

Phase-separation induced dislocation-network cellular structures in Ti-Zr-Nb-Mo-Ta high-entropy alloy processed by laser powder bed fusion

Han Chen^a, Daisuke Egusa^{a,*}, Zehao Li^b, Taisuke Sasaki^b, Ryosuke Ozasa^c, Takuya Ishimoto^d, Masayuki Okugawa^c, Yuichiro Koizumi^c, Takayoshi Nakano^c, Eiji Abe^{a,*}

^a Department of Materials Science & Engineering, University of Tokyo, Tokyo 113-8656, Japan

^b National Institute for Materials Science, Tsukuba 305-0047, Japan

^c Division of Materials and Manufacturing Science, Osaka University, Osaka 565-0871, Japan

^d Aluminium Research Center, University of Toyama, Toyama 930-8555, Japan

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ABSTRACT

Hierarchical structures, such as cellular structures, elemental segregations, and dislocation-network, are often proposed to enhance the mechanical properties of high-entropy alloys (HEAs) fabricated via additive manufacturing (AM). The formation of cellular structures is often attributed to elemental segregation during the solidification process or thermal strain resulting from the AM process. Here, we present a novel cellular structure where phase-separation and dislocation-network coupled in Ti-Zr-Nb-Mo-Ta HEA processed by laser powder bed fusion (L-PBF). Electron microscopy observations and X-ray diffraction (XRD) analyses show that this unique cellular structure consists of Zr-rich and Ta-rich body-center cubic (BCC) phases as the cell-wall and the cell-core, respectively, with their lattice constant difference of about 1 %. Moreover, a higher density of dislocations forming distinct networks is detected within this cellular structure, whose density reached $8 \times 10^{14} \text{ m}^{-2}$. Machine learning analysis reveals that the dislocations preferentially occur on the Zr-rich BCC side, thus accommodating the strains significant around the boundaries between the two BCC phases. With the aid of thermodynamic simulations, we propose a formation mechanism of the present cellular structure, which is governed by the elemental partitioning behavior of Zr and Ta during a solid-state phase separation under rapid cooling. Boundaries with this phase separation are introduced as semi-coherent interfaces with misfit dislocations, introducing a high-density dislocation in the present material. This novel cellular structure can significantly enhance the strength of AM HEAs, providing valuable insights for developing high-performance AM metals through the design of hierarchical microstructures.

1. Introduction

High-entropy alloys (HEAs) have attracted extensive attention in scientific community due to their excellent mechanical properties and damage tolerance [1–6]. HEA maximizes the configurational entropy and stabilizes the solid solution phase by consisting of five or more multicomponent elements. This can give rise to a severely distorted lattice during deformation and thus provide excellent mechanical properties and other properties [4]. Among the existing HEAs, a Ti-Zr-Nb-Mo-Ta HEA attracts increasing attention in scientific field due to its high hardness, good wear resistance and corrosion resistance, and excellent biocompatibility [7–11]. As this HEA is a good candidate for

biomaterials and is therefore referred to as BioHEA [9]. Since the melting points of constituent elements are extremely high, this BioHEA can also be utilized in industrial applications as refractory materials, similar to those reported refractory HEAs. However, due to its constituent elements' extremely high melting points, the preparation of Ti-Zr-Nb-Mo-Ta HEA often presents significant challenges [12].

The rapid development of additive manufacturing (AM) provides a new chance to prepare high-performance HEAs, especially for the HEAs with high melting point components [13–15]. AM has attracted extensive attention due to its immanent advantages, such as unrivaled design freedom and short lead times [16–19]. Most reported AM technologies use powder or wire as feedstock, during which the powder or wire

* Corresponding authors.

E-mail addresses: egusa@stem.t.u-tokyo.ac.jp (D. Egusa), abe@material.t.u-tokyo.ac.jp (E. Abe).

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suffers quick melting and subsequent rapid cooling layer-by-layer [16–18]. This special layer-by-layer formation mode would lead to repeated liquid-solid and solid-state phase transformation [16–18]. As a result, the built parts experience a specific thermal history [16–18]. This cyclic and complicated thermal history can result in the formation of hierarchical structures, including coarse columnar grains, fine equiaxed grains, molten pool boundaries, and cellular structures [20–29]. Among them, the metastable cellular structure is extensively attractive for metallic materials processed by AM. This is because the cellular structure is essential in enhancing the mechanical properties and other properties [23,26,27].

Several studies concentrate on the cellular structure in aluminum alloys, Cu alloys, 316 L steel, CrCoMo alloy, Inconel 718, and HEAs processed by AM in recent years [20–33]. Different cellular structures have been reported in these AM-processed alloys. One crucial cellular structure is the cellular structure consisting of the low-melting phase as the cellular core and the high-melting phase as the cellular wall [22,27,30]. The most common cellular structure can be seen in Al-Si or Al-Ni binary alloys, in which the cellular wall is enriched with high-melting Si or Ni, and the cellular core is rich in Al [22,30]. Due to the constitutional undercooling together with a high velocity of the solidification front, the high-melting element Si or Ni will be trapped at the solidification interface and finally segregate to the cellular wall. Such cellular structures are also observed in ternary alloys and complex alloys processed by AM, such as AlSi10Mg and CrCoMo alloys and 316 L steel [22,27]. This kind of cellular structure is usually due to the epitaxial growth during solidification [22]. The solidification starts on the substrate from the heat-affected zone, favored by cellular structure. The crystallographic orientation of the cellular structure is often preferred close to the heat flow direction.

Another important cellular structure is the dislocation-network, often observed in Cu alloys, 316 L steel, and HEAs processed by AM [20,21,23–26,32]. This cellular structure is due to the self-assembly of the high density of dislocations. Its appearance has been closely associated with the complicated stress cycles arising from the repetitive and non-equilibrium building process [25,32]. Especially in the study of Bertsch et al. [25], systematic comparison experiments were carried out to elucidate the formation of a dislocation-network in AM-processed metals, resulting to show that the formation of a dislocation-network was related to the geometric constraints provided by thermal stress. Although some elements tended to segregate to the dislocations during solidification and sometimes form the chemical cell [25,26], Bertsch et al. manifested that the formation of the dislocation-network was not due to the element segregation.

Due to the introduction of multiple elements, the solidification behavior becomes more complicated in HEAs processed by AM. As a result, the different solidification morphology containing the hierarchical structure is often observed in HEAs [14,24,34,35]. Although some studies have investigated the microstructure, mechanical properties, and even the biocompatibility of Ti-Zr-Nb-Mo-Ta HEA processed by AM [7–11], fewer studies have focused on the hierarchical structure of this HEA in AM-processed forms. Furthermore, previous studies reported that the mechanical properties and biocompatibility of AM-processed Ti-Zr-Nb-Mo-Ta alloys are improved in comparison to cast alloys; in particular, the 0.2 % proof strength is increased by approximately 1.5 times [7,11,36]. The strengthening of this alloy is believed to originate from its microstructure introduced by the AM process; however, the correlation between the microstructure and mechanical properties of AM-processed Ti-Zr-Nb-Mo-Ta HEA remains unclear, particularly the role of the cellular structure in this correlation. In the present study, we first aim to reveal the hierarchical structures of Ti-Zr-Nb-Mo-Ta HEA processed by laser powder bed fusion (L-PBF), especially focusing on the cellular structure based on experiments and theoretical calculation. We aim to highlight a novel cellular structure distinct from previously reported ones, offering new insights into the hierarchical structures of HEAs processed via AM. Furthermore, this study demonstrates that this

novel cellular structure significantly enhances strengthening, providing a promising approach for designing high-performance HEAs using AM techniques.

2. Experiments and methods

2.1. Sample preparation

Ti-Zr-Nb-Mo-Ta HEA spherical powder with the nominal atomic ratio of $\text{Ti}_{1.4}\text{Nb}_{0.6}\text{Ta}_{0.6}\text{Zr}_{1.4}\text{Mo}_{0.6}$ was prepared by electrode induction melting of pre-alloyed rods, followed by gas atomization. The diameters of used powders were in the range of 10–63 μm (D50: 26.8 μm), which can be seen in our previous study [7]. The 3D printing was carried out in the Ar atmosphere using an SLM apparatus (EOS M290, EOS, Germany) under conditions where the oxygen fraction was below 0.1 %. The parameters for printing were set as follows: laser power (360 W), scanning speed (1200 mm/s), hatch distance (80 μm), and layer thickness (60 μm). The selection of process parameters is crucial for ensuring the formation of the cellular structure. The process is inherently tied to the temperature gradient (G) and the solidification growth rate (R) [30,37,38]. Specifically, the G/R ratio dictates the solidification morphology, whereas the G-R product determines the size of the solidification structure [30,37,38]. A high G/R ratio results in a planar solidification morphology, which transitions to a cellular structure as the G/R ratio decreases. Further reduction in the G/R ratio leads to the formation of columnar or equiaxed dendritic structures. Both G and R are influenced by process parameters, such as laser power and scanning velocity. When the laser power is set between 240–360 W and the scanning velocity is within 600–1800 mm/s, the cellular structure forms consistently. Furthermore, the as-built samples exhibit excellent densification, characterized by notably low porosity [30,37,38]. The dimensions of the printed blocks were 5 mm in width, 5 mm in length, and 9 mm in height. The building direction (BD) was the Z direction during the process of 3D printing. The morphology of powder and the resultant blocks can be seen in the previous study [7].

