Materials Science & Engineering A 712 (2018) 603–607

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Transition of twinning behavior in CoCrFeMnNi high entropy alloy with grain refinement

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ARTICLE INFO

Keywords:
High entropy alloy (HEA)
Deformation twinning
Ultrafine grain
Grain size
Strain hardening

ABSTRACT

Fully recrystallized CoCrFeMnNi high entropy alloys (HEAs) with different grain sizes ranging from 503 nm to 88.9 μm were fabricated by cold rolling and controlled annealing. Tensile tests were conducted at ambient temperature, and deformation microstructures were investigated using electron channeling contrast imaging (ECCI) and transmission electron microscopy (TEM) techniques. It is found that strain-hardening curves changed dramatically with grain refinement. Deformation twinning prevails when the grain size is coarse, but it is absent when the grain size falls in the ultrafine-grained (UFG) regime. The transition of twinning behavior is supposed to be determined by the increased twinning stress with grain refinement. It is indicated that the twinning behavior of the HEAs is strongly dependent on the competition between the flow stress and critical twinning stress with grain refinement.

1. Introduction

High entropy alloys (HEAs) have drawn much interest in recent years due to their outstanding properties, such as good thermal stability and high-temperature strength, exceptional corrosion resistance, and good tribological properties [1–5]. Among the HEAs, one extensively studied HEA system is based on five transition elements in the periodic table: Cr, Mn, Fe, Co and Ni [2,6–12]. The typical CoCrFeMnNi HEA with single-phase face-centered cubic (FCC) solid solution attracted much attention due to the superior cryogenic properties [6,7]. In addition, this HEA can be employed as a model material to investigate the fundamental deformation mechanisms.

In FCC materials, it is widely known that stacking fault energy (SFE) affects significantly the deformation mechanisms. When the SFE is low (20–40 mJ/m^2), deformation twinning prevails during plastic deformation, which results in the twinning-induced plasticity (TWIP) effect [13]. According to the ab initio calculations, the SFE of CoCrFeMnNi HEAs is ~21 mJ/m^2 at room temperature [14]. Therefore, it can be inferred that deformation twinning may easily occur during the deformation of the CoCrFeMnNi HEAs. Otto et al. [6] investigated the influences of temperature on mechanical properties of CoCrFeMnNi HEAs with different grain sizes, and they concluded that the increase in ductility with decreasing temperature is related to the occurrence of deformation twinning at cryogenic temperature; in contrast, deformation twins were not observed in the samples at 293 K. Similar TWIP effect was also supposed to induce the high fracture toughness of CoCrFeMnNi HEA with grain size of 6 μm at cryogenic temperature [7]. For the CoCrFeMnNi HEA with grain size of 17 μm, Laplanche et al. [11] reported that the late onset of deformation twins at room temperature is attributed to the high critical twinning stress of ~720 MPa in tensile process. However, it has recently been reported that deformation twinning induced the multiple strain-hardening stages of the CoCrFeMnNi HEA with grain size of 17 μm and enhanced strength and elongation at room temperature [15]. These studies indicate that the twinning behavior of CoCrFeMnNi HEA may be affected by the grain size and should be further clarified.

It is also widely known that the grain size affects significantly the deformation mechanisms, i.e. deformation twinning behavior [13,16,17]. El-Danaf et al. [16] found that the grain size has a significant influence on the stress-strain response of the low-SFE metal, especially the stage A (see reference paper) of the strain-hardening response. Gutierrez-Urrutia et al. [13] investigated the strain-hardening behavior in TWIP steels with grain sizes of 3 and 50 μm. They concluded that the early dislocation substructure determined the density of nucleation sites for twins per unit grain boundary area and controlled the developing twin substructure, which resulted in the significant

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https://doi.org/10.1016/j.msea.2017.12.022
Received 12 October 2017; Received in revised form 6 December 2017; Accepted 7 December 2017
Available online 09 December 2017
0921-5093/

effect on the strain-hardening behavior. Meyers et al. [17] reported that grain sizes had a Hall-Petch effect on the critical stress for twinning, indicating that deformation twinning became difficult with grain refinement. In addition, strong grain-size effect on deformation twinning was found in an $Al_{0.1}$CoCrFeNi high entropy alloy [18]. It is thus desirable to further investigate the twinning behavior and mechanical properties of CoCrFeMnNi HEA by changing grain sizes.

