Reversible deformation-induced martensitic transformation in

Al_{0.6}CoCrFeNi high-entropy alloy investigated by *in situ*

synchrotron-based high-energy X-ray diffraction

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Abstract: The micro-mechanical behavior of Al_{0.6}CoCrFeNi high-entropy alloy during tensile deformation was investigated using an *in situ* synchrotron-based high-energy X-ray diffraction technique. The alloy consisted of face-center-cubic (FCC) and body-center-cubic-based (BCC-based) structure accompanied by a small amount of σ phase. The FCC phase yielded prior to the BCC-based phase during the tensile loading, and the BCC-based phase bore more stress partition during the plastic deformation stage in spite of only ~23% volume fraction. A reversible deformation-induced martensitic transformation from the BCC-based phase to orthorhombic phase was observed during the plastic deformation stage. The transformation preferentially occurred in the grains with an orientation of B-[001]//loading direction and B-[110]//transverse direction. The study characterized the micro-mechanical behavior

of this alloy, and the reversible martensitic transformation is believed to be beneficial to the fracture toughness of such alloys.

Keywords: High-entropy alloy; Micro-mechanical behavior; Martensitic transformation; High-energy X-ray diffraction; Lattice strain.

1. Introduction

High-entropy alloys (HEA) were originally defined by Yeh as containing at least five principal elements with approximately equiatomic concentrations [1]. HEA break the traditional alloy design philosophy and open a new arena for the exploration of new materials and unique properties. To date, various HEA have been designed for obtaining unique properties, including considerable strength at cryogenic [2], ambient [3-6] and elevated [7-9] temperatures, good ductility [10-11] and favorable resistance to wear [12] and fatigue [13]. However, an optimal combination of strength and plasticity is difficult to achieve in HEA. Typical mechanisms to further improve these mechanical properties, such as dual-phase structure [5-6], precipitation-hardening [14], twinning-induced plasticity [15], and transformation-induced plasticity [16] were introduced to HEA. Recently, [Li et al. \[16\]](#) reported a deformation-induced martensitic transformation from a metastable face-center-cubic (FCC) to hexagonal close-packed phase in the 50Fe-30Mn-10Co-10Cr (atomic per cent, at. %) alloy, which realized a good combination of strength and plasticity and provided a valuable design direction to explore superior properties for HEA.

HEA are designed to form a considerably stable solid solution phase based on the concept that high configurational entropy could restrain the phase separation and compound formation. However, only a few HEA exhibit a single solid solution phase with FCC [10-11, 17-18] or body-center-cubic (BCC) [7, 9] structure. In contrast, most

HEA are inclined to form dual-phase or even multi-phase structure [13-14, 16, 19]. The multi-phase HEA not only promote a fundamental investigation of phase separation, but also increase the achievable property spectrum for the HEA. In multi-phase alloys, the mechanical property strongly depends on the strength and plasticity configuration of the constituent phases, phase interface damage resistance, and coordination deformation ability. Understanding the micro-mechanical behavior of multi-phase alloys is so important that could shed light on the macro-mechanical behavior and guide alloy composition design and application.

Neutron and high-energy X-ray diffraction (HE-XRD) technique are powerful to study the micro-mechanical behavior of alloys [21-28], especially for the multi-phase alloys and composites [22-27]. As a new type of alloy, the investigation on the deformation mechanism of HEA is still in infancy. Limited data are available regarding the micro-deformation behaviors of single phase HEA [28-29]. Even more, both qualitative and quantitative investigations concerning the micro-deformation behavior of multi-phase HEA are also infrequent. Therefore, Neutron diffraction or HE-XRD could be employed to effectively evaluate the micro-deformation of HEA.

In the present study, *in situ* synchrotron-based HE-XRD technique was employed to investigate the micro-mechanical behavior of Al_{0.6}CoCrFeNi HEA during the tensile loading. A reversible deformation-induced martensitic transformation was found during deformation. The structural evolution characteristics of the present alloy were discussed in detail. This study provides a better understanding of mechanical mechanism of the HEA and an effective guide for their design and optimization.

2. Materials and Methods

The Al_{0.6}CoCrFeNi HEA ingots were prepared by arc melting a mixture of high-purity metals (greater than 99.9 mass %) in a Ti-gettered high-purity argon

atmosphere. Each ingot was re-melted at least five times to ensure chemical homogeneity. Then the ingots were re-melted by induction heating under high vacuum (2.5×10^{-3} Pa) and injected into a copper mold. The as-cast alloy was homogenized at 1373 K for 24 h followed by water quenching, and then was rolled in steps to a total thickness reduction of 50% at room temperature. Next, the alloy was annealed at 1123 K for 1 h. The annealed alloy was cut into a flat, dog-bone shaped specimen (Fig. 3 inset) for the *in situ* tensile tests. The length, width, and thickness of the specimen were oriented parallel to the rolling direction (RD), transverse direction (TD), and normal direction (ND), respectively. The following investigation was implemented on the annealed $\text{Al}_{0.6}\text{CoCrFeNi}$ HEA (denoted as the alloy in the following).

The microstructure of the alloy was examined by a Hitachi S4800 scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) and JEOL JEM-2100 transmission electron microscope (TEM) with selected area electron diffraction (SAED). The micro-deformation behavior of the alloy was investigated using a synchrotron-based HE-XRD technique. The experiments were performed at the 11-ID-C beam line at the Advanced Photon Source, Argonne National Laboratory, USA. The experimental set-up is schematically shown in Fig. 1. A monochromatic X-ray beam with an energy of 105.74 keV (the corresponding wavelength (λ) and wave-number (k) were $0.11725 \text{ \AA}$ and $53.6 \text{ \AA}^{-1}$, respectively.) was used to map the detailed structural evolution characteristics of the alloy during the single and cyclic tensile loading. In the first cycle of cyclic loading, the alloy was loaded to 1249 MPa. The value was greater than the yield stress. Specimen was mounted on a stress rig with the RD parallel to the loading direction (LD), and the direction of X-ray beam was parallel to the ND of the alloy. A PerkinElmer α -Si flat-panel large-area detector with quadratic pixel size of $200 \text{ }\mu\text{m} \times 200 \text{ }\mu\text{m}$ was

placed behind the specimen to collect the two-dimensional (2-D) diffraction patterns during the different loading levels. One-dimensional (1-D) HE-XRD patterns were obtained by integrating the 2-D diffraction patterns along a specific azimuth angle (η). Standard CeO₂ powder was used to calibrate the exact distance between the specimen and detector.