2.2. Microstructure characterization

The phase identification of as-built Ti-Zr-Nb-Mo-Ta HEA was performed by X-ray diffraction (XRD) technique, carried out in an XRD machine (SmartLab, Rigaku Corporation, Japan). Monochromatized Cu $\text{K}\alpha_1$ line was used for XRD measurements by a Johansson-type spectrometer. The profiles were analyzed using the Rietveld method [39]. The dislocation density in the Ti-Zr-Nb-Mo-Ta HEA was evaluated by analyzing the asymptotic behavior of the second-order and fourth-order restricted moments using the restricted moment method [40]. The microstructure and composition distribution of as-built Ti-Zr-Nb-Mo-Ta HEA were observed by two scanning electron microscope (SEM) machines. One machine is JIB-4700F, and the other machine is Zeiss 550. Both machines are equipped with an energy-dispersive X-ray spectroscopy (EDS) detector and an electron backscatter diffraction (EBSD) detector. The SEM and EBSD samples were prepared using standard metallographic procedures. Initially, the samples were polished with waterproof abrasive papers of grit sizes $\times 400$, $\times 800$, $\times 1200$, and $\times 2000$ using a grinding and polishing machine. This was followed by mechanical polishing with SiO_2 suspension liquids of particle sizes 0.1 μm and 0.05 μm . For enhanced resolution during EBSD analysis, the samples were subjected to an extended polishing procedure. They were polished using 0.1 μm and 0.05 μm SiO_2 suspensions for approximately 0.5 hours each, a relatively longer duration compared to standard practices. After completing these polishing steps, both SEM and EBSD samples were directly subjected to their respective tests. It is noteworthy that cellular structures could be clearly observed in the SEM samples through backscattered electron (BSE) imaging without the need for etching. The EBSD data was processed with the HKL Channel 5 software (Oxford instruments). The transmission electron microscope (TEM) and

scanning transmission electron microscope (STEM) observations were conducted at TEM (JEOL-2010HC) and Cs-corrected atomic-resolution STEM (JEM-ARM200F) with EDS detector. The accelerating voltage for both TEM and STEM observations was 200 kV. A convergence semi-angle of 22 mrad and a high-angle annular dark field (HAADF) detector ranging from 90 mrad and a low-angle annular dark field

(LAADF) detector ranging from 40 mrad were used for STEM observations, respectively. The TEM/STEM samples were initially polished to a thickness of approximately 30–50 μm using waterproof abrasive paper with grit sizes of $\times 400$, $\times 800$, $\times 1200$, and $\times 2000$ by hand. This was followed by ion milling in an ion beam thinner at a temperature range of 123 K to 223 K. The geometric phase analysis (GPA) [41] was used for

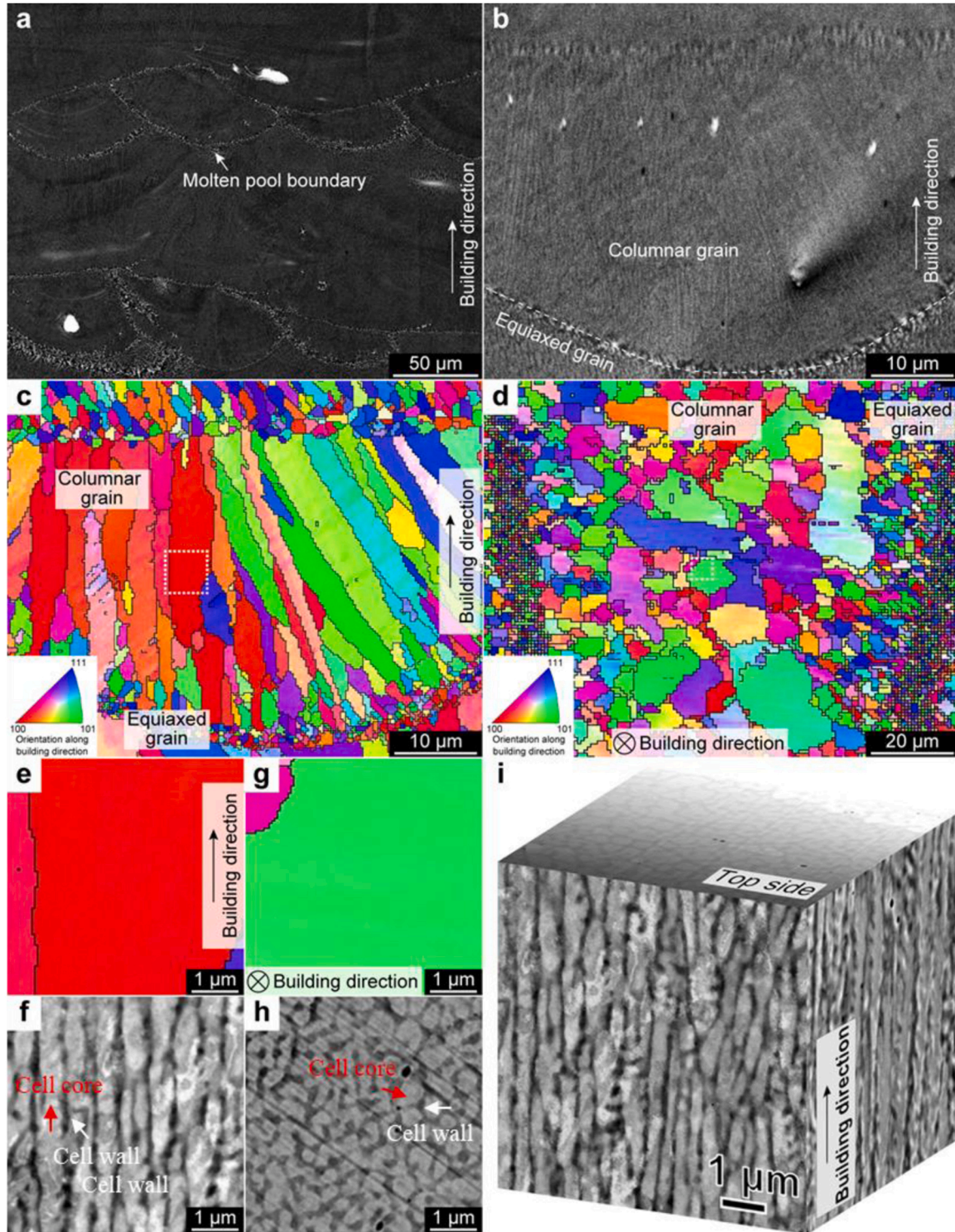


Fig. 1. Microstructure of as-built Ti-Zr-Nb-Mo-Ta HEA characterized by SEM and EBSD: (a) Low magnified SEM-BSE image showing molten pools. (b) SEM-BSE image obtained from a molten pool which includes the column grain area and equiaxed grain area. (c) Corresponding IPF map of (b). (d) IPF map of a cross-section of molten pool observed along BD. (e, g) Magnified IPF maps depicted by white rectangles in (c, d). (f, h) Corresponding SEM-BSE images of (e, g). (i) 3-dimensional morphology of columnar dendrite shown by SEM-BSE images.

strain analysis by Gatan digital micrograph software. To understand the formation mechanism of the different phases during solidification, the Scheil-Gulliver model was used to estimate the segregation behavior of elements during the solidification process. Thermodynamic data for this alloy system was obtained from Thermo-calc software [42]. The thermodynamic calculations were performed with the HEA-based databases of TCHEA5 and MBHEA2 for the segregation calculations [43]. The

Scheil-Gulliver with back diffusion calculation was used in the solid phase. The cooling rate and dendrite arm spacing are 10^6 K/s and 400 nm, respectively, which agree well with experimental results. As for the thermodynamic limitation, Scheil-Gulliver assumes that the distribution of solute elements at the solid-liquid interface is an equilibrium distribution coefficient, so the variation of the distribution coefficient with solidification rate is not considered.

