEM and TEM techniques, fracture properties of HEAs have been studied at the micrometer and nanometer scales. The extraordinarily high fracture toughness of the bulk FeCrCoMnNi HEA attracts significant attention in the materials community. The bulk single-phase FeCrCoMnNi alloy displays tensile strength levels of ~1GPa, excellent ductility (~60–70%), and exceptional fracture toughness \((K_{IC} > 200\text{MPa }\sqrt{\text{m}})\). Using *in situ* straining in a transmission electron microscope (TEM), Zhang *et al.*\(^62\) report on the atomistic to micro-scale
mechanisms underlying the origin of these properties, using an *in situ* straining test in a TEM (Fig. 10). They identified multiple deformation mechanisms in the HEA, which are rarely observed simultaneously in metallic alloys, including the easy motion of Shockley partials, their interactions to form stacking-fault parallelepipeds and arrest at planar slip bands of undissociated dislocations. These mechanisms together generate high strength, work hardening and ductility. Furthermore, crack propagation impeded by twinned, nanoscale bridges that form between the near-tip crack faces and delay fracture by shielding the crack tip (Fig. 10 (b)). Without such *in situ* fracture test, it is difficult to understand the fracture behavior in detail. Using *in situ* TEM, Cai *et al.* studied the fracture behavior of a bcc NiCrCoV HEA phase. Using this method, they can measure Young's module, fracture strength and ultimate elongation (~107 GPa, ~2.70 GPa and ~2.6%, respectively) and observe cleavage fracture with the cleavage plane of {112}.

Previous studies on bulk bcc HEAs imply that grain boundaries affect fracture behavior of bcc HEAs, but quantitative studies on their fracture properties are scarce. Using *in situ* micro-cantilever tests, the author of this review and his co-workers compared the fracture toughness of single-crystal (SC) and bi-crystal (BC) HEAs (NbMoTaW). Figs. 11(a)-(c) and (e)-(g) present snapshots from movies of typical SC- and BC-cantilevers upon loading, respectively. Figs 11(d) and 11(h) show their corresponding load-displacement curves. The SC-cantilever exhibits a linear elastic behavior at the initial loading stage, a slight yielding before reaching the maximum load, and a subsequent gradual force drop. In contrary to the SC-cantilevers, all the BC-cantilevers experienced a catastrophic event at the maximum load. They did not show any plastic yielding before fracture, and the crack tips suddenly opened and advanced along the grain boundaries (GBs) (Fig. 11(g)), indicating that the BC-specimens are more brittle than the SC ones. After *in situ* cantilever tests, fracture surfaces of the two types of cantilevers reveal distinct surface morphologies (Figs. 11(i) and (j)). Quantitatively, the fracture toughness of these cantilevers was measured: The single-crystal cantilevers fail by quasi-cleavage fracture with fracture toughness $K_{ic}$ of ~1.3-2.1 MPa·m$^{1/2}$, while the bi-crystal cantilevers exhibit brittle intergranular fracture with much lower $K_{ic}$ of ~0.2 MPa·m$^{1/2}$. The observation from small-scale testing suggests that the poor fracture resistance of the polycrystalline refractory HEAs is attributed to the GB segregation and formation of brittle oxides and nitrides at GBs.
Using in situ SEM micro-compression, Gao et al. studied mechanical properties and fracture behavior of an HEA-coated nanolattice structure, which was made by a polymetric lattice coated with an 80-nm thick HEA thin film (CoCrFeNiAl0.3) (Fig. 12). In the composite nanolattice, they observed a linear region up to 11% strain at 7.76 MPa followed by a brittle failure at 12% strain, implying an improved toughness compared to that of the polymer nanolattice. Unfortunately, the authors did not give a further evaluation of the fracture toughness of such HEA-coated nanolattice. The stress-strain curve shows structural instabilities, which is caused by the fracture of individual struts driven by the brittle HEA layers near or at the junctions. Typically, failure in such structural materials is initiated at the weakest connection, which is determined by the competing effects of stress concentrators at surface imperfections and local stresses. The optimization of lattice structure and HEA coating thickness would be interesting for future study. This concept of combining HEA with polymer lattice structures demonstrates the potential of fabricating novel architected metamaterials with tunable mechanical properties.