Diffraction data were displayed and handled against the linear reciprocal space variable. The lattice strain (ε_{hkl}) of different $\{hkl\}$ planes in each phase could be obtained by tracing the relative change of the reciprocal lattice vector (Q) using the following equation [20-21]:

$$\varepsilon_{hkl} = (Q_0 - Q)/Q \quad (1)$$

where Q could be obtained by fitting the diffraction peak position under different loading levels. Q_0 is determined from the specimen in a stress-free state (i.e., before tensile deformation). For the newly formed martensite, Q_0 is counted as the initial reciprocal lattice vector of the diffraction plane of the parent phase.

3. Results

3.1 Microstructure

Fig. 2(a) shows the XRD pattern of the alloy. Because the 100 diffraction peak of an ordered BCC (B2) phase could be found in Fig. 2(a), demonstrating that a B2 structure existed in the present alloy. Thus, the present alloy was regarded to be mainly FCC and BCC-based phase structure accompanied by a small amount of σ phase. The lattice constants of the FCC and BCC-based phases were determined to be 3.588 Å and 2.875 Å, respectively. Fig. 2(b) shows the SEM micrograph of the alloy. The dendrite and inter-dendrite morphology indicates that the present alloy did not recrystallize completely under the current experimental conditions [30]. The EDS results show that the dendritic and inter-dendritic phases were enriched with Cr-Fe and Al-Ni,

respectively (Extended Data Table 1). The Al-Ni-rich needle-like precipitates with a B2 structure [31] were distributed in the dendritic phase. Due to that the σ phase is in nano-scale [32], it is difficult to be observed in Fig. 2(b). Fig. 2(c) shows the bright-field TEM image and corresponding SAED patterns of the alloy. The 100 diffraction spot of the B2 phase also could be observed in the SAED pattern of the inter-dendrite region. Thus, the dendritic and inter-dendritic phases were identified as the FCC and BCC-based structures, respectively. The interface phase was not present between the FCC and BCC-based phases. Disregarding the small amount of the σ phase, the volume fractions of the FCC and BCC-based phases were determined to be ~77% and ~23% respectively.

3.2 Mechanical properties

Fig. 3 shows the typical tensile engineering stress-strain (σ - ϵ) curve of the alloy. The present alloy exhibited a substantial yielding strength of ~1100 MPa with a limited plastic deformation of ~2.0%. The poor plasticity of the alloy may be related to the “hard and brittle” σ phase [32] and without recrystallization [30]. The stress-strain curve could be divided into three stages based on the hardening rate: elastic regime (Stage I, $\sigma < \sim 840$ MPa), elasto-plasticity transition regime (Stage II, ~ 840 MPa $< \sigma < \sim 1150$ MPa), and stable plastic regime (Stage III, $\sigma > \sim 1150$ MPa) with a stable work hardening rate.

3.3 Structural evolution during deformation

Fig. 4 shows the 2-D diffraction patterns of the alloy when loaded at 0 and 1311 MPa. As shown in Fig. 4(a), the 111, 211, 220, and 311 diffraction rings of the FCC phase were marked by 1, 3, 5, and 7 (indexed as F- hkl), respectively. Similarly, the 110, 200, and 211 diffraction rings of the BCC-based phase were marked by 2, 4, and 6 (indexed as B- hkl), respectively. The heterogeneous intensity of the diffraction rings

before loading (shown in Fig. 4(a)) indicates that the texture existed in the alloy and was not completely eliminated after annealing. In contrast to Figs. 4(b-c), Figs. 4(e-f) show that new diffraction rings appeared near the B-110 and B-211 rings at 1311 MPa, which indicates that a martensitic transformation occurred during the tensile deformation. Moreover, the diffraction rings of the newly formed martensite appeared at the specific η , which suggests that the deformation-induced martensitic transformation in the present alloy had a selection mechanism based on a preferred orientation.

To investigate the preferred orientation selection of the martensitic transformation, the 1-D diffraction profiles of B-110, B-200, and B-211 at 1311 MPa are shown in Figs. 5(a-c) by integrating the 2-D diffraction patterns along η from 0° to 180° over a range of $\pm 5^\circ$. Fig. 5(a) shows that the diffraction peak of the martensite (noted as M) appeared between the F-111 and B-110 diffraction peaks at $\eta = \sim 0^\circ$ and $\sim 180^\circ$. Another martensite diffraction peak appeared near the B-211 diffraction peak at $\eta = \sim 50^\circ$ and $\sim 130^\circ$, as shown in Fig. 5(c). The integral intensity of the martensite diffraction peaks as a function of η , as shown in Figs. 5(d-e), directly demonstrates that the martensitic transformation had a preferred orientation selection. In addition, Fig. 5(b) shows that although no new peaks were detected near the B-200 diffraction peak, the B-200 diffraction peak exhibited a notable shift toward a lower Q value as η increased from 0° to 90° , which indicates a huge lattice strain of the $\{200\}$ plane in the BCC-based phase (indexed as B- $\{hkl\}$ plane, similarly, the $\{hkl\}$ plane in the FCC phase was indexed as F- $\{hkl\}$ plane).