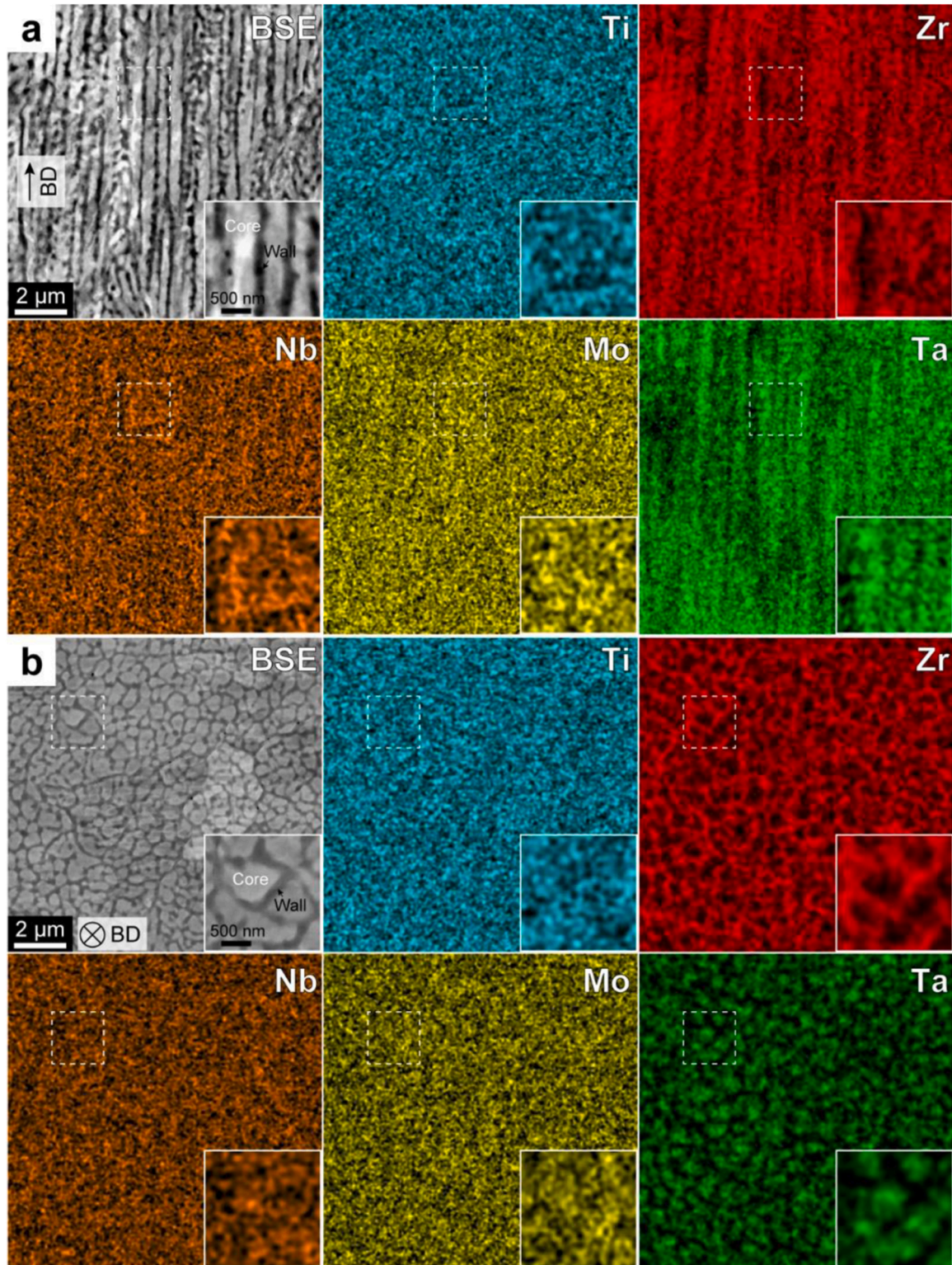


Fig. 2. SEM-BSE images and the corresponding EDS maps of the cellular structure: (a) obtained with a beam incident perpendicular to BD, (b) obtained with a beam incident parallel to BD. Insets show enlarged images/maps enclosed by the dotted rectangles.

3. Results and analysis

3.1. Microstructure analysis by SEM and XRD

Fig. 1 shows a typical microstructure of as-built Ti-Zr-Nb-Mo-Ta HEA. Fig. 1(a) shows a SEM-BSE image obtained along the direction perpendicular to BD. Molten pools with a width of several tens of micrometers are frequently observed. Fig. 1(b) shows a magnified SEM-BSE image inside a molten pool. The molten pool is mainly composed of columnar grain regions elongated to BD, and a small amount of equiaxed grains exist at the bottom of the molten pool. The formation mechanism of the equiaxed grain region has been described in the previous study [44] and [supplementary material](#). In this study, we will focus on the columnar grain regions in the following discussion. Fig. 1(c) shows an IPF map obtained by SEM-EBSD from the corresponding region of Fig. 1(b). The columnar region consists of grains that are a few micrometers wide and elongated along BD. We have evaluated in-plane morphologies of the columnar grains observed along BD, as shown in Fig. 1(d). Although slight variations exist, the in-plane grain morphology is almost isotropic, with an average diameter of about 5 micrometers. Fig. 1(e, f) show an enlarged IPF map and the corresponding SEM-BSE image observed perpendicular to BD, respectively. The SEM-BSE image reveals that the columnar grains are separated into cell walls (~200 nm in thickness) and cell cores (~400 nm in diameter), as indicated by the white and red arrows, respectively. The cellular structure size is only several hundred nanometers, which is significantly smaller than the size of the columnar grains. By analyzing the SEM-BSE images, we estimated the area fraction of each region to be $50.2 \pm 2.3\%$ for the cellular core region and $49.8 \pm 2.3\%$ for the cellular wall region. The corresponding cellular microstructure was also confirmed by the IPF map and SEM-BSE image observed along BD (Fig. 1(g, h)). A 3D magnified SEM-BSE image of the cellular structures is shown in Fig. 1(h) for a better understanding of the morphology. Moreover, it is evident that the cell wall and cell core exhibit distinct dark and bright contrasts. Additional SEM images of the cellular structure are provided in Fig. S1. Since the contrast in the SEM-BSE image reflects the change in local composition, the above results indicate the formation of a cellular microstructure with segregation within a single columnar grain. We have investigated the segregation behaviors inside the columnar grains by SEM-EDS analyses. Fig. 2(a, b) show SEM-BSE images and EDS maps of cellular structure acquired along perpendicular to and parallel to BD, respectively. Both EDS maps show the segregations of Zr and Ta elements and weak segregations of Ti, Nb, and Mo elements. A comparison

of the SEM-BSE image and EDS map shows that the bright cellular core regions correspond to Ta-rich, and the dark cellular wall regions correspond to Zr-rich. This result is consistent with the pseudo-binary segregation behavior of this alloy system suggested by thermodynamic calculations in the previous study [8]. Details of segregation behavior will be discussed later based on STEM-EDS observations.

Fig. 3(a) shows an XRD diffraction profile of as-built Ti-Zr-Nb-Mo-Ta HEA in the range of 34° – 125° , from which 110, 200, 211, 220, 310, 222 and 321 reflections are observed. All major diffraction peaks are identified as the BCC structure, and no other compounds are detected. Two close diffraction peaks are detected in each reflection, as shown in inset 211 reflection, indicating a presence of two BCC phases with slightly different lattice constants. Based on the Rietveld analysis, the lattice constants of two BCC phases are estimated to be 0.335 nm (BCC1) and 0.338 nm (BCC2), whose difference is 0.9 %. Based on the atomic radii of Zr, Ti, Nb, Ta, and Mo ($R_{Zr} > R_{Ti} \approx R_{Nb} \approx R_{Ta} > R_{Mo}$), it is inferred that the BCC2 phase with a slightly expanded lattice should be the Zr-rich region, which will be examined later. In addition, the peak widths of BCC2 show apparent broadening compared with those of BCC1. Fig. 3(b) shows a Williamson-Hall plot [45] constructed from the full width at half maxima (FWHM) of each peak estimated by two-peak Gaussian fitting. The FWHM of each peak increases almost linearly with the scattering angle, and the slope of BCC2 is equivalent to three times that of BCC1. It has been accepted that the width of XRD peaks reflects the magnitude of lattice defects such as dislocations, and a higher value of FWHM usually indicates that the sample contains a higher density of lattice defects [46,47]. Thus, the BCC2 phase includes a higher density of lattice defects than BCC1, whose details will be described later. Note that volume fractions of two bcc phases can be evaluated by area fraction of corresponding peaks, resulting in a volume fraction of $47.9 \pm 3.5\%$ for the BCC1 phase and $52.1 \pm 3.5\%$ for the BCC2 phase.

3.2. Dislocation-network cellular structures

Fig. 4(a) shows a HAADF-STEM image of a cellular structure obtained along BD. Weak bright/dark contrasts in the HAADF-STEM image can be seen, which reflects the segregation of constituent elements [48,49]. Comparison with the SEM-BSE images indicates that the bright/dark contrasts in the HAADF-STEM image correspond to the cellular core and the cellular wall, respectively. Fig. 4(b) shows a LAADF-STEM image simultaneously obtained with Fig. 4(a), whose contrasts reflect the distortions of crystals [50]. The LAADF-STEM image indicates that there are lots of dislocations in the cellular microstructure. Based on

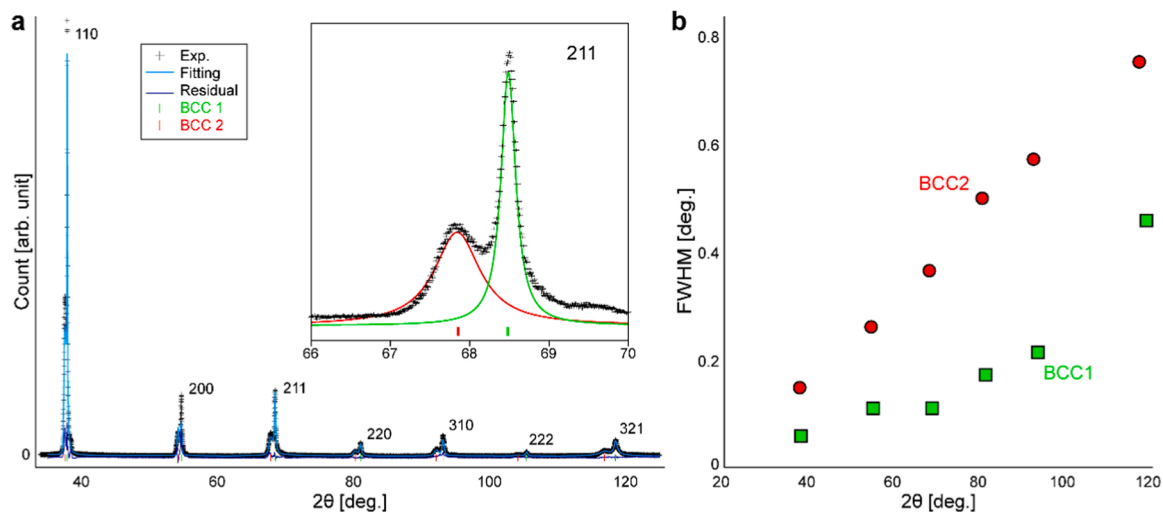


Fig. 3. Phase identification and analysis of as-built Ti-Zr-Nb-Mo-Ta HEA by XRD: (a) XRD profile with different diffraction peaks. (b) variation of FWHM versus diffraction angle. The inset figure in (a) is the magnification of the 211 diffraction peak.