Compared to nanoindentation and micro-compression studies of HEAs, fracture properties of HEAs at small length scales have been much less reported. It is mainly because experimental setup for small-scale fracture testing is relatively complicated. With more nanomechanical tools becoming mature, particularly with in situ capacities, more sophisticated experiment can be carried out to investigate fracture behavior of a large variety of HEAs.

5. Conclusions and outlook

This article reviews that nanomechanical techniques have become valuable tools to study the mechanical behavior of an emerging family of metallic systems – HEAs, offering many opportunities for scientific inquiry. A large body of literature is concentrated on nanoindentation or micro-compression of a few well-known HEAs, such as fcc FeCoCrMnNi and bcc NbMoTaW. A few interesting phenomena and useful properties have been reported, as summarized below:

- The activation volume for the onset of plasticity in HEAs is reported to be higher than in that of regular metals, suggesting a complex cooperative motion of several atoms during the dislocation nucleation process
in HEAs. But it is mainly reported by one research group and more investigations on other HEAs are needed to confirm this conclusion.

- Nanoindentation/micro-pillar strain-rate jump testing on both sx-HEAs and nc-HEAs reveals that there are competing mechanisms between dislocation mechanism (bulk behavior) and diffusion or grain-boundary sliding mechanism (nanocrystalline behavior) over a large temperature range. The fundamental difference of deformation mechanisms between HEAs and regular alloys are still not very clear.

- Nc-HEAs exhibit better creep resistant than pure fcc Ni, which might be attributed to the sluggish diffusion in HEAs, but further study is needed to confirm it.

- A study of wear and friction of a bcc HEA indicates enhanced wear resistance in HEAs, but nanoscale wear/friction of HEAs has been much less explored than other mechanical properties.

- The micro-compression method has been used to study the size dependence of plasticity in fcc and bcc HEA pillars: Fcc HEA pillars exhibit the similar size effects with pure fcc metal pillars, while bcc HEA pillars show a slightly lower size effect than those of pure bcc metals, which could be due to higher lattice friction in HEAs.

- Bcc nc-HEA micropillars exhibit substantially better mechanical and thermal stability than any previously reported nanocrystalline metals over the same homologous temperature range.

- In situ SEM and TEM capacities have been used to study the fracture properties of HEAs in various forms, including single crystals, bi-crystals, and HEA-coated nanolattices.

**Challenges:** Nanomechanical studies of HEAs are relatively new – much in contrast to the studies of regular metals, typical alloys, and metallic glasses. So far, only less than ten HEAs, among over 400 produced HEAs, have been studied using a limited number of nanomechanical methods. Sometimes, the reported results are not consistent, and many underlying mechanisms are still unknown. As a consequence, very fundamental aspects of mechanical behavior remain unresolved for HEAs at small scales. Although molecular dynamics (MD) simulations have provided helpful insight into small-scale plasticity in pure metals, and even binary alloys, it is very challenging to use MD methods to simulate the plastic deformation of HEAs. HEAs exhibit interesting an atomic-level structure
– various elements are randomly distributed in a simple lattice, but a key question is still not fully answered: What is fundamentally new in HEAs regarding their deformation mechanism?

**Perspectives:** It is worth learning from the recent literature on nanomechanics of HEAs and exploring for future studies on this topic. As many advanced nanomechanical techniques are becoming mature, they will provide new powerful tools to investigate a large variety of HEAs, both known and unknown. To conclude this article, a few unanswered questions and new directions, which would be interesting for future research, are pointed out:

- What is the deformation mechanism of HEAs at the nanometer regime of 100 nm and below? So far, the smallest HEA pillars reported are about 100 nm, mostly for the fcc FeCoCrMnNi. As critical stress increases as a sample dimension decreases, new deformation mechanisms might be activated.

- What are the nanomechanical behavior and size effects of other HEAs, except for typical fcc and bcc ones, for example, hcp HEAs, ordered HEAs and multiple-phase HEAs?

- **Compared to nanoindentation and micro-compression studies of HEAs, their fracture, fatigue, and creep properties as well as relevant environmental effects, such as oxidation and irradiation, have been much less studied and will be interesting for future investigation.**

- What is fundamentally new about atomic-level mechanical behavior in HEAs, compared to other alloys, especially stainless steels and superalloys? It is exciting to explore new mechanisms regarding dislocation nucleation, dislocation propagation, and diffusion-related deformation in HEAs.

