Phase-Transformation Ductilization of Brittle High-Entropy Alloys via Metastability Engineering

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High-entropy alloys (HEAs) in which interesting physical, chemical, and structural properties are being continuously revealed have recently attracted extensive attention. Body-centered cubic (bcc) HEAs, particularly those based on refractory elements are promising for high-temperature application but generally fail by early cracking with limited plasticity at room temperature, which limits their malleability and widespread uses. Here, the “metastability-engineering” strategy is exploited in brittle bcc HEAs via tailoring the stability of the constituent phases, and transformation-induced ductility and work-hardening capability are successfully achieved. This not only sheds new insights on the development of HEAs with excellent combination of strength and ductility, but also has great implications on overcoming the long-standing strength–ductility tradeoff of metallic materials in general.

Demand and pursuit for materials with high strength, large ductility, and high thermal stability have never faded for practical applications and scientific interests. Conventional alloys are usually composed of one principal element, with addition of some minor elements to alter local stress fields and dislocation movement, and thereby optimizing overall properties of the materials. Over the past decade, a new alloy design philosophy, i.e., high-entropy alloys (HEAs) which have equimolar or near-equimolar atomic fractions of multiple constituents, have drawn intensive interests. High configuration-entropic contribution to the decreased Gibbs free energy in these alloys retards formation of intermetallics and stabilizes single solid solution phase, such as face-centered cubic (fcc), body-centered cubic (bcc), hexagonal cubic phase (hcp), and orthorhombic crystal structures. HEAs have exhibited numerous interesting properties and unique characteristics, and developed multifarious potential applications. At elevated temperatures, this novel family of metallic materials intrinsically has high phase stability and large mechanical strength since entropic contribution predominates the thermodynamics. Vast literature data indicate that bcc HEAs, particularly bcc HEAs based on refractory elements like VNbMoTaW, exhibit not only extremely stable microstructure against temperature, but also large heat-softening resistance, even better than conventional Ni-based superalloys. Nevertheless, a great majority of such bcc HEAs developed up to date suffer from poor ductility at room temperature, which makes them difficult to be processed and thus limits their practical applications. Serious efforts have been devoted to this area, and a few approaches such as reducing the sample size and decreasing valence electron number have been proposed. However, tensile ductility was obtained only in very limited alloy systems.

The “metastability-engineering” approach was widely used in high-Mn steels and titanium alloys to promote plastic deformation via strain-induced transformation. Recently, the HEA concept was extended to non-equiatomic compositions, which greatly widens alloy design window for tailoring phase stability, stacking fault energy and associated deformation mechanisms in HEAs. As such, the “metastability-engineering” approach was successfully applied into the Fe80−xMnxCo10Cr10 (at%) HEA system, and the underlying idea is to destabilize the high-temperature fcc phase via reducing the Mn content, which promotes the TRIP (transformation-induced plasticity) effect. Consequently, both the strength and ductility were significantly increased due to concurrent interface hardening from the dual phase microstructure and transformation hardening from the metastability. In our work, we attempted to apply a similar strategy into brittle bcc HEAs for exploring the possibility of ductilization. The equiatomic TaHfZrTi HEA was selected as our prototype alloy and the content of the bcc stabilizer element, i.e., Ta, was gradually reduced in order to destabilize the bcc phase in the HEA system (TaHfZrTi, denoted as TaHEA). The ultimate goal is to enhance the comprehensive properties of brittle HEAs by fabricating dual-phase HEAs consisting of one phase with reduced mechanical stability.

Phase constitution and structural evolution of the as-cast TaHfZrTi (x = 1, 0.6, 0.5, and 0.4) alloys were characterized by X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) analysis, and the results demonstrate the targeted change of phase stability as shown in Figure 1. A single bcc phase structure was obtained in the quaternary equiatomic Ta1 HEA with only bcc diffraction peaks on its XRD trace. As the Ta

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content is decreased from 25% (i.e., Ta1) to 16.7% (i.e., Ta0.6), a small amount of hcp phase is detected from the EBSD image, but not captured by XRD. A further decrease of Ta to 14.3% and 11.8% (i.e., Ta0.5 and Ta0.4, respectively) successfully produces a dual-phase microstructure consisting of interwove hcp lamella plates embedded in the bcc matrix. The crystallographic orientation relationship between the bcc and primary hcp phase was verified to be \( \{110\}_{\text{bcc}} / \{0001\}_{\text{hcp}} \) by the corresponding pole figures (see Figure S1 in the Supporting Information). It is obvious that the volume fraction of hcp increases with decreasing Ta content, suggesting that formation of the bcc phase is suppressed while that of hcp is promoted.