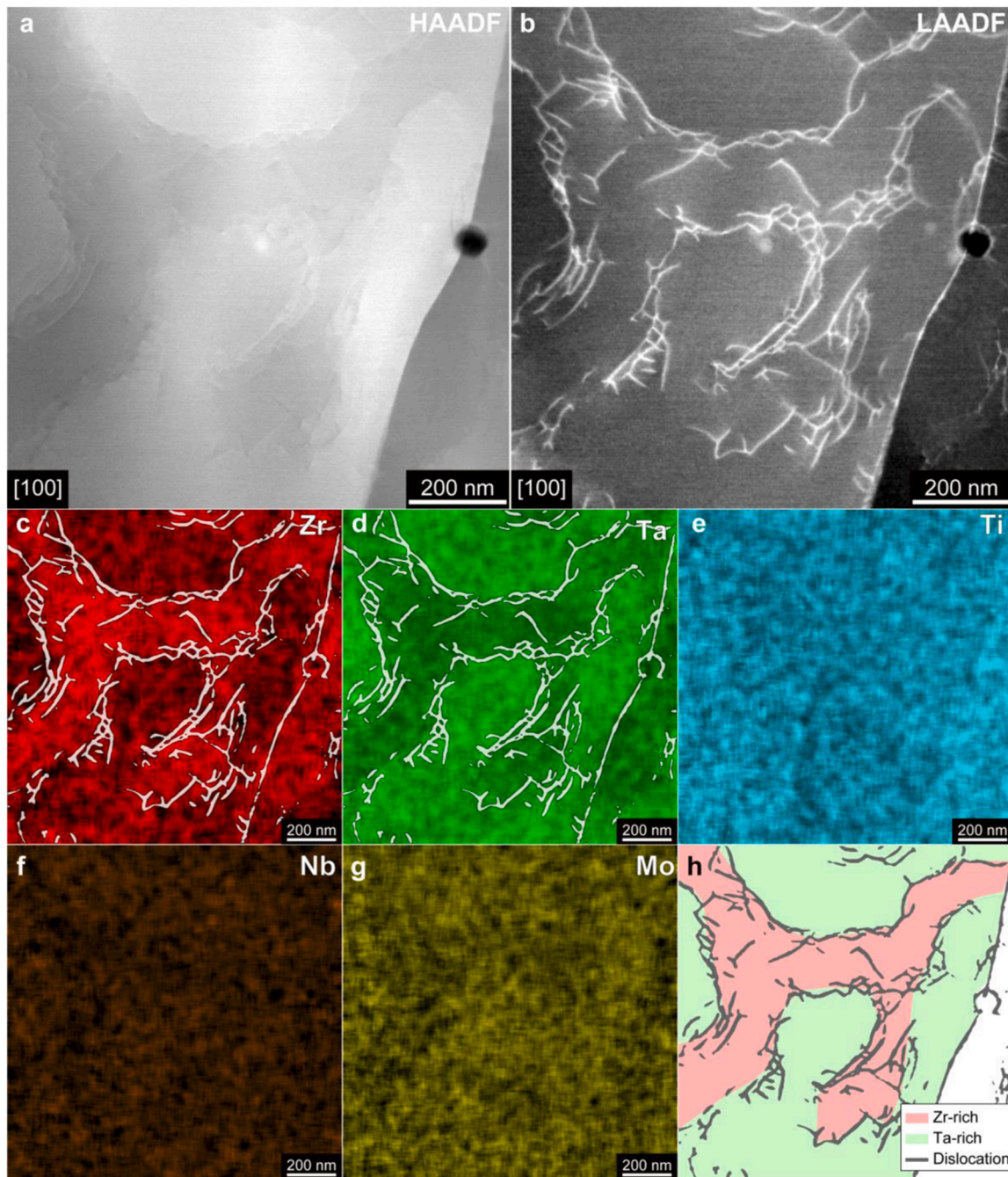


Fig. 4. STEM images and corresponding EDS maps of cellular structure: (a) HAADF-STEM image of cellular structure. (b) the corresponding LAADF-STEM image of (a). Both HAADF-STEM and LAADF-STEM images are acquired in [100] zone axis. (c-g) EDS maps of Ti, Zr, Nb, Mo and Ta elements. For comparison, the dislocation-network superimposed with the element distribution is shown in (c) and (d). (h) Schematic diagram of cellular structure with Zr-rich cellular wall and Ta-rich cellular core.

TEM/STEM observations (Fig. S3 and Fig. S4), these dislocations were identified as mixed dislocations with a Burgers vector of $1/2 \langle 111 \rangle$. Moreover, most dislocations are located around the boundaries between the cell wall and the cell core, forming a dislocation-network. Fig. S3 further clearly illustrates the dislocation-network around the cell boundaries. These results mean that the boundary of the cellular microstructure can be interpreted as a subgrain boundary composed of dislocations. Fig. 4(c-g) shows the corresponding EDS maps of Fig. 4(a) and 4 (b). The EDS maps show that the cellular wall is rich in the Zr element, while the cellular core is rich in the Ta element, which agrees well with the SEM-EDS results.

3.3. Phase identification in dislocation-network cellular structures

As stated in Fig. 3(a), there are two BCC phases (BCC1 and BCC2) in microstructure. In the XRD analysis, we have estimated BCC1 to be the Ta-rich phase and BCC2 to be the Zr-rich phase based on their lattice constants. We have verified this identification by atomic-resolution STEM observations. Fig. 5(a) shows a HAADF-STEM image containing the boundary between the Ta-rich cellular core and the Zr-rich cellular wall. Fig. 5(b) shows fast Fourier transformed (FFT) patterns constructed from the rectangle regions within Zr-rich and Ta-rich regions in Fig. 5(a). For easy comparison, the FFT patterns of each region are superimposed with red and green colors. Focusing on the peaks

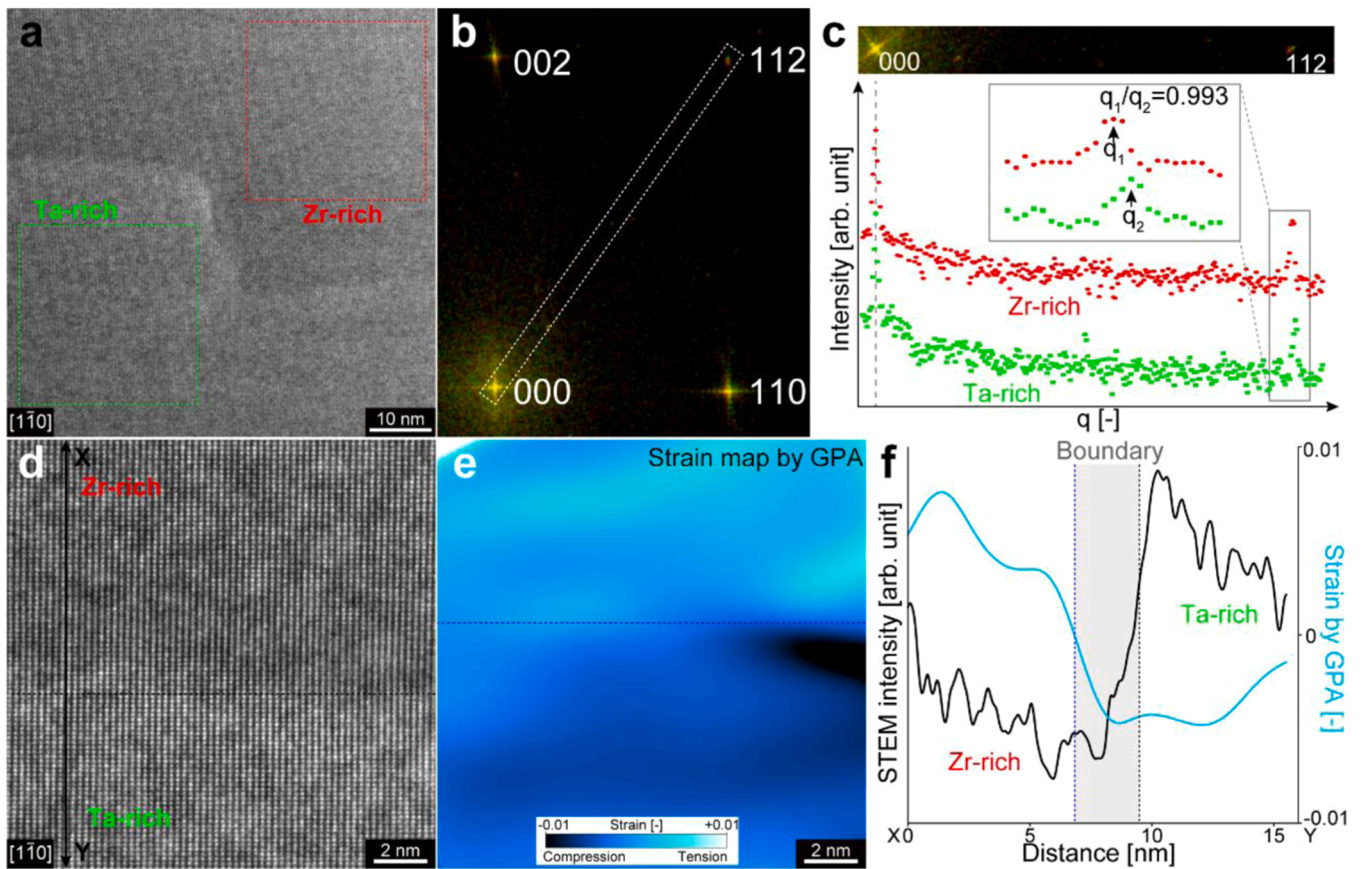


Fig. 5. Phase boundary analysis based on atomic-resolution STEM observations: (a) HAADF-STEM image of cellular structure. (b) Imposed FFT patterns obtained from Zr-rich (red) and Ta-rich (green) regions. (c) Cropped FFT pattern and corresponding intensity profiles. (d) Atomic-resolution HAADF-STEM image around the phase boundary. (e) Strain map along the vertical direction of image (ϵ_{yy}) calculated from the STEM image shown in (d). (f) Intensity profiles obtained from the HAADF-STEM image and the strain map along the X-Y direction shown in (d).