- Testing of HEAs small features for understanding their bulk properties: HEAs do not necessarily possess single-phase or fully disordered structures. Their local structures may be dramatically changed by chemical compositions and thermal treatment, producing multiple phases as well as short- or medium-range ordering. Nanomechanical testing can provide details of mechanical properties and deformation mechanisms of each phase or nanoscale cluster, giving a better understanding their bulk mechanical properties.

- High-throughput testing for new HEA design: The family of HEAs is enormous, 400 compositions have been produced and hundreds to be explored. Many HEAs contain rare or relatively rare elements, which means the process of developing HEAs is expensive. To save a significant amount of material and time,
nanomechanical testing can be used as a high-throughput screening method to search the most optimized properties and compositions, paving the way in the design for new HEAs.

• High-entropy oxides and functional properties: the concept of “high entropy” is not only limited to metals, but it can also be applied to ceramics (e.g., high-entropy oxides96). Moreover, rather than mechanical properties, many functional properties (e.g., superconductivity97 and oxidation resistance98) have also been found in HEAs. Based on nanomechanical testing platforms, the multi-field coupling of many properties of HEAs can also be measured and explored, including as mechanical, thermal, photonic, electrical and chemical-related properties.

Acknowledgments
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Table 1. A brief summary of studies of HEAs using different nanomechanical methods: nanoindentation, micro-compression, and fracture testing (cg: coarse-grained, nc: nanocrystalline, and sx: single-crystal).

<table>
<thead>
<tr>
<th>Method</th>
<th>Mode</th>
<th>Structure</th>
<th>HEAs</th>
<th>Properties</th>
<th>Representative references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoindentation</td>
<td>different loading rates</td>
<td>fcc</td>
<td>FeCoCrMnNi (cg)</td>
<td>incipient plasticity</td>
<td>Zhu et al. 2013³²</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td>different loading rates</td>
<td>bcc</td>
<td>TiZrHfNb (cg)</td>
<td>incipient plasticity</td>
<td>Zhu et al. 2017³³</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td>different indenter tips</td>
<td>fcc</td>
<td>FeCoCrMnNi (cg &amp; nc)</td>
<td>annealing effect</td>
<td>Lee et al. 2015, 2017⁵⁴, ⁵⁶</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td>strain-rate jump</td>
<td>fcc</td>
<td>FeCoCrMnNi (cg &amp; nc)</td>
<td>strain-rate sensitivity, activation volume</td>
<td>Maier-Kiener et al. 2017⁶⁰, ⁶¹</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td>holding</td>
<td>fcc</td>
<td>FeCoCrMnNi (cg &amp; nc)</td>
<td>creep property</td>
<td>Lee et al. 2016⁵⁵</td>
</tr>
<tr>
<td>Nanoindentation</td>
<td>wear &amp; friction</td>
<td>bcc</td>
<td>TiZrHfNb (cg)</td>
<td>wear rate, coefficient of friction</td>
<td>Ye et al. 2018⁶⁸</td>
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<tr>
<td>Micro-compression</td>
<td>micro-pillars</td>
<td>fcc</td>
<td>FeCoCrMnNi (cg)</td>
<td>size dependence of strength</td>
<td>Okamoto et al. 2016³³; Zhang et al. ⁸²; Raghavan et al. ²⁰¹⁷⁸¹</td>
</tr>
<tr>
<td>Micro-compression</td>
<td>micro/nano-pillars</td>
<td>fcc &amp; bcc</td>
<td>Al₀.₈CoCrCuFeNi; Al₀.₉CoCrFeNi (cg)</td>
<td>strength; size dependence</td>
<td>Liu et al. 2011⁷⁹, Giwa et al. 2016⁸⁰</td>
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<tr>
<td>Micro-compression</td>
<td>micro-pillars</td>
<td>bcc</td>
<td>NbMoTaW (sx)</td>
<td>size dependence of strength</td>
<td>Zou et al. 2014⁸⁷</td>
</tr>
<tr>
<td>Micro-compression</td>
<td>micro-pillars</td>
<td>bcc</td>
<td>NbMoTaW (nc)</td>
<td>size dependence of strength</td>
<td>Zou et al. 2015⁸⁸</td>
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<tr>
<td>Micro-compression</td>
<td>strain-rate jump/High-temperature</td>
<td>bcc</td>
<td>NbMoTaW (sx &amp; nc)</td>
<td>size effect, strain-rate sensitivity, activation volume</td>
<td>Zou et al. 2017⁶²</td>
</tr>
<tr>
<td>Micro straining</td>
<td>in situ TEM</td>
<td>fcc</td>
<td>FeCoCrMnNi (cg)</td>
<td>fracture mechanism</td>
<td>Zhang et al. 2015⁹⁹</td>
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<tr>
<td>Micro-cantilever bending</td>
<td>in situ TEM</td>
<td>bcc</td>
<td>NbMoTaW (sx and cg)</td>
<td>fracture toughness grain boundary effect</td>
<td>Zou et al. 2016⁴⁰</td>
</tr>
<tr>
<td>Nano-lattice compression</td>
<td>in situ SEM</td>
<td>fcc</td>
<td>CoCrFeNiAl₀.₃ (nc/composite)</td>
<td>fracture behavior</td>
<td>Gao et al. 2018⁹⁵</td>
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</table>

