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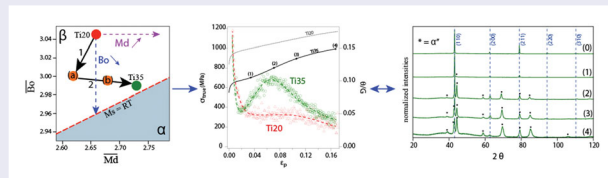
Design and tensile properties of a bcc Ti-rich high-entropy alloy with transformation-induced plasticity

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ABSTRACT

A new bcc Ti-rich high-entropy alloy (HEA) of composition $\text{Ti}_{35}\text{Zr}_{27.5}\text{Hf}_{27.5}\text{Nb}_5\text{Ta}_5$ was designed using the 'd-electron alloy design' approach. The tensile behavior displays a marked transformation-induced plasticity effect resulting in a high normalized work-hardening rate of 0.103 without loss of ductility when compared to the reference composition $\text{Ti}_{20}\text{Zr}_{20}\text{Hf}_{20}\text{Nb}_{20}\text{Ta}_{20}$. In this paper, a detailed microstructural analysis was performed to understand the deformation process, revealing architectural-type microstructures and a high volume fraction (65%) of internally twinned stress-induced martensite α'' after mechanical testing. This study opens the way to mechanical properties optimization and enhancement of titanium-based HEAs by combining multiple alloying designs.



IMPACT STATEMENT

For the first time, proof is given that transformation-induced plasticity was triggered in a bcc refractory high-entropy alloy, leading to a twofold increase in the normalized work-hardening rate.

ARTICLE HISTORY

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KEYWORDS

High-entropy alloy; mechanical properties; work hardening; martensitic phase transformation; titanium alloys

In the past decade, high-entropy alloys (HEAs) have attracted considerable attention thanks to their high thermal stability and promising mechanical properties. Originally, HEAs were defined as homogeneous solid solution alloys with body- or/and face-centered cubic (bcc or/and fcc) crystal structures consisting of at least five principal elements with concentrations between 5 and 35 at.% and displaying an enhanced phase stability driven by the high entropy of mixing.[1] A recent breakthrough in the field is the outstanding fracture toughness (exceeding $200 \text{ MPa m}^{1/2}$ at cryogenic temperature) of equiatomic fcc CrMnFeCoNi system, achieved through nano-twinning deformation mechanisms, i.e. twinning-induced plasticity (TWIP).[2] This behavior was also observed in the non-equiatomic CrMnFeCo HEA at room temperature (RT), for deformations higher than 10%; the mechanism for lower deformation levels being

dislocation glide.[3] Recently, a dual-phase fcc/hcp HEA also based on CrMnFeCo and with impressive mechanical properties was reported. The synergy of the complex alloying chemistry, twinning and dislocation glide, as well as the co-deformation of the two phases are jointly responsible for the superior mechanical properties of this dual-phase HEA.[4]

In comparison, bcc HEAs are rather similar to conventional bcc alloys with deformation controlled by screw dislocation glide.[5] Thanks to the solid solution effect, they generally display high yield strengths but still suffer from a low work-hardening rate, which prohibits their industrial applications.[5–7] Nonetheless, their appealing high-temperature performances are worth facing the challenge of significantly improving their strengthening properties.[8,9] Among the possible explored strategies used in metallurgy, one option leads naturally to the