2. Experimental procedures

Bulk CoCrFeMnNi HEAs were prepared by magnetic levitation melting technique, followed by hot forging and cold rolling into sheets 1 mm thick at room temperature. Then the cold-rolled sheets were annealed at various temperatures to obtain fully recrystallized specimens with different grain sizes. Details of the processing procedures were shown in the previous work [19]. Tensile tests were conducted at an initial strain rate of $10^{-3}\ s^{-1}$ using an Instron 5982 testing machine at room temperature. Tensile specimens with a gauge length of 10 mm, a width of 4 mm and a thickness of 1 mm were cut from annealed sheets by electrical discharge machine. Microscopic analyses before and after tensile tests were carried out using a LEO Supra 35 field emission scanning electron microscope (SEM) equipped with an electron backscattering diffraction (EBSD) system and an electron channeling contrast imaging (ECCI) component. Deformation microstructures were also characterized by an FEI Tecnai F20 transmission electron microscope (TEM). TEM foils were cut from the tensile specimens and the observation direction is parallel to the normal direction of the tensile specimen.

3. Results and discussion

CoCrFeMnNi HEAs with different grain sizes ranging from 503 nm to 88.9 µm have been obtained in this work. Fig. 1 shows typical inverse pole figure (IPF) maps, band contrast and grain boundary maps obtained by EBSD measurements of CoCrFeMnNi HEAs, which correspond to the ultrafine-grained (UFG), fine-grained (FG) and coarse-grained (CG) specimens, respectively. It is found that the maximum pole density is 2.4 (not shown here), which indicates that fully recrystallized microstructures with randomly oriented grains have been obtained. UFG samples with mean grain sizes smaller than 1 µm were obtained due to the low SFE of the CoCrFeMnNi HEAs and the numerous nucleation sites for recrystallization introduced by cold rolling process. In addition, profuse annealing TBs can be detected in each sample, especially in the FG and CG samples. The green, silver and red lines are related to low-angle grain boundaries (LAGBs), high-angle grain boundaries (HAGBs) and twin boundaries (TBs), respectively, as shown in Fig. 1d-f. The mean grain sizes of all the samples were measured by a linear intercept method after countering the HAGBs including the TBs.

Fig. 2a shows the tensile true stress-strain curves of the CoCrFeMnNi HEAs with different grain sizes. With decreasing the grain size from 88.9 µm to 503 nm, the yield strength greatly increases from 236 MPa to 888 MPa, well complying with the Hall-Petch relationship [19]. Fig. 2b shows the strain-hardening rates plotted as a function of true strains for the samples with different grain sizes. It is found that the strain-hardening curves diverse significantly when the grain size changes. The high sensitivity of the strain-hardening curves to the grain sizes is common in these materials with low SFE, which is attributed to the activation of dislocations and deformation twins at different strain levels [20,21]. It is of value to note that the strain-hardening rate can go upwards with strain when the grain size is 88.9 µm, and this upturn phenomenon is supposed to be induced by deformation twins or stacking faults [13,20]. Hence, it is inferred that deformation twinning may influence the strain-hardening behavior of the HEAs. The deformation microstructures are thus characterized after tensile tests.