corresponding to the 110, 002, and 112 reflections, a slight peak splitting can be observed. This indicates that the Zr-rich and Ta-rich regions have different lattice constants, which agrees with the XRD results. Fig. 5(c) shows a cropped FFT pattern from the region with 000 and 112 reflections and the corresponding intensity profile. The difference of lattice constants between the Zr-rich area and the Ta-rich area is expressed by a ratio between q_1 (Ta-rich area) and q_2 (Zr-rich area), which is equal to 0.993. The distance in the FFT pattern (reciprocal space) is inversely proportional to the distance in the real space. This means that the lattice constant of the Ta-rich region is larger than that of the Zr-rich region by $1/0.993$, equal to 0.7 % expansion. This value is close to the one obtained from XRD, where the difference in lattice constant of BCC2 (0.338 nm) and BCC1 (0.335 nm) is about 0.9 %. This fact demonstrates that the two BCC phases identified by the XRD analysis are equivalent to the cellular core regions and the cellular wall regions with different compositions. Based on the analysis of Figs. 1–5, this cellular structure represents a novel form, consisting of a Zr-rich BCC phase as the cell wall and a Ta-rich BCC phase as the cell core, with the cell wall being occupied by a dislocation-network. This dislocation-network cellular structure is distinct from previously reported cellular structures in Al-Si, Al-Ni, and CrCoMo alloys [22,27,30], which only exhibit phase separation. It also differs from the dislocation-network commonly observed in Cu alloys, 316 L steel, and HEAs processed by AM [20,21,23–26,32].

3.4. Phase boundary of cellular structures with dislocation-network

According to the XRD results, the microstructure of this alloy is almost explained by two BCC phases. On the other hand, the dislocation-

network structure are located around the boundaries between the BCC phases, as observed in the LAADF-STEM image. We have examined details of these boundary regions, focusing on their chemical compositions and lattice constants. Fig. 5(d) shows an atomic-resolution HAADF-STEM image containing the Zr-rich and Ta-rich regions. The upper part of the image corresponds to the Zr-rich region and the lower part to the Ta-rich region based on the contrast of the STEM image. Fig. 5(e) shows a strain map (ϵ_{yy}) of the STEM image calculated by GPA analysis. To suppress the effect of relaxation due to nearby misfit dislocations, we chose ϵ_{yy} , which corresponds to strain perpendicular to the boundary. Bright contrast on the upper part of the strain map indicates expansion of the lattice constant. Fig. 5(f) shows profiles of STEM image intensity and strain distribution along X to Y in Fig. 5(d). Based on the profiles, the segregation behavior and strain distribution are almost consistent with the results of previous analyses; that is, the Zr-rich region exhibits positive strain, i.e., the expanded lattice constant. However, the relationship between composition and lattice constant appears different behavior around the center of the profiles. Assuming that the sharp slope in the profile represents a phase boundary, the STEM image intensity indicates that the boundary is located at around 10 nm (black dashed line), while the strain distribution indicates that the boundary is located at around 7 nm (blue dashed line). This mismatch suggests a formation of a Boundary region with a few nanometers of thickness between the two BCC phases depicted as the grey-shaded area in Fig. 5(f). Moreover, the GPA results suggest an obvious strain difference at the phase boundary between the Zr-rich BCC phase and the Ta-rich BCC phase. This strain discontinuity at the phase boundary is accommodated by dislocations. The underlying reason is that the Zr-rich BCC phase and the Ta-rich BCC phase, with different lattice constants, experience

compressive and tensile strain states, respectively. To maintain continuous deformation, the strain is thus accommodated at the phase boundary. Additionally, we have examined details of the Boundary region with low-magnification HAADF/LAADF-STEM images and corresponding STEM-EDS maps. Fig. 6(a) shows profiles of HAADF, LAADF image intensity, and Zr and Ta concentration distributions obtained from the region crossing the phase boundary. The Zr-rich and Ta-rich regions can be distinguished from the intensity variation of the HAADF-STEM image. In the case of atomic-resolution STEM images, the Boundary region was detected by strain distribution based on GPA analysis, but the same analysis is difficult to perform for low-magnification STEM images. Therefore, we assumed that the regions of high intensity in the LAADF-STEM images correspond to the Boundary region. We construct a classification model using an unsupervised clustering analysis with the experimental data to identify the three types of regions automatically. Training data for the analysis are extracted from a 10×100 nm region (2000 points) including a “Boundary” region, consisting of HAADF/LAADF STEM image intensities and five element concentrations. We construct the model using the k-means clustering method ($k = 3$) [51] with the above experimental data. The misclassification rate for the analysis was 4.6 % which was assessed by comparing the classification result of models with the different training datasets. Fig. 6(b) shows a classified result of three regions based on the constructed model for the region shown in Fig. 4. Each BCC region is clearly divided, and Boundary regions with a width ranging from several to tens of nanometers are located at the phase boundary. The width of the Boundary appears wider than that observed in Fig. 5(f). This is because the Boundary is not always flat and is curved along the in-plane and depth directions, which increases the apparent width. We have evaluated average chemical compositions of each region based on the STEM-EDS results according to the classified results, as shown in Table 1. Fig. 6(c) shows differences in chemical composition from an average of the whole region to those in Boundary, Zr-rich, and Ta-rich regions. Close compositions of Boundary and Zr-rich regions indicate that Boundary region can be interpreted as a part of the Zr-rich region accompanied with a dense dislocation-network. Note that the localized dislocation distribution around the Boundary region is different from those in the cellular microstructures reported in the previous study [21, 25]. Later we will discuss the formation mechanism of phase-separated microstructures and dislocation networks.

Regarding the relationship between compositions and lattice constants a_{lat} of HEA solid solution, the following equation has been proposed by previous studies [52]:

Table 1

The chemical compositions (at%) of three types of regions evaluated by clustering analysis based on STEM and STEM-EDS observations.

	Ti	Zr	Nb	Mo	Ta
Ta-rich	30.5 ± 2.5	27.2 ± 2.9	14.1 ± 4.5	14.0 ± 3.2	14.3 ± 1.5
Zr-rich	30.6 ± 2.4	34.6 ± 2.9	11.5 ± 4.9	11.7 ± 3.4	11.5 ± 1.6
Boundary	29.9 ± 2.1	31.5 ± 2.8	13.1 ± 4.3	13.0 ± 3.3	12.4 ± 1.4

$$a_{lat} \approx \frac{\sum_{i=1}^n a_{ii}^2 K_{ii} X_i}{\sum_{i=1}^n a_{ii} K_{ii} X_i} \quad (1)$$

where a_{ii} , K_{ii} and X_i refer to the lattice constant, bulk modulus, and concentration [at%] of element i . We estimated lattice constants of the Ta-rich BCC1 and Zr-rich BCC2 phases using the physical properties of each element according to a database based on first-principles calculations (Materials Project [53]). Estimated lattice constants were as 0.334 nm for Ta-rich BCC1 and 0.336 nm for Zr-rich BCC2, which are close to the results (0.335 and 0.338 nm) evaluated by XRD. This match supports that the estimated chemical compositions of Ta-rich BCC1 phase and Zr-rich BCC2 phase are reasonable.

3.5. Mechanical property

Fig. 7(a) shows the compressive stress-strain curve of the as-built Ti-Zr-Nb-Mo-Ta HEA [7], where the yield strength and ultimate tensile strength are evaluated as 1690 MPa and 1800 MPa, respectively. This yield strength is significantly higher than that of other similar HEAs [3, 54–60] (Fig. 7(b)), indicating the excellent strength of our HEA. To better understand the reasons behind the higher strength of this HEA, we estimate the strengthening effect contributed by different strengthening mechanisms.