The structural evolution characteristics during tensile deformation were systematically studied by tracing the 1-D diffraction profiles of different reflections at different stress levels. Fig. 6(a) shows that both the F-111 and B-110 diffraction peaks

in the TD ($\eta = 0^\circ$) have shifted towards higher Q value with an increase in the tensile stress, while the B-110 diffraction peak shifted more than the F-111 diffraction peak. When the tensile stress was higher than ~ 1150 MPa, the B-110 diffraction peak rapidly widened and subsequently split into two peaks, which indicates that the deformation-induced martensitic transformation was initiated during the macroscopic plastic deformation stage. Then, with a further increase in the applied stress, the B-110 diffraction peak continued to shift towards higher Q value, whereas the diffraction peak of the martensite shifted towards lower Q value. Apparently, the B-110 diffraction peak shifted more obvious than before it split, which suggests that the continuous martensitic transformation led to severe lattice deformation in some grains of the BCC-based phase. As shown in Fig. 6(b), the B-211 diffraction peak at $\eta = 50^\circ$ also split when the stress reached ~ 1150 MPa. Figs. 6(a-b) exhibited that the martensite transformed from the BCC-based phase. This conclusion could be further confirmed by the intensity change of the B-110 and B-211 diffraction peaks, as shown in Figs. 6(c-d). The intensity of both the B-110 and B-211 diffraction peaks exhibited a slight decrease when the stress increased from ~ 800 MPa to ~ 1150 MPa, and then showed a sharp fall after the stress exceeded ~ 1150 MPa. Meanwhile, a rapid increase of the diffraction peaks intensity in the martensite was observed, which indicates an increasing volume fraction of the martensitic phase.

A cyclic tensile test was used to determine the reversibility of the martensitic transformation. The 1-D diffraction profiles of the B-110 and B-211 reflections during the cyclic loading are shown in Fig. 7. The shifting tendency of the B-110 and B-211 diffraction peaks in the first cycle was similar to that in the single loading. During the unloading process, the diffraction peaks of the BCC-based and martensitic phases shifted towards the original position and almost completely merged when the stress was

zero, which indicates that the martensitic transformation in the present alloy was nearly reversible. In contrast to the diffraction peak split during the plastic deformation stage in the first loading, the split of diffraction peaks occurred in the elastic deformation stage during the second loading.

4. Discussion

4.1 Lattice strain response during deformation

The mechanical behavior and martensitic transformation of the alloy could be further understood from the evolution of the lattice strain. Because of the high angular resolution of synchrotron-based HE-XRD, overlapping diffraction peaks could be easily separated, and the peak positions could be accurately modeled using the Lorentz function, as shown in the inset of Fig. 8(a). The lattice strain for the different planes of the FCC and BCC-based phases in the LD and TD during the single loading is shown in Fig. 8(a) as a function of the tensile stress. The curves of lattice strain versus tensile stress could also be classified into three stages, which coincides well with the tensile stress-strain curve (Fig. 3). When the tensile stress was less than ~840 MPa (stage I), the lattice strain in all planes responded linearly to the tensile stress, which indicates that only elastic deformation occurred in the FCC and BCC-based phases. The different slopes depended on the elastic anisotropy in each phase. In stage II, the non-linear response of the lattice strain to the applied stress was gradually presented. The slope of the lattice strain curve of the B-{200} plane was obviously higher than the other planes. When the stress was greater than ~1150 MPa (stage III), the lattice strain in the B-{200} plane exhibited a sudden increase as high as ~3.5%, which is consistent with the notable shift of the B-{200} diffraction peak shown in Fig. 5(b). The huge lattice strain was considered to be a result of the martensitic transformation. In addition, the lattice strain of all planes in the FCC phase decreased in stage III, which indicates the yielding

of the FCC phase. Clearly, the lattice strain of the BCC-based phase during the plastic deformation stage was higher than that of the FCC phase, which suggests that the BCC-based phase bore more stress than the FCC phase.

To understand the micro-mechanical behavior of the present alloy, the von Mises stress (σ_{VM}) was introduced to assess the stress partition of the constituent phases during deformation [23, 26]. The corresponding σ_{VM} of each phase was calculated by following [33]:

$$\sigma_{VM} = \frac{1}{\sqrt{2}} [(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2]^{1/2} \quad (2)$$

where σ_{11} is the principal stress in the LD, and σ_{22} and σ_{33} are the principal stresses in the TD, which could be obtained by the measured lattice strains:

$$\sigma_{11} = \frac{E}{1+\nu} \varepsilon_{11} + \frac{\nu E}{(1+\nu)(1-2\nu)} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) \quad (3)$$

$$\sigma_{22} = \sigma_{33} = \frac{E}{1+\nu} \varepsilon_{22} + \frac{\nu E}{(1+\nu)(1-2\nu)} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) \quad (4)$$

where ε_{11} and ε_{22} are the lattice strains parallel to the LD and TD respectively, and ε_{22} is equal to ε_{33} . E is the elastic moduli of each $\{hkl\}$ plane. Because of the relatively low symmetry and insensitivity to the inter-granular strain, the B- $\{211\}$ and F- $\{311\}$ planes were chosen to represent the average behavior of the BCC-based and FCC phases, respectively. Fig. 8(b) shows the σ_{VM} of the BCC-based and FCC phases as a function of the tensile stress. During the initial elastic deformation stage (stage I), a minimal load was transferred between the BCC-based and FCC phases. With a further increase in the tensile stress in stage II, the BCC-based phase gradually developed a more important role in the stress partition. As the tensile stress exceeded ~ 1150 MPa, the FCC phase yielded, which led to a strain relaxation of the FCC phase with more stress transferred to the BCC-based phase. When the stress in the BCC-based phase reached a critical level, the martensitic transformation was initiated in some grains of the

BCC-based phase.

As shown in Fig. 4, the diffraction peaks of martensite were obviously observed near the B-211 diffraction ring at $\eta = \sim 50^\circ$ and the B-110 diffraction ring at $\eta = \sim 0^\circ$. Besides, the B-200 diffraction peak exhibited a relative large shift to higher Q , as shown in Fig. 5(b). Therefore, to better understand the martensitic transformation characteristics of the present alloy during the cyclic loading, the lattice strain of the B- $\{110\}$, B- $\{200\}$, and B- $\{211\}$ planes along $\eta = 0^\circ$ (TD), 90° (LD), and 50° as a function of the tensile stress during the cyclic loading is shown in Fig. 9 shows. The main observations are summarized as follows:

(1) Fig. 9(a) shows that, during the first loading, the lattice strain of the B- $\{110\}$ plane in the TD exhibited a sudden increase when the stress exceeded ~ 1150 MPa. This increase corresponded to the initiating of martensitic transformation, which verifies the fact that the formation of martensite induced severe lattice deformation in some grains of the BCC-based phase. In contrast to the B- $\{110\}$ plane in the TD, when the stress was greater than ~ 1150 MPa, the B- $\{211\}$ plane at $\eta = 50^\circ$ exhibited a decrease in the lattice strain instead of an increase one (Fig. 9(c)), which indicates that the formation of martensite caused a strain relaxation in grains of the BCC-based phase along this direction.