The samples with different grain sizes after tensile tests were characterized by ECCI technique, and typical substructures of the CoCrFeMnNi HEAs are summarized in Fig. 3. Fig. 3a and b show that

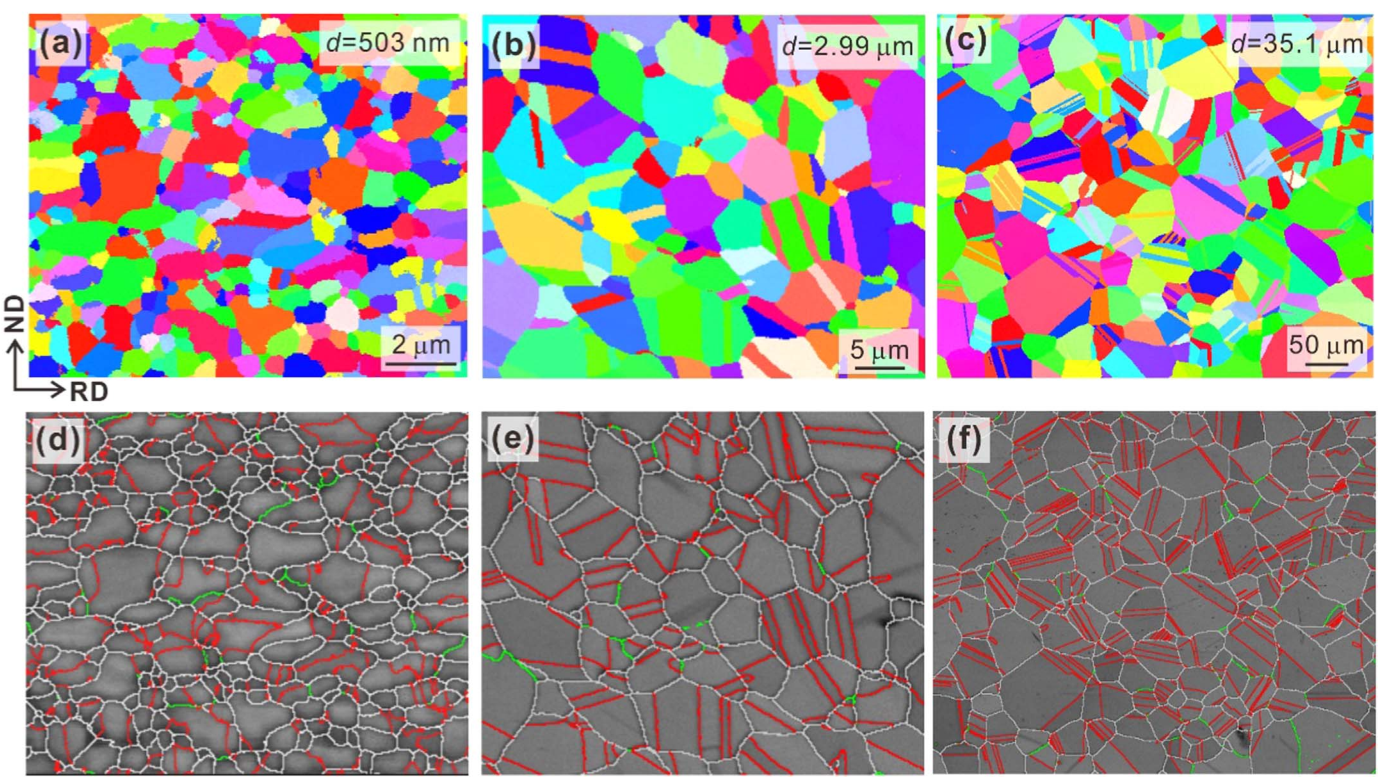

Fig. 1. (a-c) Inverse pole figures and (d-f) band contrast and grain boundary maps of fully recrystallized CoCrFeMnNi HEAs with different mean grain sizes. All the EBSD samples were examined from the RD-ND planes of the cold rolled strips. The green, silver and red lines are related to low-angle grain boundaries (LAGBs), high-angle grain boundaries (HAGBs) and twin boundaries (TBs).