First, we estimate the dislocation density for diffraction peaks of BCC1 and BCC2 phases using the X-ray line profile analysis [40]. The dislocation densities of the BCC1 and BCC2 phases are approximately $3.3 \times 10^{-4} \text{ m}^{-2}$ and $13.7 \times 10^{-4} \text{ m}^{-2}$, respectively. This observation is consistent with the XRD profile (Fig. 3), where the BCC2 phase has a broader peak width. The high dislocation density is attributed to the formation of a dislocation-network in the Zr-rich BCC2 phase, which contributes to dislocation strengthening. The dislocation strengthening effect can be estimated using the Taylor equation: $\sigma = \alpha G b \rho^{1/2}$ where α is a constant (~ 0.33) [62] and b is the Burgers vector (~ 0.29 nm), and M is the Taylor constant (~ 3) [63]. The shear modulus is calculated using the rule of mixtures, yielding a shear modulus of 44.4 GPa for our

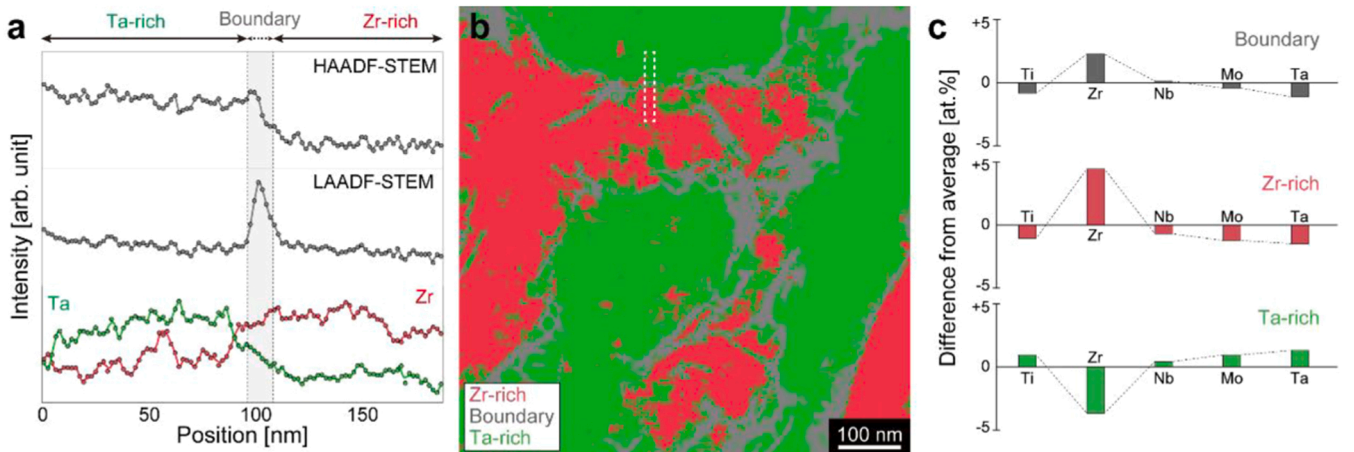


Fig. 6. Phase identification by clustering of experimental data: (a) HAADF/LAADF-STEM image intensity profiles and Zr and Ta concentration distribution obtained from the region crossing BCC phase boundary. (b) Regional distribution estimated by clustering. The profile shown in (a) is obtained from the 10×100 nm region indicated by the white dotted line. (c) Chemical composition differences in Boundary/Zr-rich/Ta-rich regions from the average composition.

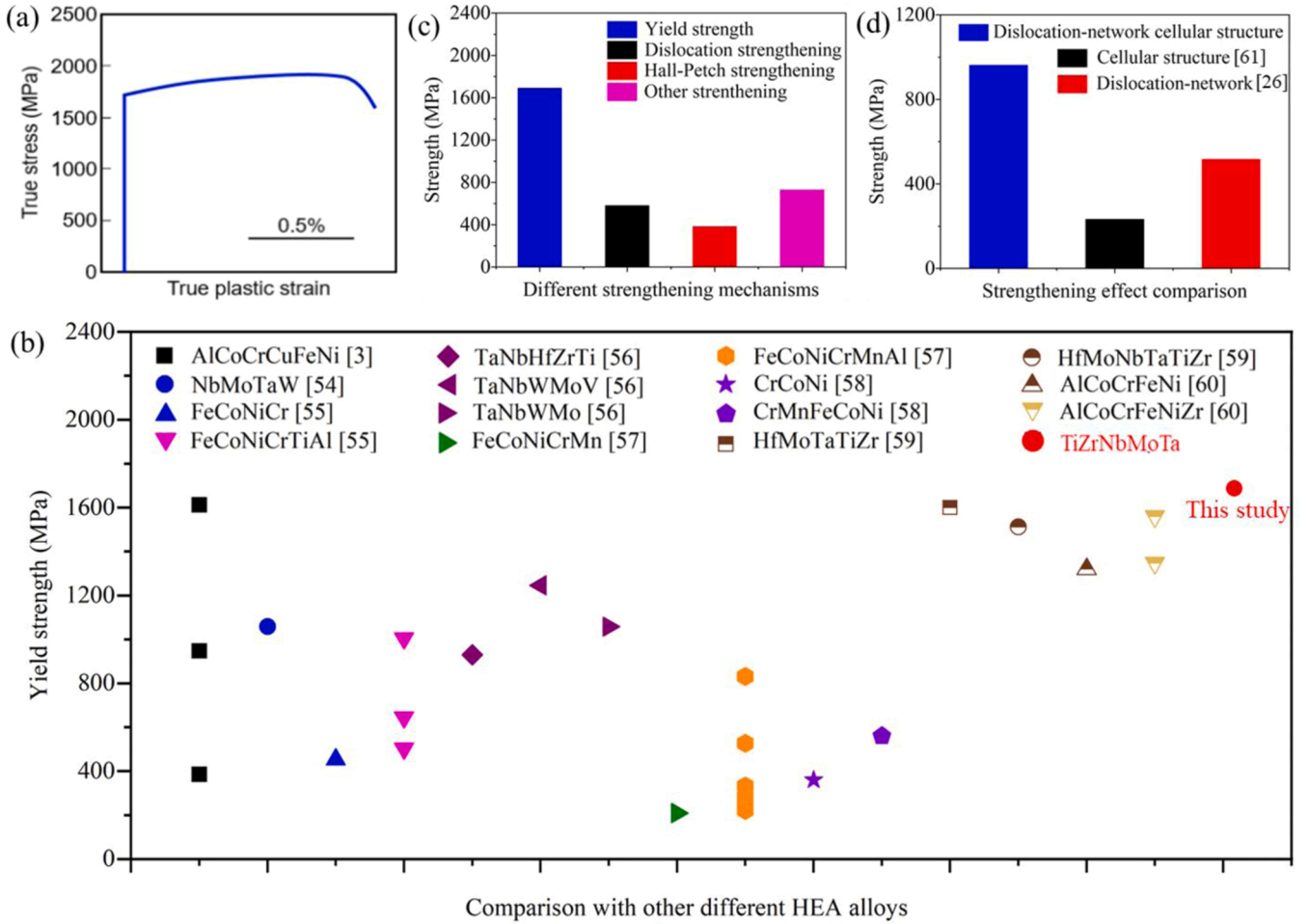


Fig. 7. Mechanical properties of the present HEA: (a) Compressive stress-strain curve of the present HEA [7], (b) Comparison between our HEA and other commonly reported HEAs [3,54–60], (c) Evaluation of strengthening from different mechanisms, (d) Comparison of the strengthening effect between our novel dislocation-network cellular structure and other commonly reported cellular structures and dislocation networks [26,61].

Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6} alloy. Using these parameters, the estimated dislocation strengthening is about 580 MPa. Next, the strengthening effect from the cellular structure is considered, using the Hall-Petch relation: $\sigma = kd^{-1/2}$ where k is the Hall-Petch strengthening factor ($\sim 270 \text{ MPa}/\mu\text{m}^{1/2}$) [64] and d is the average cell diameter ($\sim 0.5 \mu\text{m}$). The average Hall-Petch strengthening from the cellular structure is about 382 MPa. Therefore, the contribution of other strengthening mechanisms, including solution strengthening and inherent alloy component strengthening, is approximately $1690 - 580 - 382 = 728 \text{ MPa}$ (Fig. 7(c)). In summary, the total strengthening effect from the cellular structure is about 962 MPa (Fig. 7(d)), which is significantly higher than the conventional cellular structure (without dislocation-network, $\sim 232 \text{ MPa}$) [61] and dislocation-network (without phase separation, $\sim 516 \text{ MPa}$) [26].

It is important to note that the strengthening effect resulting from grain boundaries is already incorporated into the cell strengthening calculation. This is because multiple cells grow together to form coarse columnar grains, and eutectic reactions occur at both the grain and cell boundaries. As a result, there is overlap between the grain boundaries and some of the cell walls. Therefore, it can be concluded that the cells, rather than the grain boundaries of columnar grains, are the primary structures that interact with dislocations during deformation [61,65]. As a result, there is no need to conduct a separate evaluation of the strengthening effect from the grain boundaries in this context.

4. Discussion

4.1. Phase separation during L-PBF

In recent years, the metastable cellular structures in metallic materials processed by AM have been reported extensively in aluminum alloys, CrCoMo alloy, 316 L steel, Inconel 718, Cu alloys, and HEAs [20–33]. Although the cellular structures in these alloys after AM are different, the formation process of cellular structure is demonstrated to have a close relationship with temperature gradient (G) and solidification velocity (V) [30,31,66]. Generally, G/V ratio determines the solidification morphology. A very high ratio of G/V leads to a planar solidification morphology. With the continuous decrease of G/V ratio, the planar solidification morphology will gradually change to the cellular structure, columnar dendrite, or equiaxed dendrite. In Fig. S1, the main solidification structure in a molten pool is column dendrite, suggesting that the column dendrite growth mode dominates the solidification front.