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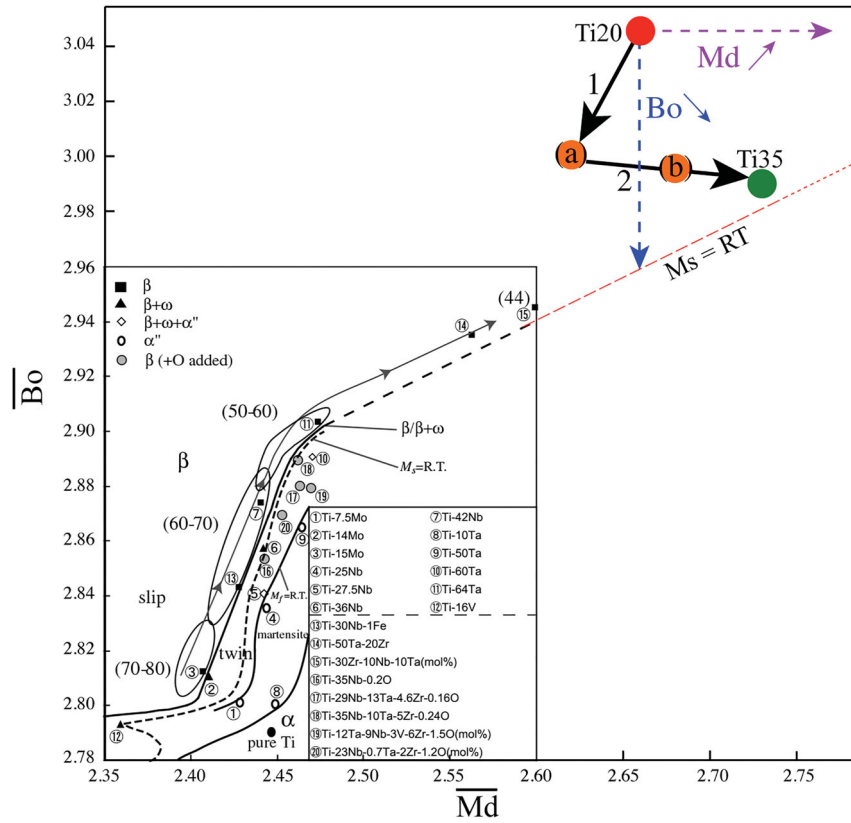


Figure 1. Bo–Md diagram extrapolated to the high-Bo–high-Md domain. Compositions (a) and (b) described in Table 1 (from [15]).

traditional precipitation hardening approach. However, unlike recent studies of fcc HEAs,[10,11] and to the authors' best knowledge, published results dealing with hardening precipitation for bcc HEAs are limited to the AlCrMnFeNi system with still complicated or ambiguous hardening mechanisms [12,13]; up to now, no systematic studies are reported for refractory compositions. Another option to improve the strengthening properties considers the possibility of TWIP and/or transformation-induced plasticity (TRIP) as for austenitic steels.[14] This approach was already successfully applied to fcc-based high- and medium-entropy alloys.[2,4] In bcc structures, this approach was developed in great detail for β -titanium alloys with the definition of empirical tools such as the Bo–Md diagram (Figure 1), to achieve specific mechanical properties through chemical design.[15–18] Bo is the bond order and describes the bond strength between Ti and the alloying elements and is defined as $Bo = \sum_i x_i Bo_i$. $Md = \sum_i x_i Md_i$ relates to the energy level of the d -orbitals and takes into account the atomic radius and the electronegativity of the elements.

This latest strategy is explored here, providing proof of concept that tools developed for conventional Ti-alloys can be successfully applied to Ti-rich HEA, including the tuning of the mechanical properties that is implied. The

design of a 'transformable' refractory HEA is proposed, using both HEA concept [19] and 'd-electron alloy design' through the Bo–Md parameters. A combination of high strength, superior work-hardening rate and good ductility can be expected from the proposed alloy design.

The present study concerns the titanium-containing system TiZrHfNbTa.[7] In order to maintain a concentrated solid solution and therefore an enhanced solid solution hardening, the composition optimization was done as a first approach within the boundaries of five elements in concentration ranging between 5 and 35 at.% suggested by Yeh et al.[1] These limits, leading to compositions with high configurational entropy of mixing, were used as a frame for the study. In order to obtain a β -metastable structure, the concentration of the five elements was changed, since the equiatomic Ti₂₀Zr₂₀Hf₂₀Nb₂₀Ta₂₀ (hereafter referred to as Ti20) was proved to display a stable bcc structure with respect to temperature and deformation, which is in good agreement with its position in the Bo–Md diagram (Figure 1).[5,9] The design procedure is illustrated in Figure 1 and relies on the Bo–Md diagram: in order to get closer to the $M_s = RT$ line and to destabilize the β -phase, the Bo parameter must be decreased (blue arrow) or Md increased (purple arrow). As Ti has almost the lowest Md parameter of the five elements [15] and with the aim of

Table 1. Concentration (at.%) of each element for the alloys plotted in Figure 1, with the corresponding total Bo and Md values.