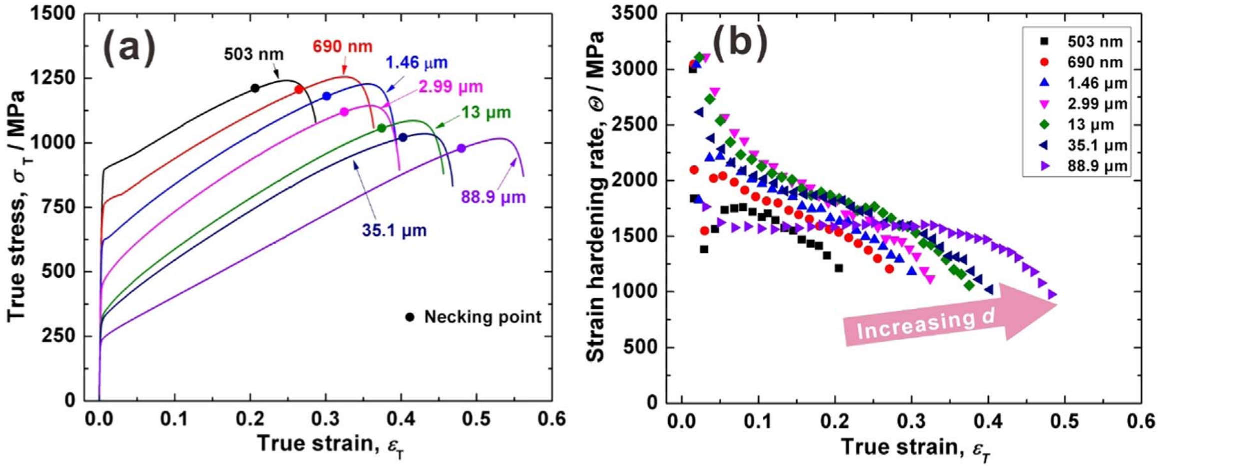

Fig. 2. (a) Tensile true stress-strain curves and (b) strain-hardening rate curves of CoCrFeMnNi HEAs with different grain sizes. Necking points were indicated for each curve.

numerous annealing twins (AT) exist in the samples. Deformation twins (DT) cannot be clearly detected by ECCI in the samples with ultrafine grain size (Fig. 3a) and fine grain size ($d = 1.46$ μm, not shown here). For the HEA with a mean grain size of 2.99 μm, deformation twins can be found in some grains, and one example is shown in Fig. 3b. In contrast, deformation twins can be frequently observed in the HEA with coarse grain sizes, and some of these deformation twins are indicated with arrows, as shown in Fig. 3c and d. It is further observed that deformation twins are in bundles consisting of thinner twins.

To further reveal the effect of grain sizes on the deformation mechanisms of the samples, detailed microstructures were characterized by TEM, as shown in Fig. 4. Here we can see numerous dislocations accumulated in the grain interior (Fig. 4a) and the annealing twins (Fig. 4a1) in the UFG samples. Note that dislocation cells can be stored in the grain interior even though the grain size is small, as shown in Fig. 4a. This high-density dislocation storage can be attributed to the restrained dislocation recovery and planar dislocation slip modes in this HEA with low SFE [6]. In addition, stacking faults (SF) were observed at high magnifications, as shown in Fig. 4a2. However, deformation twins were rarely detected, indicating that the twinning capability of the UFG HEA was highly restrained. Fig. 4b shows that deformation twins are found in some grains of the sample with grain size of 2.99 μm, although the fraction of deformation twins is still small. More twin bundles are observed in the samples with grain size of 13 μm, as shown in Fig. 4c. In addition, obvious dislocation cell structures were found, and the cell size can be as small as 200 nm. With further increase in the grain size to 35.1 μm, deformation twins in different twinning systems were activated, and the resultant twin interactions were also frequently observed, as shown in Fig. 4d. At a higher magnification (Fig. 4d1), the thickness of the twins can be as small as 10 nm after observing from the < 110 > zone axis. The selected area electron diffraction pattern of the deformation twins is shown in Fig. 4d2.