(2) After the first unloading, a residual lattice strain of 0.2% remained in the B- $\{110\}$ plane (Fig. 9(a)), which suggests that the recovery of the B- $\{110\}$ plane in the TD was hindered at some level. The B- $\{200\}$ plane in the LD had a larger residual lattice strain than the B- $\{110\}$ plane (Fig. 9(b)). Compared with the B- $\{110\}$ and B- $\{200\}$ planes, the B- $\{211\}$ plane at $\eta = 50^\circ$ exhibited a nearly complete recovery and the residual lattice strain approached zero, as shown in Fig. 9(c).

(3) Fig. 7 shows that the B-110 and B-211 diffraction peaks split during the plastic

deformation stage in the first loading but split during the elastic deformation stage in the second loading, which indicates that the martensitic transformation occurred during the plastic deformation in the first loading but during the elastic deformation in the second loading. The lattice strain shown in Fig. 9 was consistent with the results depicted in Fig. 7. As shown in Fig. 9, the lattice strain of martensite was traced when the stress was greater than ~1150 MPa (the alloy underwent a plastic deformation) in the first loading (Fig. 9(a)). However, in the second loading (Fig. 9(c)), the lattice strain of martensite was obtained when the stress was in the range of ~400-600 MPa (the alloy underwent an elastic deformation).

(4) Moreover, Fig. 9 shows an evident increase in the lattice strain in all planes of the BCC-based phase during the first loading (marked by the blue arrow A), which corresponds to the initiation of the martensitic transformation. Compared with the first loading, the stress corresponding to an apparent increase in the second loading (marked by the blue arrow B) was higher. This finding means that although the martensite formed during the elastic deformation stage in the second loading, the formation of additional martensite required an even greater stress in the second loading than in the first loading.

The different responses of the lattice strain of the B-{110}, B-{200}, and B-{211} planes listed in observations (1-2) could be ascribed to the combined action of the inter-phase [34-36] and inter-granular stress [37-39], which refer to the phase-to-phase and grain-to-grain interactions, respectively. This combined action could be understood from the “microstructure evolution” schematic, as shown in Fig. 10, which was obtained by adjusting and extending the “bicrystal model” used in a NiTi alloy [38]. Before loading, the alloy was in a stress-free state (Fig. 10(a)). When the alloy was loaded to the plastic deformation stage in the first loading, the martensitic

transformation occurred in grains A and B of the BCC-based phase at different levels depending on the crystal orientations [24, 36, 39]. Simultaneously, the plastic deformation occurred in the FCC phase and some grains of the BCC-based phase (Fig. 10(b)). The internal stress in grain A was believed to be higher than that in grain B [38]. After the first unloading (Fig. 10(c)), the strain caused by the plastic deformation could not be recovered, while the strain caused by the elastic deformation and martensitic transformation did recover. Therefore, for coordinating deformation, a strong coupling between the two constituent phases and different grains promoted the appearance of inter-phase stress between the FCC and BCC-based phases and inter-granular stress between grains A and B of the BCC-based phase. Both inter-phase and inter-granular stress led to different levels of residual lattice strain in the two phases and the slightly retained martensite in grains of the BCC-based phase. The preserved martensite was inevitable during the deformation-induced martensitic transformation in the plastic deformation stage because of the simultaneous onset of plastic deformation in the other phases and/or grains with different orientations [35-37]. Therefore, the lattice strain in all planes of the BCC-based phase exhibited different recovery levels.

The different responses in lattice strain between the first and second loading listed in observations (3-4) also could be understood from Fig. 10. Observation (3) indicates that the martensitic transformation was initiated during both the plastic deformation stage in the first loading (Fig. 10(b)) and during the elastic deformation stage in the second loading (Fig. 10(d) and (e)). In addition, as listed in observation (4), a higher tensile stress was required to further stimulate the martensitic transformation in the second cycle (Fig. 10(b) and (e)). Actually, both observations (3) and (4) have previously been reported in a dual-phase composite with the phase transformation [34] and in several superelastic alloys with a martensitic deformation [35, 38]. It is

speculated that these observations could be attributed to both the preexisting internal stress (strain) in the two phases and the slightly retained martensite in the BCC-based phase after the first unloading (Fig. 10(c)), which were also caused by inter-phase and the inter-granular stress [34-35, 39-40]. This consideration highlights the ability of the constituent phase to accommodate deformation in this type of multi-phase alloy. Additionally, the continuously increasing lattice strain of the martensite in the second loading indicates that the martensitic transformation was not complete until the alloy fractured.

4.2 Martensitic transformation mechanism

As shown in Fig. 6, when the tensile stress was greater than ~1150 MPa, new diffraction peaks appeared near the B-110 and B-211 diffraction peaks, which indicates that a deformation-induced martensitic transformation occurred in the present alloy during tensile deformation. In addition, the B-{200} plane shows an uncommonly large lattice strain up to ~3.3% in the TD, as seen in Fig. 8, which could not be explained by the elastic or plastic deformation [22, 24]. It could, however, be explained by a phase transformation [41]. The martensitic transformation in the present alloy began at the plastic deformation stage, which lagged remarkably behind the Al-Co-Ni alloys [42-43], the transformation in which occurred during the elastic stage. Similarly, the initial stress of the martensitic transformation in Ti-based amorphous alloy composites also lagged behind traditional Ti alloys. It was speculated that the addition of solution elements, such as Zr and Sn, could suppress the occurrence of the martensitic transformation [24, 27]. For the HEA, a different atomic radius of each element leads to lattice parameter variations and severe lattice distortions, which result in an inhibition effect on the phase transformation. In addition, for those composites and alloys with a multi-phase structure, the stress partition of each phase and the compatible deformation

ability of the constituent phases play an important role regarding the activation of the phase transformation [34-35]. The present alloy mainly consisted of “soft” FCC and “hard” BCC-based phases, and the volume fraction of the FCC phase was greater than the BCC-based phase. When the macro-tensile stress was greater than ~1150 MPa, the FCC phase yielded, and the BCC-based phase bore more stress. Then, the martensitic transformation occurred in some grains of the BCC-based phase with a preferred orientation selection. Therefore, the grain-to-grain and phase-to-phase interactions in the present alloy could also significantly affect the micro-deformation behavior and structural evolution of each constituent phase [22].