	Ti (2.79; 2.45)	Zr (3.09; 2.93)	Hf (3.11; 2.98)	Nb (3.10; 2.42)	Ta (3.14; 2.53)	Bo	Md
Ti20	20	20	20	20	20	3.05	2.66
(a)	35	16.25	16.25	16.25	16.25	3.00	2.62
(b)	35	22.5	22.5	10	10	2.99	2.68
Ti35	35	27.5	27.5	5	5	2.99	2.73

Note: The couples (Bo_i ; Md_i) used for the calculation of the total Bo and Md are given in the first row with the corresponding element.[15]

keeping a ‘Ti-rich’ concentration, decreasing Bo is preferred. Since Ti has the lowest Bo value, in the first step (black plain arrow 1 in Figure 1), a composition (a) with 35 at.% of Ti and equal concentrations of the other 4 elements is proposed. However, this alloy is still quite far from the $M_s = RT$ line. In the second step (black plain arrow 2 in Figure 1), the amount of β -stabilizers (Nb and Ta) is thus progressively reduced down to 5 at.%, which corresponds to the minimum of the compositional frame chosen for the high-entropy nature of the alloy. Zr and Hf concentrations are adjusted in order to keep the balance. Intermediate compositions that have a higher Nb and Ta content such as alloy (b) are still located too far from the $M_s = RT$ line. The limit composition $Ti_{35}Zr_{27.5}Hf_{27.5}Nb_5Ta_5$ (hereafter referred to as ‘Ti35’) with Bo and Md parameters close to the $M_s = RT$ line (in the ‘stress transformation range’ region of the Bo/Md stability map) was finally selected (Table 1).

The Ti35 alloy was prepared via classical arc and frequency induction melting. Details on the preparation technique and the as-cast microstructure are described in a previous study.[20] The obtained ingots were 10 mm in diameter and 60 mm long. The control of structure and the grain size was carried out by cold rolling with a 60% and 70% reduction in thickness followed by 30 min solution treatment under helium at 900°C and 800°C, respectively, and subsequent air quenching. Only the final state is considered in the following, and referred to as ‘solution treated’. The composition was confirmed by the electron probe microanalysis with a Cameca SX100 micro-analyzer operating at an accelerating voltage of 15 kV. The solution treated alloy displays a fully bcc structure with lattice parameter $a = 345.0$ pm and an average grain size of 40 μ m. Tensile testing was performed on the dog-bone shaped specimen (4 mm wide and 0.8 mm thick) in the rolling direction at RT under a strain rate of $10^{-4} s^{-1}$ and controlled with a 10 mm gauge length extensometer. The crystal structures and the microstructures of the deformed specimens (after unloading) were characterized by X-ray diffraction (XRD) using Co-K α radiation ($\lambda = 0.179$ nm), electron back-scattered diffraction (EBSD) and transmission electron microscopy (TEM). Samples for the EBSD analysis were prepared by mechanical and electrochemical polishing with a solution of HClO₄ and methanol, at

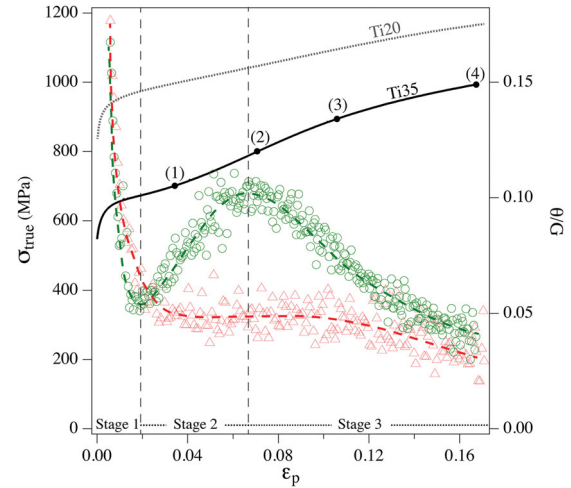


Figure 2. Tensile true stress σ_{true} (black) and normalized work-hardening rate θ/G (green) of Ti35 as a function of the plastic strain for a deformation rate of $10^{-4} s^{-1}$. For convenience the curves are plotted until 0.17 of plastic deformation; macroscopic localization is observed at about 0.2 and fracture at 0.23. In grey and red: true stress versus plastic strain (compression testing) of Ti20 (grey dotted line) and the corresponding normalized work-hardening rate θ/G (in red) as a function of the plastic strain. The dashed lines are guide for the eyes to highlight the trend of θ/G . [5,22]