To further understand the formation mechanisms of cellular structures with phase separations, we performed a thermodynamic simulation for the phase separation with a dataset within the Thermo-Calc software. Fig. 8(a) shows a property diagram of the Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6} alloy, which is a type of phase diagram showing the volume fraction of constituent phases as a function of temperature. In the equilibrium condition, the following transformation process occurs: Liquid $\rightarrow$ BCC $\rightarrow$ Zr-rich BCC and Ta-rich BCC (denoted as BCC_{Zr} and

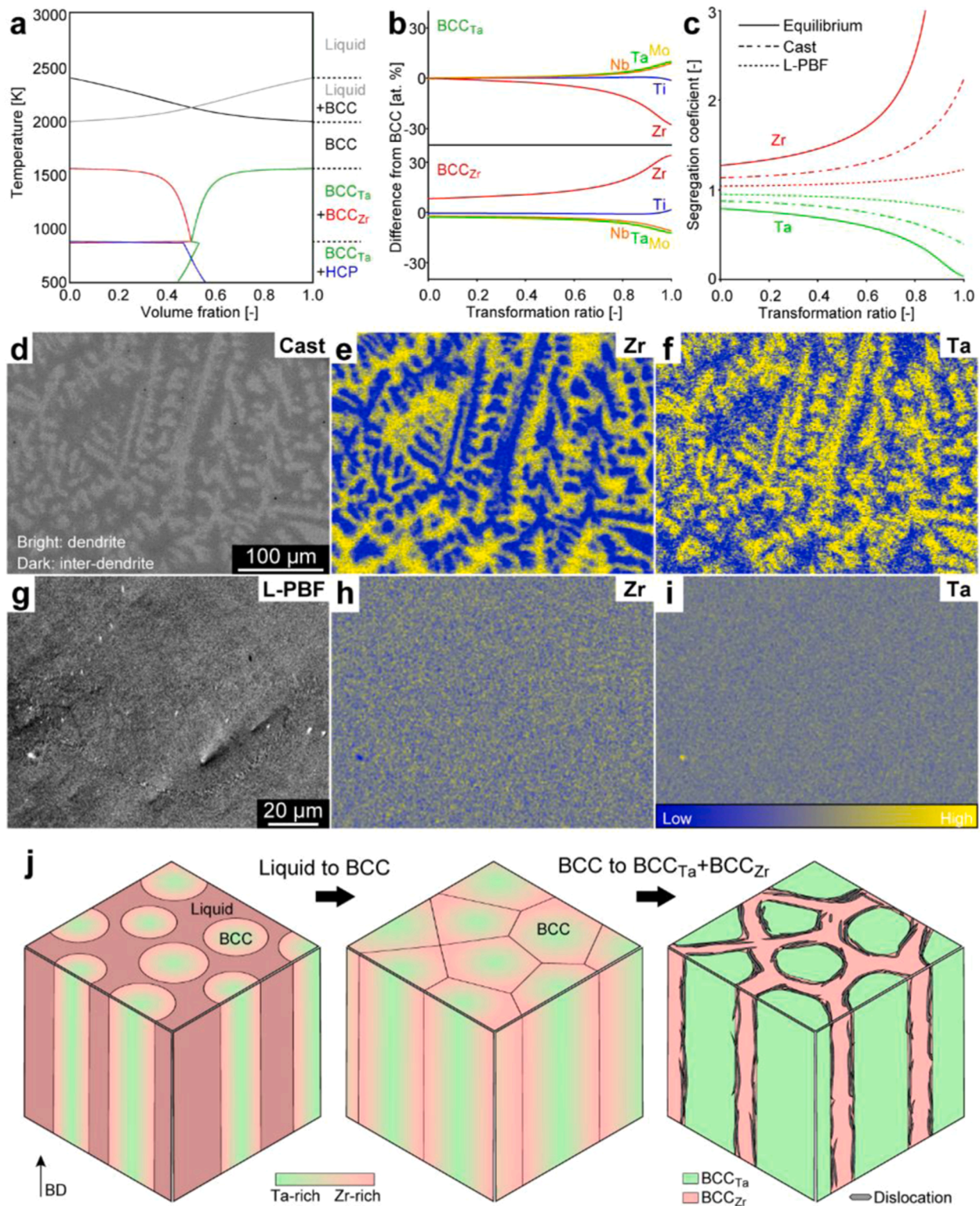


Fig. 8. Effect of fabrication condition on the segregation behavior: (a) Property diagram of the $\text{Ti}_{1.4}\text{Nb}_{0.6}\text{Ta}_{0.6}\text{Zr}_{1.4}\text{Mo}_{0.6}$ alloy under the equilibrium condition. (b) Segregation behavior of constituent elements during BCC to $\text{BCC}_{\text{Zr}}/\text{BCC}_{\text{Ta}}$ phase transformation. (c) The variation of segregation coefficients of Zr and Ta elements during BCC to $\text{BCC}_{\text{Zr}}/\text{BCC}_{\text{Ta}}$ phase transformation. (d-f) SEM-BSE image of as-cast HEA and its corresponding EDS maps of Zr and Ta, which are reproduced from ref [7] with permission. (g-i) SEM-BSE image of L-PBF processed HEA and corresponding EDS maps of Zr and Ta. (j) Schematic illustration of phase transformation.

BCC_{Ta} hereafter) $\rightarrow \text{BCC}_{\text{Ta}}$ and HCP. Due to the nonequilibrium conditions of ultra-rapid cooling of L-PBF, the actual transformation have terminated up to the transformation to $\text{BCC}_{\text{Zr}}/\text{BCC}_{\text{Ta}}$, which is supported by the fact that no HCP phase was observed in the experiment. XRD and

electron microscopy analyses indicate that the observed microstructure can be identified as two BCC phases with different compositions, suggesting that the solid-to-solid transformation process had a significant influence on the microstructure formation. Fig. 8(b) shows an elemental

segregation behavior during BCC phase separation under equilibrium conditions. As phase separation proceeds, the original BCC phase will transform into the Nb-Ta-Mo-rich BCC_{Ta} and the Zr-rich BCC_{Zr} . Table 2 shows chemical compositions of the BCC_{Zr} and BCC_{Ta} in the equilibrium condition, in the as-cast alloy [9] and in the present L-PBF fabricated Ti-Zr-Nb-Mo-Ta alloys. The chemical composition differences between BCC_{Zr} and BCC_{Ta} in the cast and LPBF samples are notably distinct. Specifically, in the cast sample, the differences for Ti, Zr, Nb, Mo, and Ta are approximately 4 at%, 21 at%, 5 at%, 6 at%, and 14 at%, respectively. In contrast, in the LPBF sample, the differences for Ti, Zr, Nb, Mo, and Ta are significantly reduced to approximately 1 at%, 8 at%, 2 at%, 2 at%, and 2 at%, respectively. A direct comparison of the chemical compositions between the as-cast and L-PBF conditions reveals a significant reduction in the degree of segregation in the L-PBF-processed samples. For a quantitative representation of changes in segregation behaviors, we have evaluated segregation coefficients for Zr (k_{Zr}) and Ta (k_{Ta}) by the following equations:

$$k_{Zr} = \frac{\text{Zr concentraion in } BCC_{Zr}}{\text{Zr concentraion in } BCC_{Ta}}, \quad k_{Ta} = \frac{\text{Ta concentraion in } BCC_{Zr}}{\text{Ta concentraion in } BCC_{Ta}} \quad (2)$$

In Fig. 8(c), the solid line illustrates changes in the segregation coefficients under the equilibrium condition with respect to the transformation ratio. The “Transformation ratio” indicates the progress of the phase separation, which is calculated as the ratio of the current volume fraction of BCC_{Zr} to the maximum volume fraction of BCC_{Zr} (45 %). In the equilibrium case, segregation coefficients for Zr and Ta become $k_{Zr} = 24$ (1/0.042) and $k_{Ta} = 0.03$ when the transformation is accomplished. On the other hand, the segregation coefficients estimated from the compositions of the cast and L-PBF alloys become $k_{Zr} = 2.2$ (1/0.45) and $k_{Ta} = 0.39$ for casting and $k_{Zr} = 1.2$ (1/0.81) and $k_{Ta} = 0.75$ for L-PBF, which are illustrated by dashed lines in Fig. 8(c). Note that the volume fraction of BCC_{Zr} estimated by SEM observations and XRD analysis was about 50 %. This fraction is consistent with the maximum volume fraction of BCC_{Zr} in the property diagram (45 %), suggesting that the phase transformation from BCC to BCC_{Zr}/BCC_{Ta} has been completed in the present sample.

The change in segregation behavior due to fabrication procedures is also confirmed by experimental results. Fig. 8(d-f) show the SEM-BSE image of the as-cast alloy and the corresponding Zr/Ta map by SEM-EDS [7]. The observed microstructure shows evident segregation behavior on a large scale (~ several hundred micrometers). Fig. 8(g-i) show a SEM-BSE image of the L-PBF HEA and the corresponding Zr/Ta map in the present study. Although there is also the element segregation of Zr and Ta in L-PBF processed HEA (Figs. 2 and 4), the element segregation on a large scale is not apparent. Through the comparison, the element segregation can be effectively suppressed by fast-cooling in the L-PBF fabrication, which may be an origin of excellent properties of this alloy not only for high strength but also for improved biocompatibility [7].