Table 2

Activation volumes for the pop-ins in fcc and bcc materials (after Zhu et al.⁴³).

<table>
<thead>
<tr>
<th>Materials</th>
<th>fcc-Pt</th>
<th>fcc-Ni</th>
<th>bcc-Mo</th>
<th>fcc-HEA</th>
<th>bcc-HEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation volume (Ω)</td>
<td>~0.5</td>
<td>~1</td>
<td>~1</td>
<td>~3</td>
<td>~3-5</td>
</tr>
</tbody>
</table>
Fig. 1. (a) Length scales associated with structure defects and dislocation systems from the macroscopic scale to the nanometer scale (the concept is adapted from Zaiser and Seeger\textsuperscript{100} and the schematic illustrations are from Refs. \textsuperscript{101, 102, 103, 104, 105}). (b) Examples of available nanomechanical techniques (from left to right): nanoindentation, micro-compression, micro-cantilever bending, micro/nano-tensile tests, and in situ TEM (representative images from Refs. \textsuperscript{11, 106-109}, respectively). (c) The increasing chemical and structure complexity from single-element fcc metals to multi-component metallic glasses, a couple of intermediate states such as ordered intermetallic compounds, high-entropy alloys, and quasicrystals. The periodicity and structural order of materials decrease from left to right (the schematic illustrations from Refs.\textsuperscript{110-112}). (Reproduced with permissions)

Fig. 2. (a) Typical load–displacement (P–h) curves from three different FeCoCrMnNi HEA grains tested at room temperature, showing pop-in phenomena when dislocation nucleation occurs. (b) Extracting the activation volume from room-temperature experimental data at different loading rates, where \( P \) is cumulative probability and \( P \) is a pop-in load. (c) Typical P–h curves at temperatures of 22, 50, 100 and 150 °C, showing a decreased pop-in load with an increasing temperature. (d) The variation of maximum shear stress as a function of temperature, suggesting a thermally activated dislocation nucleation process.\textsuperscript{42} The activation energy and volume for the onset of plasticity can be calculated according to equation (1) and (2). (Reproduced with permission from Ref.\textsuperscript{42})

Fig. 3. Typical microstructure of (a) the as-cast (average grain size ~40 µm) and (b) HPT-processed (average grain size ~40 nm) FeCoCrMnNi HEA. (c) Hardness as a function of the grain size in the HEA, following the Hall-Petch relation. (d) Estimated stress-strain relations calculated from nanoindentation data, showing a strong indentation-size effect in annealed HEAs and annealing-induced hardening (1A: annealing at 450 °C for one hour; 10A annealing at 450 °C for ten hours). (e) Typical TEM image and (f) the corresponding EDS map for the subsurface region underneath the nanoindenter (Berkovich tip for the sample HPT +10A), indicating phase separation and formation of new intermetallics.\textsuperscript{54, 56} (Reproduced with permission from Refs.\textsuperscript{54, 56})