The diffraction peaks of the martensite phase appeared at the specific η (Fig. 5), which indicates that the martensitic transformation had a preferred orientation selection. To better investigate the preferred orientation selection of the transformation, the 2-D diffraction patterns with the calculated diffraction patterns of BCC-based phase and orthorhombic martensite were illustrated in Fig. 11(a). The diffraction profiles of the martensite exhibit definite symmetry along $\eta = 90^\circ$ (LD), which conformed to the transmission geometry principle of HE-XRD [44]. Moreover, the orientation of grains occurring martensitic transformation was in accordance with the calculated diffraction patterns of BCC-based phase along the $[1\bar{1}0]$ zone axis and orthorhombic martensitic phase along the $[00\bar{1}]$ zone axis. Both the intensity variation shown in Figs. 6(c-d) and the diffraction patterns shown in Fig. 11(a) suggest that the newly formed martensite preferentially transformed from the grains of the BCC-based phase with an orientation relationship of B-[001]//LD and B-[110]//TD.

The deformation-induced martensitic transformation from the BCC-based phase to orthorhombic phase has been shown to occur in many Ti alloys or Co-Ni-Al alloys, along with a shape memory effect or super-elasticity [24, 41-43]. Generally, for this

type of martensitic transformation, the parent and the martensite phases maintain a strict orientation relationship, i.e., B-(110)//M-(020), B- ($\bar{1}\bar{1}0$) //M-(001) and B-(002)//M-(200) (B-(112)//M-(220)), which could be used to calculate the lattice parameter of martensite [45]. Fig. 11(b) plots a visualized schematic map of the unit cells transformation from the BCC-based to orthorhombic structure, and the corresponding orientation relationship between the parent and martensite phases. Because the phase transformation was considered to be incomplete, the lattice parameters of the martensite were determined by the stress state of 1311 MPa. In terms of the inter-planar spacing of the M-{020} and M-{220} planes, based on the corresponding orientation relationship, parameters (*a*) and (*b*) were determined to be 2.954 Å and 4.082 Å, respectively. Because no other diffraction peaks of martensite were observed along the present diffraction direction, the lattice parameter (*c*) could not be calculated directly. Both the chemical composition and phase transformation characteristics of the present alloy are consistent with the Co-Ni-Al alloys. Therefore, the unit cell volume change in the Co-Ni-Al alloys was used to calculate the lattice parameter (*c*). In contrast to the near zero volume change in the Ni-Ti-Cu and Fe-Ni-Ga alloys, the unit cell volume change in the Co-Ni-Al alloys was estimated to be 2% [43]. Ultimately, the lattice parameter (*c*) of the martensite was determined to be 3.942 Å.

As mentioned above, the grains in the BCC-based phase with an orientation relationship of B-[001]//LD were also severely deformed. It was observed that the BCC-based phase expanded along the B-[001] direction and compressed along the B-[110] direction. In addition, the grain size (*d*) of the martensite was determined to be 15.2 nm at the stress state of 1311 MPa in accordance with the Scherrer formula. The martensite formed on the habit planes and formed by changing of stacking, and then grew by continually transforming from the parent to the martensitic phase. The

nano-scale phase caused by composition separation is general in many HEA systems [46-47]. Thus, it was speculated that the martensitic transformation in the present alloy just occurred in nano-scale parent phase with the specific composition. The nano-scale size of the parent phase restricted the further growth of the martensite. In consequence, the size of martensite in the present alloy is in nano-scale.

5. Conclusion

An *in situ* synchrotron-based high-energy X-ray diffraction technique was employed to investigate the micro-mechanical behavior of Al_{0.6}CoCrFeNi high-entropy alloy during the tensile loading. The main conclusions are summarized as follows:

(1) Al_{0.6}CoCrFeNi high-entropy alloy samples, rolled to a thickness reduction of 50% and annealed for 1 h at 1123 K, exhibited a face-center-cubic (FCC, dendrite morphology) and body-center-cubic-based (BCC-based, inter-dendrite morphology) structure accompanied by a small amount of σ phase.

(2) During the tensile deformation, the FCC phase yielded prior to the BCC-based phase, and the BCC-based phase bore more stress in the plastic deformation stage despite having less volume fraction.

(3) A reversible deformation-induced martensitic transformation from the BCC-based to orthorhombic phase was found during tensile deformation. The transformation preferentially occurred in the grains with an orientation of B-[001]//loading direction and B-[110]//transverse direction.

(4) In the process of cyclic loading, the martensitic transformation initiated during the plastic deformation stage in the first loading, but initiated during the elastic deformation stage in the second loading.

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References

- [1] J.W. Yeh, S.K. Chen, S.J. Lin, J.Y. Gan, T.S. Chin, T.T. Shun, C. Tsau, S.Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes, *Adv. Eng. Mater.* 6 (2004) 299-303.
<http://dx.doi.org/10.1002/adem.200300567>
- [2] B. Gludovatz, A. Hohenwarter, D. Catoor, E.H. Chang, E.P. George, R.O. Ritchie¹, A fracture-resistant high-entropy alloy for cryogenic applications, *Science* 345 (2014) 6201.
<http://dx.doi.org/10.1126/science.1254581>
- [3] F. Otto, A. Dlouhy, Ch. Somsen, H. Bei, G. Eggeler, E.P. George, The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy, *Acta Mater.* 6 (2013) 5743-5755.
<http://dx.doi.org/10.1016/j.actamat.2013.06.018>
- [4] Y. J. Zhou, Y. Zhang, Y. L. Wang, G. L. Chen, Solid solution alloys of AlCoCrFeNiTi_x with excellent room-temperature mechanical properties, *Appl. Phys. Lett.* 90 (2007) 181904.
<http://dx.doi.org/10.1063/1.2734517>
- [5] Y.P. Lu, Y. Dong, S. Guo, L. Jiang, H.J. Kang, T.M. Wang, B. Wen, Z.J. Wang, J.C. Jie, Z.Q. Cao, H.H. Ruan, T.J. Li, A promising new class of high-temperature alloys:

eutectic high-entropy alloys, *Sci. Rep.* 4 (2014) 6200.

