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Hot Deformation and Dynamic Recrystallization Behavior of CoCrNi and (CoCrNi)₉₄Ti₃Al₃ Medium Entropy Alloys

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Abstract: The CoCrNi and precipitate-hardened (CoCrNi)₉₄Ti₃Al₃ medium entropy alloys (MEAs) have attracted much attention, due to their exceptional mechanical properties, whereas the hot deformation characteristics have not been revealed. In the present study, we investigated the dynamic recrystallization behavior and microstructure evolutions of the two MEAs hot-compressed at single-phase temperatures. The constitutive equation was obtained, and microstructures were observed. Discontinuous dynamic recrystallization acted as a key mechanism of grain refinement at a relatively higher temperature and lower strain rate, which leads to the formation of a homogeneous grain structure. The addition of Ti and Al promoted dynamic recrystallization due to the solid solution hardening effect. The results provide valuable guidelines for microstructure refinement via thermomechanical processing.

Keywords: medium entropy alloy; hot deformation; recrystallization; constitutive equation; microstructure

1. Introduction

High entropy alloys (HEAs) comprising more than four principles elements have attracted much academic attention, due to their unusual structures and properties [1,2]. Among those HEAs, the face-centered cubic (fcc) single-phase CoCrFeMnNi and CoCrFeNi alloys are the most widely investigated, which exhibit exceptional mechanical properties at both ambient and cryogenic temperatures [2–5]. To date, much effort was devoted to improving mechanical performance, where meta-stabilization is one of the most widely utilized methods [6–9]. The stacking fault energy (SFE) will be decreased along with the reduction of fcc-phase stability, which determines the plastic behavior and mechanical properties. An intermediate SFE (15–45 mJ/m²) promotes the formation of mechanical twinning [10], whereas a low SFE (<15 mJ/m²) leads to the strain-induced martensitic transformation [11,12]. Both of them contribute to the enhancement of mechanical properties by twinning-induced plasticity effect and transformation induced plasticity effect [7–12].

The fcc-phase CoCrNi medium entropy alloy (MEA) was reported to exhibit mechanical properties superior to that of the CoCrFeMnNi and CoCrFeNi HEAs because of the relatively lower SFE value (18 mJ/m²) than the HEAs counterparts (~27 mJ/m²) [13,14]. However, the insufficient room temperature strength of those alloys impedes their applications. To further improve the



mechanical properties, precipitation-hardened MEAs were designed by minor-addition of strong γ' -phase former (Ti, Al) into the CoCrNi matrix [15–18]. For instance, a large number of nanosized coherent L1₂-(Co,Ni,Cr)₃(Ti,Al)-type particles could be formed in the (CoCrNi)₉₄Ti₃Al₃ alloy, which enhance the yield strength and ultimate tensile strength of CoCrNi alloy by approximate 70% and 40% [16], respectively. The nano-particles are thermally stable up to around 800 °C but re-dissolved at temperatures higher than 850 °C, which means that the alloy is dual-phase at temperatures lower than 800 °C but single fcc-phase at temperatures higher than 900 °C [18]. The precipitation-hardened alloys are convincing candidates for various applications.

It is known that grain size has a significant influence on the yield strength and strain hardening behavior of alloys, where the grains are generally regulated via hot and/or cold processing. Thus, the investigation of hot deformation behavior and dynamic recrystallization mechanism is a prerequisite for controlling the grain size and morphology [19–21]. The hot compression behaviors of CoCrFeMnNi HEA at various temperatures higher than 800 °C have been studied, and the constitutive equations were formulated for describing the interdependency between deformation temperature, strain rate, flow stress, and strain [22–26]. It was found that the microstructure evolution at the temperatures is accompanied by discontinuous dynamic recrystallization (dDRX), where the dynamic recrystallization (DRX) grains nucleated along initial grain boundaries resulting in the necklace like structures [24–26]. The nucleation of DRX is without any preferential orientation selections, and the resultant grains exhibit relatively weak texture [24]. The results provide guidelines for modulating grain structures.

However, the hot deformation behavior and the DRX mechanism of the CoCrNi and $(CoCrNi)_{94}Ti_3Al_3$ MEAs have not been reported. The present study aimed to reveal the hot deformation and DRX behavior of the two MEAs compressed at various temperatures in the single fcc-phase regime. The constitutive equation was constructed and the relationship between DRX mechanism and compression condition was clarified, which offers a guideline for regulating grain structures and mechanical properties by hot processing of the alloys.

2. Materials and Methods

The ingots of CoCrNi and (CoCrNi)₉₄Ti₃Al₃ MEAs were produced by a high-frequency induction melting and casting under high-purity argon atmosphere. The ingots were hot forged and homogenized at 1200 °C for 4 h, followed by water quenching. Then, samples with a height of 12 mm and a diameter of 8 mm for hot compression tests were cut from the ingots by electric discharge machining. After that, the compression tests were carried out by using Gleeble 1500 machine (Dynamic systems Inc., Poestenkill, NY, USA).