Fig. 4. Nanoindentation strain-rate jump tests on a <100> orientation grain in (a) the coarse-grained and (b) the nanocrystalline (nc) FeCoCrMnNi HEA. Representative curves are showing hardness versus indentation depth for different temperatures. The inset shows an enlarged segment of the slowest strain-rate region for all temperatures. (c) Strain-rate sensitivity and activation volume (\( V \)) as functions of testing temperature up to 400 °C, indicating different mechanisms of thermally activated deformation in the coarse-grained and nanocrystalline HEAs.\textsuperscript{60} (Reproduced with permission from Ref.\textsuperscript{60})
Fig. 5. Strain-rate as functions of holding time for (a) ~33-nm grain, (b) ~49-nm grain, and (c) coarse-grain FeCoCrMnNi HEA. The inserts show creep strain vs. holding time. (d) Relationship between quasi-steady-state (QSS) creep strain rates as functions of stress (slopes correspond to the creep-stress exponent \( n \)), indicating the nanocrystalline (nc) HEAs exhibit significantly lower creep rates than that of nanocrystalline Ni.\(^{55}\) (Reproduced with permission from Ref.\(^{55}\))

Fig. 6. Typical SEM images of the TiZrHfNb HEA under (a,b) ramping mode from 0-1000 µN, (c,d) constant load at 500 µN, and (e, f) constant load at 1000 µN. (g, h) The high-resolution TEM image along zone axis of [111] shows severely distorted lattice and high density of dislocations with Burgers vectors. (i) adhesion coefficient of friction (COF) as a function of the normal force for Nb, Nb-based C103 alloy and the HEA in the plasticity-dominated regime, indicating the HEA has the lowest COF and best wear resistance among them.\(^{68}\) (Reproduced with permission from Ref.\(^{68}\))

Fig. 7. (a) Typical SEM images of the fcc FeCoCrMnNi HEA micro-pillars after deformation (1-10 µm in diameter, cylinder shape); Scaling of the yield strength as a function of the pillar diameter, with a size-effect exponent of about -0.32.\(^{81}\) (b) SEM image of the fcc FeCoCrMnNi HEA micro-pillars after deformation (~1-8 µm in diameter, rectangular shape) deformed along [-123] orientation. The size-effect exponent is about -0.6.\(^{83}\) (c) Micro-compression of a fcc Al\(_{0.7}\)CoCrFeNi HEA micro-pillars (450 nm – 2 µm in diameter, cylinder shape), the size-effect exponent is about -0.6.\(^{80}\) (Reproduced with permission from Refs.\(^{80, 81, 83}\))

Fig. 8. SEM images of post-compressed [316]-oriented sx-HEA Nb\(_{25}\)Mo\(_{25}\)Ta\(_{25}\)W\(_{25}\) pillars with approximate diameters of: (a) 2 µm, (b) 1 µm. An enlarged image which presents sharp slip bands is shown in the inset of (a). (c) Stress-strain curves for the sx-HEA pillars. (d) Schematic illustration of size-dependent strengths for different metallic systems: FIB-milled pure fcc and bcc pillars. The HEA bcc pillars exhibit both higher absolute and normalized strength levels than any other bcc metals but a relatively low size dependence of strengths.\(^{87}\) (e)-(j) Compression results for the pillars prepared from the HEA films. (e)-(h) SEM images of typical as-deformed HEA pillars (IBAD) with the diameter \( D \) ranging from approximately 1 µm to 100 nm. (i) Representative stress-strain curves of the HEA pillars, showing a size-dependent strength. (j) A comparison of the strength-size relationships for the columnar-structured HEA pillars, single-crystal HEA (based on the specimen and method in Ref.\(^{87}\)) and W pillars\(^{72, 75, 88}\). (Reproduced with permission from Refs.\(^{87, 88}\))
**Fig. 9.** Compression results for the sx- and nc-HEA micro-pillars from room temperature to 600 °C. Representative SEM images of the deformed sx-HEA pillars ((a), (b), (c), and (d)) and nanostructured columnar-grained HEA pillars ((e), (f), (g), and (h)). Corresponding engineering stress–strain curves of (i) the sx-HEA and (j) nc-HEA pillars, showing how flow stresses changes by temperature. Strain-rate jump tests are applied to measure the strain-rate sensitivity using initial and final strain rates of $10^{-3}$ s$^{-1}$ and four other strain rates of $2\times10^{-4}$ s$^{-1}$, $2\times10^{-3}$ s$^{-1}$, $5\times10^{-4}$ s$^{-1}$, and $5\times10^{-3}$ s$^{-1}$. (j) Normalized critical resolved shear stress ($\tau/\mu$) as a function of homologous temperature ($T_t/T_m$) for the sx- and nc-HEA pillars, indicating the nc-HEA pillars exhibit the highest normalized strength ($\sim1/50$-$1/30$) among all the bulk and nanostructured metals ($\tau$ is critical resolved shear strength, $\mu$ is the corresponding shear modulus, $T_t$ is testing temperature, and $T_m$ is melting temperature. (k) The Ashby-inspired map of specific strength (strength-to-density ratio) versus test temperature, showing that the nc-HEAs exhibit the highest strength-to-density ratio in all the nc-metals at the same tested temperatures. (Reproduced with permission from Ref.62)