As an example, details of the dual-phase structure were carefully analyzed in alloy Ta0.5. The bcc matrix with a grain size of around 100 µm and the primary hcp phase, i.e., the interlaced lamella plates ranging from tens of nanometers to several micrometers in width, constitute the as-cast alloy Ta0.5. Bright-field transmission electron microscopy (TEM) image (Figure 2a) reveals the laminate appearance with inner parallel plate structure of the primary hcp phase. The \([2110]\) selected area diffraction (SAD) pattern of hcp is provided to identify the interior structure and as shown in Figure 2b \([01\bar{T}1]\) twinning is occasionally observed. The twins in several nanometers width (Figure 2c) are likely formed by post-transformation shear.\(^{[36]}\) To reveal chemical distribution at the atomic scale, 3D atom probe tomography (APT) tests of tip specimens taken from the region around phase boundaries between bcc and hcp were conducted and the corresponding results are shown in Figure 2d. Clearly, no apparent elemental segregation is observed in the 3D reconstructions, indicating a uniform distribution of all the elements even at phase boundaries, and the equivalent level of solid solution strengthening of the two phases. Analogous energy dispersive spectroscopy (EDS) observation was conducted on alloy Ta0.6, and the elemental partitioning among the interleaved bcc and hcp phase is also ruled out (Figure S2, Supporting Information). The homogenous elemental distribution confirms the diffusionless transformation from high-temperature bcc to hcp during solidification. Based on all the above observations, it is clear that the bcc matrix is metastable and further destabilized as the Ta content is reduced. In other words, our design strategy was successfully realized by lowering the Ta concentration.

Representative tensile true stress–strain curves of the as-cast Tax HEAs are shown in Figure 3a. Distinct variation can be seen from the alloys with different Ta concentrations. Ta1 (#1) shows high strength (≈1500 MPa) but very limited plasticity (≈4%). Decreasing the Ta content significantly ductilizes Ta0.6 (#2) and Ta0.5 (#3); the uniform strain is increased over 20% and 27%, respectively, although the fracture strength in both alloys is slightly lowered to 1100 MPa. Further decrease of Ta (i.e., Ta0.4, #4), the stress–strain curve displays a double yielding behavior, which is usually observed in shape memory alloys as a signal of stress/strain-induced martensitic phase transformation.\(^{[26]}\)

The strain-hardening rate \( (d \sigma / d \varepsilon) \) of these HEAs determined from the corresponding true stress–strain curves is shown in Figure 3b. Alloy Ta1 (#1) shows a sharp decrease in the strain-hardening rate for its quick failure after elastic stage. The strain-hardening rate of alloy Ta0.6 (#2) gradually decreases to below 0 (where necking happens) at its late deformation stage, while alloy Ta0.5 (#3) retains a steady hardening rate of about 1.4 GPa until plastic instability. Moreover, the strain-hardening behavior of alloy Ta0.4 (#4) exhibits a nonmonotonous evolution (i.e., a large hump after the decrease in the early stage), and three hardening stages are visible in this specific alloy. It is known that continuously decreasing strain-hardening rate correlates to a dislocation-slip-dominated plastic deformation mechanism.\(^{[17]}\) The initial drop in the strain-hardening rate, which was observed in all the alloys and characterized as stage I.
in alloy Ta0.4, corresponds to the conventional elastic to plastic transition and dislocation-slip-dominated plastic deformation. The obvious increase in the hardening rate up to \( \varepsilon = 5\% \) in Stage II can be attributed to the activation of martensitic transformation in the early plastic stage as analogous to that in titanium alloys.\[26,27\] In stage III, the hardening effect resulted from phase transformation tends to saturate and deformation is dominated by dislocation slip again. Compared with alloy Ta0.4, dislocation slip overwhelms phase transformation in alloy Ta0.6 while in alloy Ta0.5, the two deformation mechanisms simultaneously influence hardening rate. As a result, alloy Ta0.5 exhibits a plateau in its hardening rate at the late deformation stage. Based on the strain-hardening analysis, we draw a conclusion that transformation and dislocation slip continuously occur throughout the whole plastic straining range, resulting in a good balance of strength and ductility. It is noted that the predominant mechanism defines the shape of strain-hardening rate curve, rendering either a monotonous decreasing form or a nonmonotonous shape with a plateau or hump.