For the CoCrFeMnNi HEAs tensioned at room temperature, deformation twinning prevails when the grain size is larger than 13 μm,

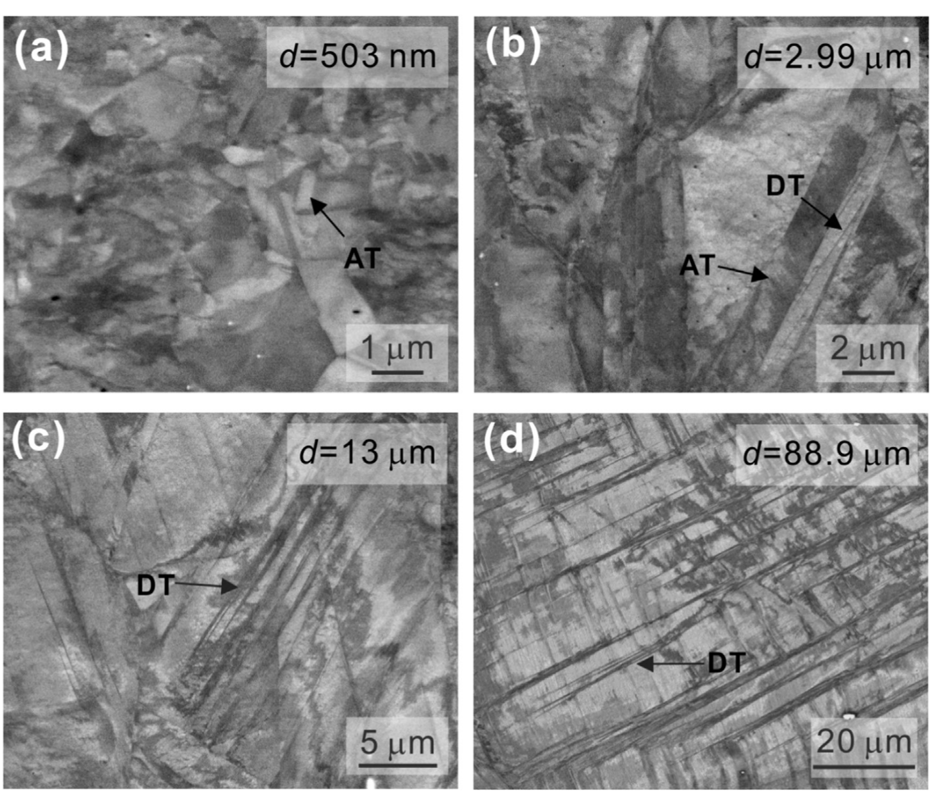

Fig. 3. ECCI images of the CoCrFeMnNi HEAs with different grain sizes after tensile test: (a) 503 nm, (b) 2.99 μm, (c) 13 μm and (d) 88.9 μm.