0°C and 15 V for 15 s. Scanning electron microscopy analyses were performed using a field emission gun Zeiss Merlin scanning electron microscope operating at 20 kV and equipped with an Oxford EBSD camera (step size between 0.3 and 0.66 μ m). TEM analyses were performed after mechanical polishing followed by electropolishing using a solution of HClO₄, butanol and methanol at 15 V and $-35^\circ C$. The observations were done using a Tecnai F20 operating at 200 kV equipped with the precession automated crystal orientation mapping (P)ACOM-TEM using the Astar package.[21]

The tensile true stress/true strain and work-hardening curves of Ti35 are depicted in Figure 2 for a plastic strain up to 17%. The alloy displays a Young’s modulus of $E = 79$ GPa, an offset yield strength at 0.2% and an ultimate tensile strength of 540 and 995 MPa, respectively, and an elongation at fracture as high as 23%. The yield strength of Ti35 is in the upper range of the obtained values for other β -metastable alloys based on similar elements but less alloyed, typically ranging between

200 and 600 MPa, illustrating a moderate solid solution hardening effect.[16,18,23,24] As expected from the chosen alloying design, cyclic stress-strain curves display a double yielding behavior (detailed in Figure 1(b) of the Supplementary material), typically observed in metastable β -alloys.[25,26] This behavior is reflected in the evolution of the normalized work-hardening rate ($\theta/G, \theta = d\sigma_T/d\varepsilon_p$), with the shear modulus G estimated from $G/E = 3/8$ as experimentally found for polycrystalline metallic materials.[27] Three stages as visible in Figure 2 (green curve): first, a classical decrease in θ/G until $\varepsilon_p = 0.018$ (stage 1), then an increase in θ/G in stage 2 up to a maximum of about $\theta/G = 0.103$ and finally a decrease from $\varepsilon_p = 0.07$ to the end. As seen in Figure 2, compared to equimolar $\text{Ti}_{20}\text{Zr}_{20}\text{Hf}_{20}\text{Nb}_{20}\text{Ta}_{20}$ the work-hardening rate of this Ti-rich multi-component alloy is greatly enhanced with no ductility loss,[5] confirming the efficiency of the Ti-alloys design tools.

In order to understand the deformation mechanisms behind such remarkable hardening properties, specific disrupted tensile tests were performed. The XRD patterns are shown in Figure 3 after loading at a chosen strain (samples numbered (1)–(4) in Figure 2) and unloading.

The pattern (0) corresponds to the solution treated state, before deformation: the structure is bcc, the presence of some minor amounts of omega phase was evidenced by TEM. XRD patterns for samples (2), (3) and (4) highlight the appearance of another phase identified as orthorhombic. As for sample (1) strained at a plastic strain of 0.034, the first small reflection of the martensitic orthorhombic phase appears at $2\theta = 44.1^\circ$, corresponding to the (111) reflection. This stress-induced martensitic orthorhombic α'' phase originates in the so-called TRIP effect, which was characterized in all the samples by EBSD analyses (cf. Figure 2 of the Supplementary material). These analyses allowed quantification of the

Table 2. Percentage of each phase at the different deformation stages obtained by EBSD phase mapping.

Sample/ ε_p	(1)/0.034	(2)/0.070	(3)/0.105	(4)/0.166
% β	97.3	44.3	28.2	15.9
% α''	1.4	53.7	62.4	67.6
% non-indexed	1.3	2.0	9.4	16.5

respective percentages of the two β and α'' coexisting phases, given in Table 2. As illustrated by the XRD pattern (1) and Table 2, the phase transformation is almost fully reversible up to $\varepsilon_p = 0.034$ since martensite transforms back to obtain an almost 100% bcc structure after unloading. At higher strains illustrated by the samples (2), (3) and (4), the reversibility of the phase transformation is not complete. The martensitic phase fraction after unloading increases, and is calculated to level off around 65% (Table 2) evidencing an impressive ability of this alloy to deform through phase transformation.

It should also be mentioned that the percentage of non-indexed points corresponding to the severely deformed areas increases (Table 2). EBSD analyses did not evidence twinning of the β -phase, which excludes twinning-induced deformation as a possible deformation mechanism also known from metastable β -titanium alloys. It may be linked to the low amount of β -stabilizers in Ti35, favoring phase transformation against twinning.