To understand deformation mechanism of the designed HEAs, in situ neutron diffraction was conducted on alloy Ta0.4 to monitor the structural evolution upon tensile loading. The deep penetration ability of neutrons enables us to monitor the structural information of bulk materials instead of surfaces. Additionally, the relationship between lattice strain and applied stress could be accurately measured by such technique. Figure 4a shows diffraction patterns of alloy Ta0.4 under a loading-unloading cycle. As can be seen, the diffraction patterns obtained at the early loading stage mainly exhibit bcc reflections. In response to the increased tensile stress, diffraction peaks slightly shift rightward but the peak intensities keep unchanged before the macroscopic yielding. The hcp peak, i.e., (101)\(_{hcp}\), increases at \( \approx 400 \) MPa, which accounts for the first macroscopic yielding. This observation can be illustrated more clearly in Figure 4 b, which shows the variation of the relative intensities of (110)\(_{bcc}\) and (101)\(_{hcp}\) as a function of loading stress. The relative intensity of (101)\(_{hcp}\) emerges, while that of (110)\(_{bcc}\) starts to decrease at the stress about 400 MPa. The intensity of (101)\(_{hcp}\) continues increasing at the expense of the (110)\(_{bcc}\) peak with further loading and preserves the intensity throughout subsequent unloading process, demonstrating a characteristic of irreversible phase transformation. Figure 4c shows variation of lattice strains of (110)\(_{bcc}\), (200)\(_{bcc}\), (211)\(_{bcc}\), and (101)\(_{hcp}\) as a function of loading stress. Before the phase transformation starts (i.e., below the yielding stress of \( \approx 400 \) MPa), both the bcc lattice strains increase linearly with the applied stress, exhibiting typical elastic deformation behavior. A comparison between the slopes of applied stress versus lattice strain curves (elastic constants) of the three bcc planes indicates the elastic anisotropy of the bcc structure, which is due to different correlation between crystallographic orientation and elastic stiffness in single crystals.\[38\] The slopes of the (110)\(_{bcc}\) and (200)\(_{bcc}\) planes deviate from initial linearity around the yield stress, suggesting different internal stress redistribution among differently oriented \{hkl\} grain families.\[39\] As the deformation-induced transformation proceeds, (110)\(_{bcc}\) and (200)\(_{bcc}\) planes show further deviation from the initial linearity, which is due to the load partition of the newly formed hcp phase. These data vividly manifest cooperative deformation behavior between the transformed hcp crystallites and untransformed bcc crystallites.
Therefore, it is clear that the phase transformation from bcc to hcp did occur upon loading of alloy Ta0.4. To further understand influences of the phase transformation on deformation modes of the current HEAs, changes in the fracture and lateral surfaces (along loading direction) of the deformed samples with different Ta concentrations are presented in Figure 5. As the Ta content is decreased, the fractography changes from typical brittle fracture surface to ellipse or equiaxed dimples. The quantity of dimples increases but the size decreases, suggesting a brittle-ductile transition on deformation. Embossment of grains can be clearly seen on the lateral surface of Ta1, indicating that deformation is mainly at grain boundaries. On the contrary, extensive slip/shear bands (or laths) are observed inside the grains of alloys Ta0.5 and Ta0.4. In situ scanning electron microscope (SEM) observation of the lateral morphology evolution in alloy Ta0.5 as a function of loading is shown in Figure 5e. Lamellar hcp phase starts to form inside grains after the macroscopic yielding of this alloy (about 700 MPa, see Figure 3a) and then multiplies and coarsens with further loading. The hcp plates span or extend across the entire grain of the parent bcc matrix. Similar trends were observed in alloy Ta0.4, plates start to appear right after yielding and multiplies as the case in Ta0.5 (see Figure S3 in the Supporting Information for details). This observation indicates that the phase transformation promotes deformation inside grains and changes the deformation behavior obviously. It is also observed that the amount of hcp laths formed during deformation increases as the Ta content decreases, indicating the potency of transformation drops with Ta increasing, coinciding with the XRD results and EBSD images of deformed specimens (Figure S4, Supporting Information).

Mechanical properties of the designed HEAs mainly benefit from the deformation-induced phase transformation via the “metastability-engineering” approach. Phase transformation generates the transformation strain, releases the stress concentration on the interface between the two phases, and then the continued plastic deformation inclines to take place in the remained bcc phase, preventing the early crack. It has been reported that the martensitic hcp phase has a higher Young’s modulus than the matrix bcc phase in most titanium alloys.[35,40] Therefore, the newly formed hcp crystallites would share the load at the late deformation stage and promote workhardening. As deformation continues, a considerable amount

Figure 3. Mechanical behavior of the as-cast Tax HEAs at room temperature. a) Representative tensile true stress–strain curves. b) The corresponding strain-hardening rate curves.