Changes in segregation behavior as a function of cooling rate have been reported in previous studies based on the phase-field modeling [67]. In particular, under rapid cooling processes such as L-PBF, the equilibrium condition at the phase transformation boundary is not

always satisfied, and the segregation coefficient approaches 1 as the cooling rate increases. These studies have shown that the reduction of segregation tendency occurs during the solidification process, i.e., liquid-to-solid transformation. In the present study, we assume that a reduction of segregation tendency also occurs during the solid-to-solid phase transformation, i.e., $BCC \rightarrow BCC_{Zr}/BCC_{Ta}$ processes, which provides formation of dislocation-network coupled with phase separation. Fig. 8(j) shows a schematic illustration of microstructural development during Liquid $\rightarrow$ BCC $\rightarrow$ BCC_{Zr}/BCC_{Ta} processes. During the solidification process, the BCC phase forms a dendrite microstructure elongated along the BD direction. Zr is preferentially ejected into the liquid phase, resulting in the formation of a BCC single-phase microstructure with segregation at the end of solidification. Subsequently in the solid-solid transformation, this segregation leads to the phase separation of BCC to BCC_{Ta} and BCC_{Zr} . To accommodate the difference in lattice constants between BCC_{Ta} and BCC_{Zr} , the dislocations-networks are introduced around the phase boundaries, whose details are discussed in the next section.

It is worth noting that if one assumes that the formation of dislocation-network is due to the microstructural developments during the solidification process, there are two points that are difficult to explain. The first is the distinct peak separation that appeared in the XRD analysis. During the solidification, segregation coefficients change gradually depending on the volume fraction of the solid phase, like the behavior in Fig. 8(c). Therefore, in the as-solidified microstructure, the local composition appears a variety depending on the solidification timing. Based on this assumption, the XRD profile should appear as broad peaks with a single BCC phase, which does not correspond to the experimental results. The second is the localized distribution of the dislocation-network in the cellular structure. When dislocations are introduced to relax internal stresses during solidification, they are localized in the final solidification zone, the cellular wall region. In this case, the dislocation density is expected to be approximately uniform within the cellular wall, as observed in AM-processed 316 L steel [25]. However, LAADF-STEM observations and machine-learning analysis indicate that the dislocation-network is localized near the Boundary region, contrary to the above assumption. The results support the idea that the observed dislocation network was introduced during the solid-solid phase separation to accommodate strains between two BCC phases. In the present alloy system, Zr is the softest element, as indicated by its small Young's modulus, which may lead to preferential strain accommodation by BCC_{Zr} .

4.2. Formation mechanism of dislocation-network

Microstructures with dislocation-networks have been reported in AM-processed metallic materials [20,21,23–26,32]. One of the proposed mechanisms for forming dislocation-networks in AM-processed alloys is due to cellular/column dendrite growth mode under conditions of high temperature gradient and high growth rate [30,66]. Other mechanisms have been reported in which dislocation structures are introduced to relax thermal stresses introduced by cyclic heating under laser irradiation [20,25]. However, the dislocation-network that overlaps with the phase separation-induced cellular structure is seldom reported to the best of our knowledge. In the present L-PBF fabricated HEA, we consider that the dislocation-network structure was introduced to compensate for the strain caused by phase separation during the solid phase transformation. In this case, the degree of strain due to phase separation, i.e., the difference in lattice constants between two BCC phases, is essential. In the case of the L-PBF condition, the difference in lattice constants between two BCC phases is less than 1 %, which is sufficiently small to be accommodated by introducing a dislocation-network as geometrically necessary dislocations (GND) [32]. If the segregation coefficient between the two BCC phases is far from 1, the difference in lattice parameters will increase. Based on Eq. (1) and compositions listed in Table 2, the differences in lattice constants for the cast condition and the

Table 2

The chemical compositions of BCC phases in Ti-Zr-Nb-Mo-Ta HEA under equilibrium condition and experimentally processed by casting and L-PBF (at%).

	Phase	Ti	Zr	Nb	Mo	Ta
Equilibrium	BCC_{Ta}	29	2.7	22	23	23
	BCC_{Zr}	32	65	2	0.6	0.8
Cast	BCC_{Ta}	27	17	17	17	23
	BCC_{Zr}	31	38	12	11	9
	Difference	4	21	5	6	14
	BCC_{Ta}	30	27	14	14	14
L-PBF	BCC_{Zr}	31	35	12	12	12
	Difference	1	8	2	2	2

equilibrium condition are estimated at 2.6 % and 7.2 %, respectively, which should be difficult to accommodate with the introduction of GND.

We will discuss a fraction of the GND caused by this phase separation in the high dislocation density of this material. The GND can be regarded as misfit dislocations that relax the strain between the two BCC phases, their density can be estimated from the density of the phase boundary and the difference in lattice constants. From the results of the SEM observations, the phase boundary is approximately coincident with the surface of the cell core, which has rod-shaped elongated along the BD direction. From the results of the TEM observations as shown in Fig. S3, the density of the phase boundary in a single columnar grain was estimated to be approximately $4.5 \times 10^{-3} \text{ nm/nm}^2$. In addition, GND is introduced at a density that relaxes a 1.0 % mismatch between BCC phases, average interval of dislocation become 0.29 nm/0.01, equal to 29 nm along one direction. Assuming the misfit dislocations arranged as grid-like on the phase boundary, their density per unit area becomes $6.9 \times 10^{-2} \text{ nm/nm}^2$. The overall dislocation density is calculated by the product of these two values, $3.1 \times 10^{-4} \text{ nm/nm}^3$, equals to $3.1 \times 10^{14} \text{ m}^{-2}$. This density correspond to about 40 % of the overall dislocation density of the sample, which is calculated by XRD to be $8.5 \times 10^{14} \text{ m}^{-2}$. At present, formation mechanism of residual dislocation is still unclear; however, we considered following mechanism; dislocation-networks are initially introduced as GND by the solid phase separation during the first rapid cooling of L-PBF, then cyclic heating and cooling will multiply the dislocations to accommodate thermal distortions. This two-stage accommodation process will lead to a higher dislocation density of present BioHEA than previously reported AM alloys [68].

The relationship between phase separation and dislocation-network in the present study suggests that the dislocation-network structure can be controlled by designing the nano-to-micron scale segregation behavior of the constituent elements [69]. For example, recent studies suggest that senary Ti-Zr-Nb-Mo-Ta-Hf alloys with weaker segregation behavior can indeed form homogeneous microstructures with less dislocation-networks [70], leading to easier control of properties across micro to macro scales. Simultaneous design of phase separation and dislocation-network structure is expected to lead to the development of materials with a novel microstructure that will pave a path to expand their functionality. Moreover, such novel dislocation-network cellular structure can contribute to an evident strengthening effect (Fig. 7(d)) as 962 MPa, which is much higher than the common cellular structures [26,61]. Thus, the present HEA having an excellent strength. This suggests that such dislocation-network cellular structure can be proposed to develop high-performance metals processed by AM.

5. Conclusions

We have investigated microstructure formed in as-built Ti-Zr-Nb-Ta-Mo HEA processed by L-PBF based on XRD, SEM, TEM, and STEM observations. On the basis of observations, the microstructure was characterized by cellular structure in which microscopic phase separation and dislocation-network coupled whose formation mechanism was proposed with the aid of thermodynamic calculations. The main results are summarized as follows.

- (1) Based on SEM analysis, cellular structures with solute segregation are confirmed in as-built Ti-Zr-Nb-Ta-Mo HEA processed by L-PBF. This cellular structure consists of Ta-rich cellular wall regions and Zr-rich cellular core regions with a hundred nm width. XRD analysis reveals that this cellular structure is identified as independent two BCC phases with a slight difference of lattice constant.
- (2) Combination of STEM/STEM-EDS measurements and clustering analysis provide that the cellular structure can be classified into two BCC phases with different compositions and lattice constants, accompanied by nano-scale Boundary regions containing high density of dislocation-networks. Compositional differences

between the BCC phases were less than a few at%, which is much weaker than that of the cast HEA.

- (3) The effect of the cooling rate on segregation behavior was investigated by thermodynamic simulation, indicating that the degree of segregation becomes weak under fast cooling conditions such as L-PBF. In addition, based on the observed cellular microstructure, it is suggested that their formation process is dominated by the phase separation process of $\text{BCC} \rightarrow \text{BCC}_{\text{Zr}}/\text{BCC}_{\text{Ta}}$ in the solid phase transformation.
- (4) Based on the estimated phase-segregation behavior of L-PBF HEAs, we propose a process in which a dislocation-network is introduced as a GND for strain relaxation caused by solid phase transformation. Since the phase transformation behavior is affected by the segregation behavior of the constituent elements, the dislocation-network structure may be controlled by optimizing the composition and process conditions that weaken the segregation behavior. This mechanism provides insight into the control of microstructures in which cooperative reactions between phase separation and strain accommodation.
- (5) The strengthening effects of the dislocation-network cellular structure were quantitatively analyzed. This unique structure contributes to a combined strengthening mechanism, including dislocation strengthening due to the high-density dislocation network and Hall-Petch strengthening resulting from the fine cellular size. These combined effects result in the excellent strength of the present HEA. This novel cellular structure offers significant potential for designing and developing high-performance AM metals

CRediT authorship contribution statement

Egusa Daisuke: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chen Han:** Writing – original draft, Visualization, Methodology, Investigation. **Koizumi Yuichiro:** Writing – review & editing, Supervision, Resources. **Okugawa Masayuki:** Visualization, Validation, Software, Formal analysis. **Abe Eiji:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Nakano Takayoshi:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Sasaki Taisuke:** Visualization, Supervision, Resources, Methodology. **Li Zehao:** Investigation. **Ishimoto Takuya:** Writing – review & editing, Resources, Project administration, Methodology, Investigation. **Ozasa Ryosuke:** Resources, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.addma.2025.104737](https://doi.org/10.1016/j.addma.2025.104737).

Data availability

Data will be made available on request.

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