Based on the EBSD analysis of sample (2) strained up to $\varepsilon_p = 0.07$ (Figure 4), the classical crystallographic relationship between α'' and β was found (blue Miller indices in Figure 4(c)): $(110)_{\alpha''} // \{112\}_{\beta}$ and $[001]_{\alpha''} // \langle 110 \rangle_{\beta}$. The martensitic phase is structured into two sub-domains with different orientations, one being obtained from the other by a rotation of about 80° along $\langle 3-12 \rangle$ (in red in Figure 4(c)). Considering the close relationship between the orthorhombic lattice and a hexagonal one,[28] this relation described in the latter structure would be a rotation of 80° along $\langle -1101 \rangle$, which corresponds to a $\langle 10-1-2 \rangle \{10-11\}$ twin. Smaller magnifications indicate that up to three different orientations of martensite can be observed in each former β grain.

The nano-scale structure of sample (1) investigated by TEM and automated crystal orientation mapping is given in Figure 5. The hexagonal indexation due to an orthorhombic to hexagonal transformation during TEM sample preparation, related to the close hcp structure and orthorhombic one of this alloy, which has an orthorhombicity of 98%, has been discussed elsewhere.[20] After straining at $\varepsilon_p = 0.034$, the first non-reversible martensite needles are already nano-structured with twins. The latter are identified as the classical $\langle 10-11 \rangle \{10-12\}$ mechanical twins for hexagonal structures. Combining data from Figures 4 and 5 illustrates that at least two

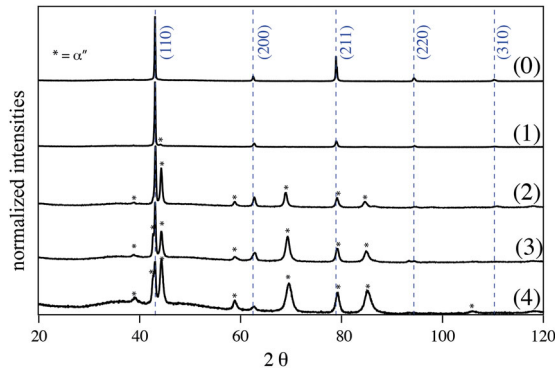


Figure 3. XRD pattern of samples (1)–(4) (Figure 2) after unloading. The bcc reflections are indicated by the dashed lines and the orthorhombic ones by an asterisk. The (0) pattern corresponds to the reference bcc state.

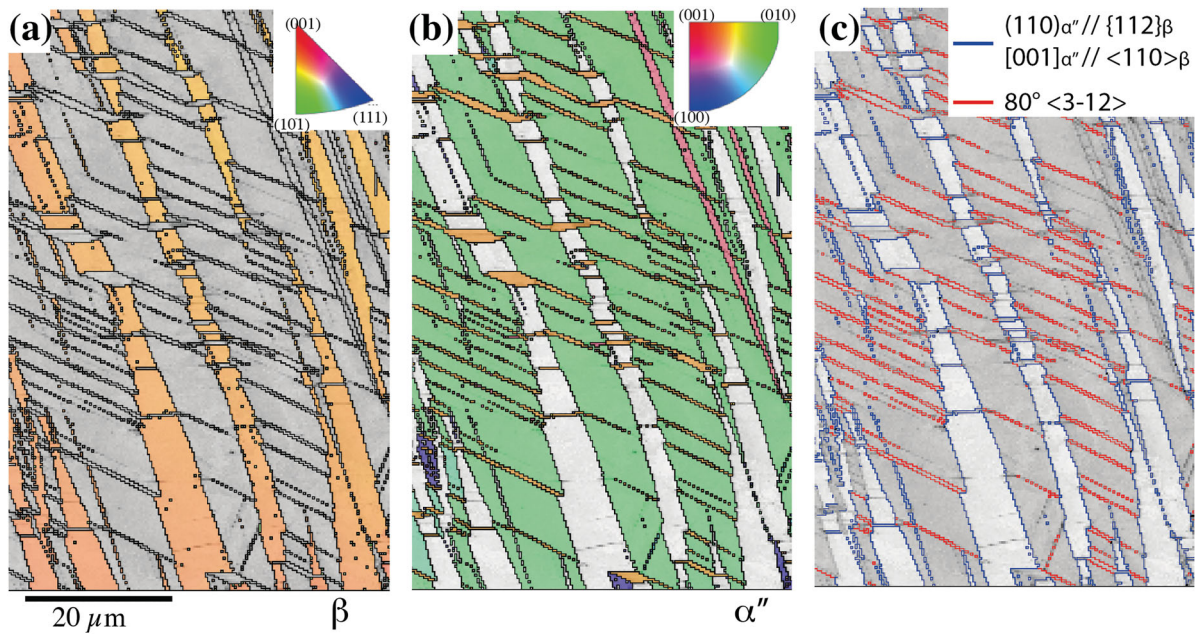


Figure 4. (a and b) EBSD orientation maps of sample (2) for β and α'' , respectively, with the corresponding stereographic triangles. (c) Band contrast and special orientation boundaries.