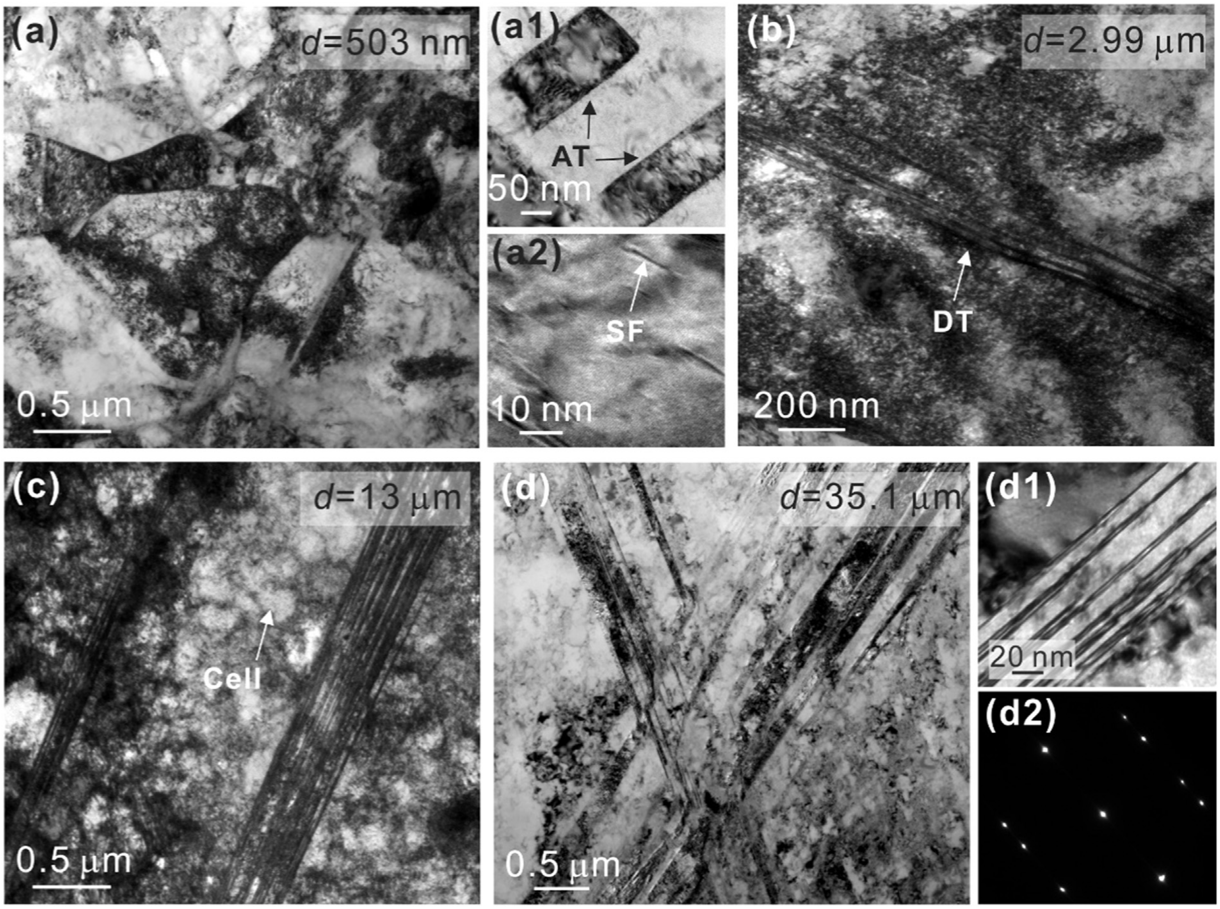

Fig. 4. TEM images of the CoCrFeMnNi HEAs with different grain sizes after tensile test: (a) 503 nm, (b) 2.99 μm, (c) 13 μm and (d) 35.1 μm.

but is drastically suppressed when the grain size approaches to 2.99 μm. Furthermore, deformation twinning is completely absent in the UFG regime. This indicates that grain size can impact significantly on the deformation twinning behavior of the HEA. It has been observed that the twinning capability of FCC metallic materials will be weakened with grain refinement [22,23]. This can be related to the increase of the critical stress for twinning with grain refinement [24], and the twinning stress can be calculated by:

$$\sigma_T = m\frac{\gamma}{b_p} + \frac{k_T}{\sqrt{d}} \tag{1}$$

where m is the Taylor factor ($m = 3.06$ [25]), γ is the SFE (γ = 21 mJ/m^2 [14]), b_p is the Burgers vector of a partial dislocation ($b_p = \frac{\sqrt{6}}{6}a = 1.46 \times 10^{-10}$ m [26]), k_T is the Hall–Petch constant for twinning and d is the grain size. Furthermore, for FCC metallic materials, $k_T = 2 \times k_S$ is approximately estimated based on the correlations between k_T and k_S [17], where $k_S = 490$ MPa μm$^{1/2}$ is the Hall–Petch constant for dislocation slip [19]. The calculated twinning stress and the maximum flow stress at necking are plotted with grain size in Fig. 5. It should be noted that the maximum flow stress at necking changes slightly, but the calculated twinning stress increases drastically with grain refinement. When the grain size is larger than 2.99 μm, the maximum flow stress is higher than the twinning stress, indicating that deformation twins can be activated which was confirmed experimentally. When the grain size falls into the UFG regime, it is found that the twinning stress is much larger than the maximum flow stress, indicating that deformation twin is difficult to activate. The above approach can give reasonable explanation on the grain size effect on the twinning behavior of the HEA. In fact, there is an experimental attempt in determining the twinning stress of CoCrFeMnNi HEA with a mean grain size of 17 μm, and the