<http://dx.doi.org/10.1038/srep06200>

[6] I.S. Wani, T. Bhattacharjee, S. Sheikh, Y.P. Lu, S. Chatterjee, P.P. Bhattacharjee, S. Guo, N. Tsuji, Ultrafine-Grained AlCoCrFeNi_{2.1} Eutectic High-Entropy Alloy, *Mater. Res. Lett.* 4 (2016) 174-179.

<http://dx.doi.org/10.1080/21663831.2016.1160451>

[7] O.N. Senkov, G.B. Wilks, J.M. Scott, D.B. Miracle, Mechanical properties of Nb₂₅Mo₂₅Ta₂₅W₂₅ and V₂₀Nb₂₀Mo₂₀Ta₂₀W₂₀ refractory high entropy alloys, *Intermetallics* 19 (2011) 698-706.

<http://dx.doi.org/10.1016/j.intermet.2011.01.004>

[8] W.P. Huhn, M. Widom, Prediction of A2 to B2 Phase Transition in the High-Entropy Alloy Mo-Nb-Ta-W, *JOM* 65 (2013) 1772-1779.

<http://dx.doi.org/10.1007/s11837-013-0772-3>

[9] N.N. Guo, L. Wang, L.S. Luo, X.Z. Li, Y.Q. Su, J.J. Guo, H.Z. Fu, Microstructure and mechanical properties of refractory MoNbHfZrTi high-entropy alloy, *Mater. Des.* 81 (2015) 87-94.

<http://dx.doi.org/10.1016/j.matdes.2015.05.019>

[10] Z. Wu, H. Bei, G.M. Pharr, E.P. George, Temperature dependence of the mechanical properties of equiatomic solid solution alloys with face-centered cubic crystal structures, *Acta Mater.* 81 (2014) 428-441.

<http://dx.doi.org/10.1016/j.actamat.2014.08.026>

[11] F. Otto, N.L. Hanold, E.P. George, Microstructural evolution after thermomechanical processing in an equiatomic, single-phase CoCrFeMnNi high-entropy alloy with special focus on twin boundaries, *Intermetallics* 54 (2014) 39-48.

<http://dx.doi.org/10.1016/j.intermet.2014.05.014>

[12] C.Y. Hsu, T.S. Sheu, J.W. Yeh, S.K. Chen, Effect of iron content on wear behavior of AlCoCrFeMo_{0.5}Ni high-entropy alloys, *Wear* 268 (2010) 653-659.

<http://dx.doi.org/10.1016/j.wear.2009.10.013>

[13] M.A. Hemphill, T. Yuan, G.Y. Wang, J.W. Yeh, C.W. Tsai, A. Chuang, P.K. Liaw, Fatigue behavior of Al_{0.5}CoCrCuFeNi high entropy alloys, *Acta Mater.* 60 (2012) 5723-5734.

<http://dx.doi.org/10.1016/j.actamat.2012.06.046>

[14] J.Y. He, H. Wang, H.L. Huang, X.D. Xu, M.W. Chen, Y. Wu, X.J. Liu, T.G. Nieh, K. An, Z.P. Lu, A precipitation-hardened high-entropy alloy with outstanding tensile properties, *Acta Mater.* 102 (2016) 187-196.

<http://dx.doi.org/10.1016/j.actamat.2015.08.076>

[15] Y. Deng, C.C. Tasan, K.G. Pradeep, H. Springer, A. Kostka, D. Raabe, Design of a twinning-induced plasticity high entropy alloy, *Acta Mater.* 94 (2015) 124-133.

<http://dx.doi.org/10.1016/j.actamat.2015.04.014>

[16] Z.M. Li, K.G. Pradeep, Y. Deng, D. Raabe, C.C. Tasan, Metastable high-entropy dual-phase alloys overcome the strength-ductility trade-off, *Nature* 534 (2016) 227-230.

<http://dx.doi.org/10.1038/nature17981>

[17] N. Kumar, Q. Ying, X. Nie, R.S. Mishra, Z. Tang, P.K. Liaw, R.E. Brennan, K.J. Doherty, K.C. Cho, High strain-rate compressive deformation behavior of the Al_{0.1}CrFeCoNi high entropy alloy, *Mater. Des.* 86 (2015) 598-602.

<http://dx.doi.org/10.1016/j.matdes.2015.07.161>

[18] M. Laurent-Brocq, A. Akhatova, L. Perrière, S. Chebini, X. Sauvage, E. Leroy, Y. Champion, Insights into the phase diagram of the CrMnFeCoNi high entropy alloy,

Acta Mater. 88 (2015) 355-365.

<http://dx.doi.org/10.1016/j.actamat.2015.01.068>

[19] L.L. Ma, C. Li, Y.L. Jiang, J.L. Zhou, L. Wang, F.C. Wang, T.Q. Cao, X.F. Xue, Cooling rate-dependent microstructure and mechanical properties of $\text{Al}_x\text{Si}_{0.2}\text{CrFeCoNiCu}_{1-x}$ high entropy alloys, J. Alloy. Comp. 694 (2017) 61-67.

<http://dx.doi.org/10.1016/j.jallcom.2016.09.213>

[20] K.D. Liss, A. Bartels, A. Schreyer, H. Clemens, High-energy x-rays: a tool for advanced bulk investigations in materials science and physics, Textures and Microstructures, 35 (2003) 219-252.

<http://dx.doi.org/10.1080/07303300310001634952>

[21] K.D. Liss, A. Bartels, H. Clemens, S. Bystrzanowski, A. Stark, T. Buslaps, F.P. Schimansky, R. Gerling, C. Scheu, A. Schreyer, Recrystallization and phase transitions in a γ -TiAl-based alloy as observed by *ex situ* and *in situ* high-energy X-ray diffraction, Acta Mater. 54 (2006) 3721-3735.