**Fig. 10.** (a) Bright-field TEM image of a growing crack during *in situ* straining of the fcc FeCoCrMnNi HEA. Submicron/nano-scale voids at the intersection of slip systems are observed. (scale bar, 200 nm) (b) TEM images show nanoscale fibres bridge the cracks (scale bar, 200 nm). Nanotwins can be seen to form in the fibres, which enhance ductility and toughness. (c) High-resolution TEM image of deformation twinning during *in situ* TEM tensile test (scale bar, 5nm). (d) HAADF-STEM image of the atomic structure of the deformation nanotwins (scale bar, 2 nm). (Reproduced with permission from Ref.99)

**Fig. 11.** Representative *in situ* TEM images of deflected single-crystalline (SC) - (a, b, and c) and bi-crystal (BC)- (e, f, and g) cantilevers: (a) and (e) initial contacts; (b) and (f) crack tip opening at the maximum load; (c) and (g) fracture and load drops. (d) and (h) the corresponding indenter load-displacement curves for the SC- and BC-cantilevers, respectively. The indenter displacement was evaluated using an image correction software. Typical post-mortem SEM images of the fracture surfaces: (i) the SC-cantilever specimen shows a quasi-cleavage feature with river markings, suggesting SC-HEAs are not intrinsically brittle; (j) the BC-cantilever specimen exhibits a typical feature of brittle intergranular fracture. (Reproduced with permission from Ref.40)