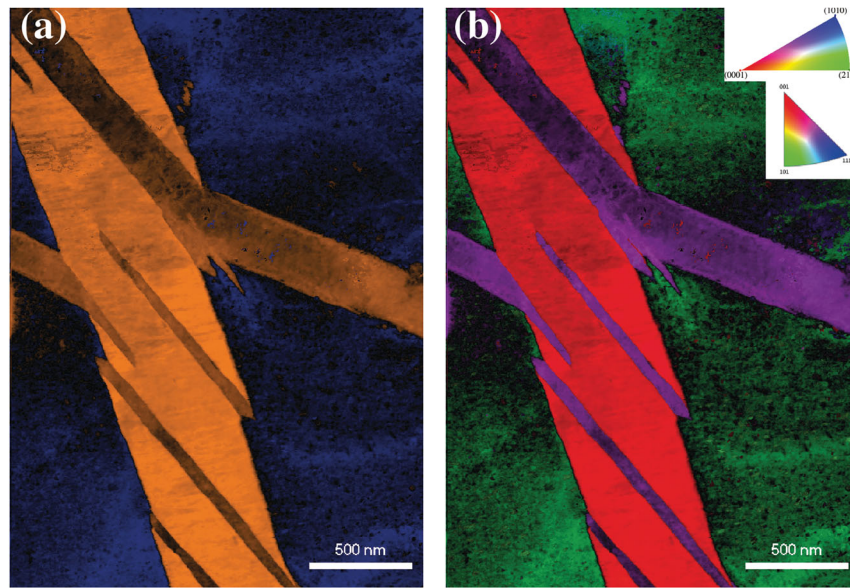


Figure 5. ACOM-TEM mappings. (a) Phase mapping; bcc: blue; hexagonal: orange. (b) Orientation mapping.

twinning systems can be activated in this martensitic structure, allowing a large potential of deformation.

Based on these observations and in comparison with the equiatomic TiZrHfNbTa HEA, several synergic features seem to operate in this alloy which explain the mechanical properties: both the strongly alloyed nature of Ti35 and the presence of a stress-induced phase transformation lead to a good yield strength and a strong strengthening effect due to the plastic deformation of the two coexisting phases. Some hypotheses can be made based on two complementary effects related to

phase transformation that could give information about the hardening mechanism. The first one would be the dynamical Hall–Petch effect that considers that the dislocation glide becomes more limited with increasing deformation due to the continuous creation of new boundaries by the TRIP effect.[29] The second one would be the dynamical composite effect, which is usually applied to TWIP but may be used here. With phase transformation, necessary dislocations would accommodate the deformation gradient at the interfaces to allow homogeneous deformation of the material. Due to their localization,

they would prevent further phase transformation nearby these interfaces and growth of the martensite needles: if the phase transformation proceeds, it would take place in areas with less dislocation, i.e. far away from the existing martensite needles.

In conclusion, a new TRIP alloy was found within the HEA family. According to the Bo–Md diagram developed for titanium alloys, the HEA of composition $\text{Ti}_{35}\text{Zr}_{27.5}\text{Hf}_{27.5}\text{Nb}_5\text{Ta}_5$ was considered as a good β -metastable candidate. Successful thermo-mechanical treatments were performed on the as-cast alloy in order to obtain a bcc single solid solution. Tensile tests were performed and microstructural analyses demonstrate that this alloy is deformed by stress-induced phase transformation, conferring it a very high work-hardening rate compared to classical multi-component alloys. The tools developed for the Ti-alloys design proved to be efficient to predict the deformation mechanism in this optimized composition. This allows creating work hardening in a bcc HEA. The study of this composition also illustrates the ‘cocktail effect’, meaning that the properties of the multi-component alloy can be adjusted by varying the concentration of one of the elements, here titanium. A proof of concept is given in this study that TRIP mechanism can be triggered in bcc HEAs. No further optimization was done, and future efforts will be dedicated to improve the microstructure and composition, with the aim to enhance the mechanical properties presented here.

Disclosure statement

No potential conflict of interest was reported by the authors.

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