<http://dx.doi.org/10.1016/j.actamat.2006.04.004>

[22] N. Jia, Z.H. Cong, X. Sun, S. Cheng, Z.H. Nie, Y. Ren, P.K. Liaw, Y.D. Wang, An *in situ* high-energy X-ray diffraction study of micromechanical behavior of multiple phases in advanced high-strength steels, Acta Mater. 57 (2009) 965-997.

<http://dx.doi.org/10.1016/j.actamat.2009.05.002>

[23] S. Cheng, Y.D. Wang, H. Choo, X.L. Wang, J.D. Almer, P. Liaw, Y.K. Lee, An assessment of the contributing factors to the superior properties of a nanostructured steel using *in situ* high-energy X-ray diffraction, Acta Mater. 58 (2010) 2419-2429.

<http://dx.doi.org/10.1016/j.actamat.2009.12.028>

[24] J. Mu, Z.W. Zhu, R. Su, Y.D. Wang, H.F. Zhang, Y. Ren, An *in situ* high-energy X-ray diffraction study of micromechanical behavior of multiple phases in advanced

high-strength steels, *Acta Mater.* 61 (2013) 5008-5017.

<http://dx.doi.org/10.1016/j.actamat.2013.04.045>

[25] K. Yan, K.D. Liss, I.B. Timokhina, E.V. Pereloma, *In situ* synchrotron X-ray diffraction studies of the effect of microstructure on tensile behavior and retained austenite stability of thermo-mechanically processed transformation induced plasticity steel, *Mater. Sci. Eng. A* 662 (2016) 185-197.

<http://dx.doi.org/10.1016/j.msea.2016.03.048>

[26] X.Q. Zhang, L.L. Ma, Y.F. Xue, Q.B. Fan, Z.H. Nie, L. Wang, J.M. Yin, H.F. Zhang, H.M. Fu, Temperature dependence of micro-deformation behavior of the porous tungsten/Zr-based metallic glass composite, *J. Non-Cryst. Solids* 436 (2016) 9-17.

<http://dx.doi.org/10.1016/j.jnoncrysol.2016.01.005>

[27] J. Xu, L.L. Ma, Y.F. Xue¹, Z.H. Nie, Y.H. Long, L. Wang, Y.B. Deng, Work-hardening behavior, strain rate sensitivity, and failure behavior of *in situ* CuZr-based metallic glass matrix composite, *J. Mater. Sci.* 51 (2016) 5992-6001.

<http://link.springer.com/article/10.1007/s10853-016-9900-0>

[28] W.C. Woo, E.W. Huang, J.W. Yeh, H. Choo, C. Lee, S.Y. Tu, *In-situ* neutron diffraction studies on high-temperature deformation behavior in a CoCrFeMnNi high entropy alloy, *Intermetallics* 62 (2015) 1-6.

<http://dx.doi.org/10.1016/j.intermet.2015.02.020>

[29] Y. Wu, W. H. Liu, X. L. Wang, D. Ma, A. D. Stoica, T. G. Nieh, Z. B. He, Z. P. Lu, *In-situ* neutron diffraction study of deformation behavior of a multi-component high entropy alloy, *Appl. Phys. Lett.* 104 (2014) 051910.

<http://dx.doi.org/10.1063/1.4863748>

[30] S.G. Ma, J.W. Qiao, Z.H. Wang, H.J. Yang, Y. Zhang, Microstructural features and

tensile behaviors of the $\text{Al}_{0.5}\text{CrCuFeNi}_2$ high-entropy alloys by cold rolling and subsequent annealing, *Mater. Des.* 88 (2015) 1057-1062.

<http://dx.doi.org/10.1016/j.matdes.2015.09.092>

[31] Y.F. Kao, T.J. Chen, S.K. Chen, J.W. Yeh, Microstructure and mechanical property of as-cast, -homogenized, and -deformed $\text{Al}_x\text{CoCrFeNi}$ ($0 \leq x \leq 2$) high-entropy alloys, *J.*

Alloy. Comp. 488 (2009) 57-64.

<http://dx.doi.org/10.1016/j.jallcom.2009.08.090>

[32] W.R. Wang, W.L. Wang, J.W. Yeh, Phases, Phases, microstructure and mechanical properties of $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloys at elevated temperatures, *J. Alloy. Comp.* 589 (2014) 143-152.

<http://dx.doi.org/10.1016/j.jallcom.2013.11.084>

[33] G.E. Dieter, D. Bacon, *Mechanical Metallurgy*, McGraw-Hill, New York, 1986.

[34] S.J. Hao, L.S. Cui, D.Q. Jiang, X.D. Han, Y. Ren, J. Jiang, Y.N. Liu, Z.Y. Liu, S.C. Mao, Y.D. Wang, Y. Li, X.B. Ren, X.D. Ding, S. Wang, C. Yu, X.B. Shi, M.S. Du, F. Yang, Y.J. Zheng, Z. Zhang, X.D. Li, D.E. Brown, J. Li, Transforming metal nanocomposite with large elastic strain, low modulus, and high strength, *Science* 339 (2013) 1191-1194.

<http://dx.doi.org/10.1126/science.1228602>

[35] S. Cai, M.R. Daymond, R.A. Holt, E.C. Oliver, Evolution of internal strains in a two phase zirconium alloy during cyclic loading, *Acta Mater.* 59 (2011) 5305-5319.

<http://dx.doi.org/10.1016/j.actamat.2011.05.007>

[36] R.D. Dar, Y. Chen, Nanoindentation studies of small-scale martensitic transformations and ductile precipitate effects in dual-phase polycrystalline shape memory alloys, *Acta Mater.* 91 (2015) 112-127.

<http://dx.doi.org/10.1016/j.actamat.2015.03.019>

[37] P. Castany, A. Ramarolahy, F. Prima, P. Laheurte, C. Curfs, T. Gloriant, *In situ* synchrotron X-ray diffraction study of the martensitic transformation in superelastic Ti-24Nb-0.5N and Ti-24Nb-0.5O alloys, *Acta Mater.* 88 (2015) 102-111.

<http://dx.doi.org/10.1016/j.actamat.2015.01.014>

[38] P. Sedmák, P. Šittner, J. Pilch, C. Curfs, Instability of cyclic superelastic deformation of NiTi investigated by synchrotron X-ray diffraction, *Acta Mater.* 94 (2015) 257-270.