**Fig. 12.** Compression tests on an HEA-coated nanolattice structure. (a) *In situ* SEM compression test set up for testing the composite nanolattice. (b) Screenshot SEM images of the composite nanolattice during the compression test (side view). (c) and (d) Side and top view of crushed composite nanolattice structure after the compression test. (e)–(g) Close-up view of a shell fragment from (d). (h) Stress-strain plots of a polymer-only nanolattice and a composite nanolattice that were tested under the same condition. The scale bars in (b)–(d) is 5mm, and 500nm in (e)–(g), respectively. (Reproduced with permission from Ref.95)
Fig. 1. (a) Length scales associated with structure defects and dislocation systems from the macroscopic scale to the nanometer scale (the concept is adapted from Zaiser and Seeger\textsuperscript{100} and the schematic illustrations are from Refs. \textsuperscript{101, 102 103 104, 105}). (b) Examples of available nanomechanical techniques (from left to right): nanoindentation, micro-compression, micro-cantilever bending, micro/nano-tensile tests, and \textit{in situ} TEM (representative images from Refs. \textsuperscript{11, 106 107-109}, respectively). (c) The increasing chemical and structure complexity from single-element fcc metals to multi-component metallic glasses, a couple of intermediate states such as ordered intermetallic compounds, high-entropy alloys, and quasicrystals. The periodicity and structural order of materials decreases from left to right (the schematic illustrations from Refs.\textsuperscript{110-112}). (Reproduced with permissions)
Fig. 2. (a) Typical load–displacement ($P$–$h$) curves from three different FeCoCrMnNi HEA grains tested at room temperature, showing pop-in phenomena when dislocation nucleation occurs. (b) Extracting the activation volume from room-temperature experimental data at different loading rates, where $F$ is cumulative probability and $P$ is a pop-in load. (c) Typical $P$–$h$ curves at temperatures of 22, 50, 100 and 150 °C, showing a decreased pop-in load with an increasing temperature. (d) The variation of maximum shear stress as a function of temperature, suggesting a thermally activated dislocation nucleation process. The activation energy and volume for the onset of plasticity can be calculated according to equation (1) and (2). (Reproduced with permission from Ref. 42)
Fig. 3. Typical microstructure of (a) the as-cast (average grain size ~40 µm) and (b) HPT-processed (average grain size ~40 nm) FeCoCrMnNi HEA. (c) Hardness as a function of the grain size in the HEA, following the Hall-Petch relation. (d) Estimated stress-strain relations calculated from nanoindentation data, showing a strong indentation-size effect in annealed HEAs and annealing-induced hardening (1A: annealing at 450 °C for one hour; 10A annealing at 450 °C for ten hours). (e) Typical TEM image and (f) the corresponding EDS map for the subsurface region underneath the nanoindenter (Berkovitch tip for the sample HPT +10A), indicating phase separation and formation of new intermetallics.54, 56 (Reproduced with permission from Refs.54, 56)
Fig. 4. Nanoindentation strain-rate jump tests on a <100> orientation grain in (a) the coarse-grained and (b) the nanocrystalline (nc) FeCoCrMnNi HEA. Representative curves are showing hardness versus indentation depth for different temperatures. The inset shows an enlarged segment of the slowest strain-rate region for all temperatures. (c) Strain-rate sensitivity and activation volume ($V$) as functions of testing temperature up to 400 °C, indicating different mechanisms of thermally activated deformation in the coarse-grained and nanocrystalline HEAs.60 (Reproduced with permission from Ref.60)
Fig. 5. Strain-rate as functions of holding time for (a) ~33-nm grain, (b) ~49-nm grain, and (c) coarse-grain FeCoCrMnNi HEA. The inserts show creep strain vs. holding time. (d) Relationship between quasi-steady-state (QSS) creep strain rates as functions of stress (slopes correspond to the creep-stress exponent \( n \)), indicating the nanocrystalline (nc) HEAs exhibit significantly lower creep rates than that of nanocrystalline Ni. \(^{55}\) (Reproduced with permission from Ref.\(^{55}\))
Fig. 6. Typical SEM images of the TiZrHfNb HEA under (a,b) ramping mode from 0-1000 µN, (c,d) constant load at 500 µN, and (e, f) constant load at 1000 µN. (g, h) The high-resolution TEM image along zone axis of [111] shows severely distorted lattice and high density of dislocations with Burgers vectors. (i) adhesion coefficient of friction (COF) as a function of the normal force for Nb, Nb-based C103 alloy and the HEA in the plasticity-dominated regime, indicating the HEA has the lowest COF and best wear resistance among them. (Reproduced with permission from Ref.68)