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Figure 4. In situ neutron diffraction data reveal structural evolution as a function of applied stress in alloy Ta0.4. a) Evolution of diffraction patterns with the applied stress. b) Evolution of relative intensities of the (110)_{bcc} and (101)_{hcp} peak as a function of applied stress. c) Evolution of lattice strain on (110)_{bcc}(200)_{bcc}, and (101)_{hcp} during loading-unloading.
of hcp forms via plasticity-induced phase transformation and bear more loads. Continual generation of hcp with increasing strain also generates new boundaries, through which the dislocation movement is effectively limited. Therefore, global deformation and work-hardening capability were enhanced from the stress/strain-induced phase transformation in the currently developed HEAs.

Figure 6 shows a comparison of the yield strength, ultimate tensile strength (UTS) and total ductility of our current HEAs with various advanced steels, titanium alloys and other refractory HEAs (rHEAs). In the elongation-yield strength plot (Figure 6a), the currently developed HEAs are located on the top-right regime, whereas in the elongation-UTS plot (Figure 6b), they are actually above the general trend for the other metallic materials, clearly indicating that these ductilized HEAs outperform most of the advanced steels, titanium alloys, and reported bcc HEAs. The tensile ductility and fracture strength of the currently developed HEAs are 2–3 times and 1.2–1.5 times that of the other ductile bcc HEAs, respectively (see Table S1 in the Supporting Information and Figure 6b). From the standpoint of structural applications, nevertheless, it is important to point out that the first yield strength of Ta0.4 is not sufficiently high. In other words, thermal and mechanical stability of the transformable phase need to be appropriately tailored so that a good combination of strength and ductility can be achieved. The mechanical performance of Ta0.5 and Ta0.6 HEAs is significantly improved via the metastability-engineering strategy which gave rise to multiple benefits; i) phase transformation-induced ductility, ii) microcomposite-effect-induced hardening due to a dual-phase microstructure, and iii) transformation-induced hardening due to a dynamic strain–stress partitioning effect.

In conclusion, the bcc phase of the brittle TaHfZrTi HEA was successfully destabilized via metastability-engineering strategy, leading to formation of a composite structure with interleaved hcp and mechanically instable bcc phases. Tantalum played a significant role in controlling the phase constitution, transformation potency and most importantly, the mechanical performance in the developed HEAs. The strain-hardening behavior of the alloys were dictated by the competition between dislocation slip and phase transformation mechanism, which was observed in the destabilized bcc phase under loading. Phase transformation yielded intensive strain-hardening effect by dynamic strain–stress partitioning between the bcc and hcp phases and promote plastic deformation inside grains, which effectively suppressed early cracking and eventually gave rise to an outstanding combination of strength and ductility. Our findings not only provide a useful approach to enhancing the
comprehensive properties of brittle bcc HEAs, but also shed insights into strengthening and ductilization of other types of advanced metallic materials.

**Experimental Section**

Alloy ingots with a nominal composition of Ta$_x$HfZrTi ($x$ is from 0 to 1) were prepared by arc-melting a mixture of pure metals with purity over 99.9 at% in a Ti-gettered argon atmosphere. All ingots were remelted at least five times to eliminate chemical inhomogeneity, and eventually drop-cast into a 10 mm x 10 mm x 60 mm copper mold. Dog-bone-shaped specimens with a thickness of 1.5 mm for tensile tests were cut from the rods by electrical discharge machining. The gauge length and width of the tensile samples are 15 and 5 mm, respectively. Prior to deformation, the samples were polished down to a 2000-grit SiC paper. Tensile tests were performed on a CMT4105 universal electronic tensile testing machine at the strain rate of 1 x 10$^{-3}$ s$^{-1}$. For each alloy, at least five tensile tests were conducted and detailed data of mechanical performance of all the tested samples are compiled in Table S1 (Supporting Information).

Phase constitution and microstructure of the alloys were characterized by X-ray diffractometer with Cu K$_\alpha$ radiation in a 2$\theta$ range from 20° to 100°, a Zeiss Supra55 SEM equipped with an HKL channel 5 system operated at 20 kV and EDS, and a transmission electron microscope (TEM, Tecnai F30) operated at 300 kV. Chemical homogeneity in the alloys was investigated using a LEAP 5000XR APT. Both the APT tip specimens from the region across the phase boundaries between bcc and hcp and TEM specimens were prepared using a focused ion beam (FEI Helios Nanolab 600i). In situ SEM with a maximum load of 1.2 kN was carried on a SEM-servo in situ fatigue testing machine to monitor the lateral surface change under tensile loading. In situ neutron diffraction loading was also conducted by using a MTS load-frame on the VULCAN engineering materials diffractometer, at the Spallation Neutron Source, Oak Ridge National Laboratory. The authors thank Matt Frost for the technical support of neutron experiment. This manuscript has been coauthored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (http://energy.gov/downloads/doe-public-access-plan).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.