<http://dx.doi.org/10.1016/j.actamat.2015.04.039>

[39] L.L. Chang, Y.D. Wang, Y. Ren, *In-situ* investigation of stress-induced martensitic transformation in Ti-Nb binary alloys with low Young's modulus, *Mater. Sci. Eng. A* 651 (2016) 442-448.

<http://dx.doi.org/10.1016/j.msea.2015.11.005>

[40] M. Tahara, H.Y. Kim, H. Hosoda, S. Miyazaki, Cyclic deformation behavior of a Ti-26 at. % Nb alloy, *Acta Mater.* 57 (2009) 2461-2469.

<http://dx.doi.org/10.1016/j.actamat.2009.01.037>

[41] J.P. Liu, Y.D. Wang, Y.L. Hao, H.L. Wang, Y. Wang, Z.H. Nie, R. Su, D. Wang, Y. Ren, Z.P. Lu, J.G. Wang, X.D. Hui, R. Yang, High-energy X-ray diffuse scattering studies on deformation-induced spatially confined martensitic transformations in multifunctional Ti-24Nb-4Zr-8Sn alloy, *Acta Mater.* 8 (2014) 476-486.

<http://dx.doi.org/10.1016/j.actamat.2014.08.019>

[42] H. Seiner, J. Kopeček, P. Sedlák, L. Bodnárová, M. Landa, P. Sedmák, O. Heczko, Microstructure, martensitic transformation and anomalies in c'-softening in Co-Ni-Al ferromagnetic shape memory alloys, *Acta Mater.* 61 (2013) 5869-5876.

<http://dx.doi.org/10.1016/j.actamat.2013.06.035>

[43] S. Dilibal, H. Sehitoglu, R.F. Hamilton, H.J. Maier, Y. Chumlyako, On the volume

change in Co-Ni-Al during pseudoelasticity, Mater. Sci. Eng. A 528 (2011) 2875-2881.

<http://dx.doi.org/10.1016/j.msea.2010.12.056>

[44] G.A. Sun, X.L. Wang, Y.D. Wang, W.C. Woo, H. Wang, X.P. Liu, B. Chen, Y.Q. Fu, L.S. Sheng, Y. Ren, *In-situ* high-energy synchrotron X-ray diffraction study of micromechanical behavior of multiple phases in Ni₄₇Ti₄₄Nb₉ shape memory alloy, Mater. Sci. Eng. A 560 (2013) 458-465.

<http://dx.doi.org/10.1016/j.msea.2012.09.090>

[45] Collings E. Materials properties handbook: titanium alloys. Materials Park, OH: ASM International; 1994.

[46] X.D. Xu, P. Liu, S. Guo, A. Hirata, T. Fujita, T.G. Nieh, C.T. Liu, M.W. Chen, Nanoscale phase separation in a fcc-based CoCrCuFeNiAl_{0.5} high-entropy alloy, Acta Mater. 84 (2015) 145-152.

<http://dx.doi.org/10.1016/j.actamat.2014.10.033>

[47] S. Singh, N. Wanderka, B.S. Murty, U. Glatzel, J. Banhart, Decomposition in multi-component AlCoCrCuFeNi high-entropy alloy, Acta Mater. 59 (2011) 182-90.

<http://dx.doi.org/10.1016/j.actamat.2010.09.023>

Al_{0.6}CoCrFeNi high entropy alloy

Reversible martensitic transformation

Fig. 1. Schematic of the *in situ* synchrotron-based HE-XRD experimental set-up.

Fig. 2. (a) XRD pattern, (b) SEM micrograph, and (c) TEM image with the corresponding SAED patterns of the alloy. The reciprocal space units in the SAED patterns is $1/d$, where d is the positive space lattice vector.

Fig. 3. Tensile engineering stress-strain curve of the alloy.

Fig. 4. 2-D diffraction patterns of the alloy under different loading levels: (a-c) 0 MPa (1, 3, 5, and 7 represent the F-111, F-211, F-220, and F-311 diffraction rings, respectively; 2, 4, and 6 represent the B-110, B-200, and B-211 diffraction rings, respectively); (d-f) 1311 MPa.

Fig. 5. 1-D diffraction profiles of (a) B-110, (b) B-200, and (c) B-211 by integrating the 2-D diffraction patterns along the specific η from 0° to 180° over a range of $\pm 5^\circ$ at 1311 MPa (M denotes the martensite.); (d) and (e) are the integral intensity of the martensite diffraction peaks shown in (a) and (c), respectively.

Fig. 6. 1-D diffraction profiles of (a) B-110 at $\eta = 0^\circ$ (TD) and (b) B-211 at $\eta = 50^\circ$ during the single loading (M denotes the martensite.). (c) and (d) are the integral intensity of the diffraction peaks shown in (a) and (b), respectively.

Fig. 7. 1-D diffraction profiles of (a) B-110 at $\eta = 0^\circ$ (TD) and (b) B-211 at $\eta = 50^\circ$ during the cyclic loading (M denotes the martensite.).

Fig. 8. (a) Response of lattice strain to tensile stress of the FCC and BCC-based phases in the LD and TD during the single loading (The inset shows the overlapping diffraction peaks were separated using the Lorentz function.); (b) Von Mises stress of the BCC-based and FCC phases as a function of tensile stress.

Fig. 9. Response of lattice strain to tensile stress of (a) B-110 plane at $\eta = 0^\circ$ (TD), (b) B-200 plane at $\eta = 90^\circ$ (LD), and (c) B-211 plane at $\eta = 50^\circ$ in the BCC-based phase and martensite during the cyclic loading (M denotes the martensite; 1st and 2nd indicate the first and the second loading, respectively; A and B indicate the evident increase of lattice strain in the first and second loading, respectively.).

Fig. 10. Schematic of the “microstructure evolution” of the alloy during the cyclic loading: (a) before loading; (b) the plastic deformation stage in the first loading; (c) after unloading; (d) the elastic deformation stage in the second loading; (e) the plastic deformation stage in the second loading.

Fig. 11. (a) 2-D diffraction schematic pattern with the calculated diffraction patterns of the BCC-based phase and orthorhombic martensite; (b) Schematic map of the unit cells transformed from the BCC-based phase to orthorhombic martensite.