Fig. 7. (a) Typical SEM images of the fcc FeCoCrMnNi HEA micro-pillars after deformation (1-10 µm in diameter, cylinder shape); Scaling of the yield strength as a function of the pillar diameter, with a size-effect exponent of about -0.32.81 (b) SEM image of the fcc FeCoCrMnNi HEA micro-pillars after deformation (~1-8 µm in diameter, rectangular shape) deformed along [−123] orientation. The size-effect exponent is about -0.6.83 (c) Micro-compression of a fcc Al0.7CoCrFeNi HEA micro-pillars (450 nm – 2 µm in diameter, cylinder shape), the size-effect exponent is about -0.6.80 (Reproduced with permission from Refs.80, 81, 83)
Fig. 8. SEM images of post-compressed [316]-oriented sx-HEA Nb$_{25}$Mo$_{25}$Ta$_{25}$W$_{25}$ pillars with approximate diameters of: (a) 2 µm, (b) 1 µm. An enlarged image which presents sharp slip bands is shown in the inset of (a). (c) stress-strain curves for the sx-HEA pillars. (d) Schematic illustration of size-dependent strengths for different metallic systems: FIB-milled pure fcc and bcc pillars. The HEA bcc pillars exhibit both higher absolute and normalized strength levels than any other bcc metals but a relatively low size dependence of strengths. (e)-(j) Compression results for the pillars prepared from the HEA films. (e)-(h) SEM images of typical as-deformed HEA pillars (IBAD) with the diameter ($D$) ranging from approximately 1 µm to 100 nm. (i) Representative stress-strain curves of the HEA pillars, showing a size-dependent strength. (j) A comparison of the strength-size relationships for the columnar-structured HEA pillars, single-crystal HEA (based on the specimen and method in Ref.87) and W pillars. (Reproduced with permission from Refs.87, 88)
Fig. 9. Compression results for the sx- and nc-HEA micro-pillars from room temperature to 600 °C. Representative SEM images of the deformed sx-HEA pillars ((a), (b), (c), and (d)) and nanostructured columnar-grained HEA pillars ((e), (f), (g), and (h)). Corresponding engineering stress–strain curves of (i) the sx-HEA and (j) nc-HEA pillars, showing how flow stresses changes by temperature. Strain-rate jump tests are applied to measure the strain-rate sensitivity using initial and final strain rates of $10^{-3}$ s$^{-1}$ and four other strain rates of $2 \times 10^{-4}$ s$^{-1}$, $2 \times 10^{-3}$ s$^{-1}$, $5 \times 10^{-4}$ s$^{-1}$, and $5 \times 10^{-3}$ s$^{-1}$. (j) Normalized critical resolved shear stress ($\tau/\mu$) as a function of homologous temperature ($T_t/T_m$) for the sx- and nc-HEA pillars, indicating the nc-HEA pillars exhibit the highest normalized strength ($\sim 1/50$-$1/30$) among all the bulk and nanostructured metals ($\tau$ is critical resolved shear strength, $\mu$ is the corresponding shear modulus, $T_t$ is testing temperature, and $T_m$ is melting temperature. (k) The Ashby-inspired map of specific strength (strength-to-density ratio) versus test temperature, showing that the nc-HEAs exhibit the highest strength-to-density ratio in all the nc-metals at the same tested temperatures.62 (Reproduced with permission from Ref.62)
**Fig. 10.** (a) Bright-field TEM image of a growing crack during *in situ* straining of the fcc FeCoCrMnNi HEA. Submicron/nano-scale voids at the intersection of slip systems are observed. (scale bar, 200 nm) (b) TEM images show nanoscale fibres bridge the cracks (scale bar, 200 nm). Nanotwins can be seen to form in the fibres, which enhance ductility and toughness. (c) High-resolution TEM image of deformation twinning during *in situ* TEM tensile test (scale bar, 5nm). (d) HAADF-STEM image of the atomic structure of the deformation nanotwins (scale bar, 2 nm). (Reproduced with permission from Ref. 99)
Fig. 11. Representative *in situ* TEM images of deflected single-crystalline (SC) - (a, b, and c) and bi-crystal (BC)- (e, f, and g) cantilevers: (a) and (e) initial contacts; (b) and (f) crack tip opening at the maximum load; (c) and (g) fracture and load drops. (d) and (h) the corresponding indenter load-displacement curves for the SC- and BC-cantilevers, respectively. The indenter displacement was evaluated using an image correction software. Typical post-mortem SEM images of the fracture surfaces: (i) the SC-cantilever specimen shows a quasi-cleavage feature with river markings, suggesting SC-HEAs are not intrinsically brittle; (j) the BC-cantilever specimen exhibits a typical feature of brittle intergranular fracture.\(^{40}\) (Reproduced with permission from Ref.\(^{40}\))
**Fig. 12.** Compression tests on an HEA-coated nanolattice structure. (a) *In situ* SEM compression test set up for testing the composite nanolattice. (b) Screenshot SEM images of the composite nanolattice during the compression test (side view). (c) and (d) Side and top view of crushed composite nanolattice structure after the compression test. (e)-(g) Close-up view of a shell fragment from (d). (h) Stress-strain plots of a polymer-only nanolattice and a composite nanolattice that were tested under the same condition. The scale bars in (b)–(d) is 5mm, and 500nm in (e)-(g), respectively.⁹⁵ (Reproduced with permission from Ref.⁹⁵)