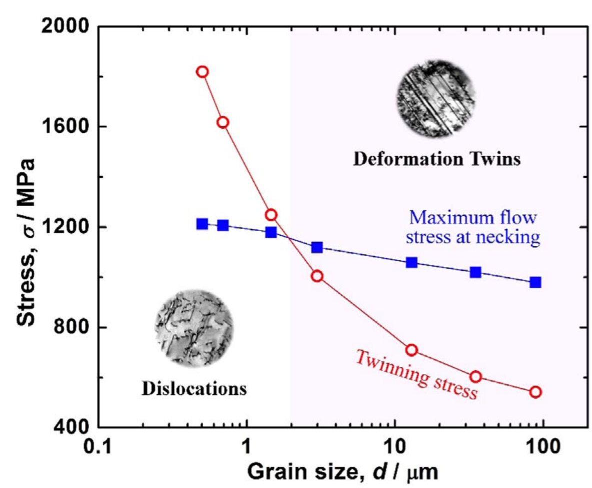

Fig. 5. Comparison between predicted twinning stress σ_T and maximum flow stress at necking σ_N for the HEA with different grain sizes.

twinning stress is reported to be 720 MPa at 77 K and 680–820 MPa at 293 K [11]. It should be noted that the grain size was measured by excluding the twin boundaries in their work, so the grain size should be ~10 μm by including the twin boundaries during grain size determination. Accordingly, the twinning stress was calculated to be 750 MPa by Eq. (1), which matches well with the experimental value. This indicates that Eq. (1) can be applicable for determining the twinning stress of CoCrFeMnNi HEA.

It should be noted that the recrystallized UFG HEA shows superior strength and ductility though deformation twins are absent during the tensile test at room temperature. This can be largely attributed to the excellent capability for dislocation storage, which is determined by the low SFE of the HEA. In addition, stacking faults can contribute to the high strength of the UFG HEA. Among the HEAs with different grain sizes, it is of value to note that the strain-hardening rate firstly drops and then upturns slightly with strain in the HEA with coarse grain size of 88.9 μm, which is a typical phenomenon induced by deformation twins [22] or stacking faults [27]. This phenomenon is frequently observed in FCC metallic materials with low SFE and coarse grain sizes [22]. In this work, dislocation cells were clearly observed, as shown in Fig. 4c, which was originated from reorganization of planar dislocations formed at low strains [6]. The concurrent appearance of dislocation cells and deformation twins is similar to these observed in medium-to-low SFE materials [21]. The retained high strain-hardening rate of the CG CoCrFeMnNi HEA is supposed to be induced by the continuous emergence of deformation twins with strain, which leads to the obvious strength enhancement via the dynamic Hall-Petch effect [28].

4. Conclusions

We have fabricated fully recrystallized CoCrFeMnNi HEAs with grain sizes ranging from 503 nm to 88.9 μm, and the effects of grain size on the strain-hardening behavior and deformation mechanisms were investigated. The strain-hardening curves change dramatically with decreasing the grain size. Deformation twinning was suppressed with grain refinement due to the increased critical stress for twinning. Deformation twinning was readily observed when the grain size is larger than 2.99 μm. No deformation twin was observed when the grain size approaches to 503 nm. The twinning stress can be calculated by a Hall-Petch type equation. The present study reveals that, while SFE determines the fundamental deformation modes, grain size can also control the transition of the deformation behavior in CoCrFeMnNi HEA.

Acknowledgements

Y.Z.T. acknowledges the IMR Foundation for “Young Merit Scholars”. This work was supported by the National Natural Science Foundation of China (NSFC) under grant 51331007, 51501196 and 51501198.

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