The hot compression routes of the CoCrNi and (CoCrNi)₉₄Ti₃Al₃ MEAs were described in Figure 1. All of the samples were heated up to 1200 °C with a heating rate of 10 °C/s, and then isothermally held for 300 s at 1200 °C, followed by cooling to compression temperatures with a cooling rate of 10 °C/s. The samples were held at each temperature for 10 s before compression. The formation of any possible precipitates could be prevented by the heat treatment routine. Then, the samples were hot compressed up to a 63% reduction in height (an equivalent true strain of 1.0). The CoCrNi samples were compressed at temperature of 850, 900, 950 and 1000 °C, and at strain rate of 1, 0.1, 0.01 and 0.001 s⁻¹, respectively. The (CoCrNi)₉₄Ti₃Al₃ samples were compressed at temperature of 900, 1000 and 1100 °C, and at strain rate of 0.1, 0.01 and 0.001 s⁻¹, respectively. During compression, displacement and load were recorded for stress-strain curves. The samples were water quenched immediately after the compression. For each condition, at least three independent samples were tested to ensure the repeatability of the results.



Figure 1. Schematic diagram showing the experimental procedure and conditions for the hot compression of the CoCrNi and (CoCrNi)₉₄Ti₃Al₃ alloys.

Microstructures of the hot compressed samples were characterized by scanning electron microscope (SEM, Hitachi S-3400N, HITACHI, Tokyo, Japan) equipped with an electron backscatter diffraction (EBSD, OIM Analysis, AMETEK Inc., Berwyn, PA, USA) detector, operated at an acceleration voltage of 20 kV. For the EBSD observation, the cylindrical hot-compressed samples were sectioned vertically through the center parallel to the compression direction, and the central regions were observed. The samples were polished by abrasive paper and mirror-finished by using colloidal silica suspension (OP-U).

3. Results

3.1. Flow Behaviors

Figure 2 shows the true stress-strain (σ - ε) curves of the CoCrNi alloy compressed at (a) 850 °C, (b) 900 °C, (c) 950 °C, (d) 1000 °C, and at strain rate of 1, 0.1, 0.01 and 0.001 s⁻¹, respectively. All the σ - ε curves exhibit work hardening (flow stress increases with an increase of strain) at small strain but flow softening (flow stress decreases with an increase of strain) at large strain. The discontinuous yielding phenomena [19–21], which was reported in the Titanium alloys hot-compressed at single α -hcp phase region, is not observed in the present study. Table 1 shows the peak stresses during hot-compression. The peak flow stress increases with the increase of strain rate. As is known, the accumulation of dislocations and dynamic recovery of dislocations are competitive processes. Less of the dislocations are dynamically recovered when the samples were compressed at high strain rates, and a larger amount of dislocations were accumulated. The high density of dislocations prevents further plastic deformation of samples, leading to high peak stresses. At low strain rates, dynamic recovery of dislocations is more prevailing, resulting in low peak stresses due to the weak strain hardening effects. The flow softening at large strain indicates the occurrence of DRX, and steady flow stresses tend to be reached.

Figure 3 shows the true σ - ε curves of the (CoCrNi)₉₄Ti₃Al₃ alloy compressed at temperature of (a) 900 °C, (b) 1000 °C, (c) 1100 °C, and at strain rate of 0.1, 0.01 and 0.001 s⁻¹, respectively. All the curves exhibit strain hardening at the initial stage and flow softening after peak stress, and the flow stress increases with the increase of strain rates at any given temperature. It is noteworthy that sharp flow softening is observed in the samples compressed at 900 °C, which is notably different from that of CoCrNi alloy. Table 2 shows the peak flow stress of the (CoCrNi)₉₄Ti₃Al₃ alloy. It can be seen that the values are decreased with the increase in temperature and decrease in strain rate.



Figure 2. True stress-strain curves of the CoCrNi alloy hot-compressed at (**a**) 850 °C, (**b**) 900 °C, (**c**) 950 °C, and (**d**) 1000 °C. The strain rate is 1, 0.1, 0.01 and 0.001 s⁻¹.

Table 1. The peak stress (σ_{max}) of the CoCrNi alloy hot-compressed at 850, 900, 950 and 1000 °C, respectively. The strain rate is 1, 0.1, 0.01 and 0.001 s⁻¹.

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	Temperature	σ_{max} (MPa) 1 s^{-1}	σ _{max} (MPa) 0.1 s ⁻¹	σ _{max} (MPa) 0.01 s ⁻¹	σ _{max} (MPa) 0.001 s ⁻¹
	850 °C	427.6	380.1	313.9	206.8
	900 °C	410.4	331.9	239.8	165.3
	950 °C	336.2	254.0	178.2	119.9
	1000 °C	274.3	197.1	141.5	90.2
	1000 °C	274.3	197.1	141.5	90.2



Figure 3. True stress-strain curves of the $(CoCrNi)_{94}Ti_3Al_3$ alloy hot-compressed at (**a**) 900 °C, (**b**) 1000 °C, and (**c**) 1100 °C. The strain rate is 0.1, 0.01, and 0.001 s⁻¹.

Table 2. The peak flow stress (σ_{max}) of the (CoCrNi)₉₄Ti₃Al₃ alloy hot-compressed at 900, 1000 and 1100 °C, respectively. The strain rate is 0.1, 0.01, and 0.001 s⁻¹.

Temperature	σ _{max} (MPa) 0.1 s ⁻¹	σ _{max} (MPa) 0.01 s ⁻¹	σ _{max} (MPa) 0.001 s ⁻¹
900 °C	390.6	310.6	231.5
1000 °C	193.9	144.2	92.3
1100 °C	134.3	78.1	51.0

3.2. Calculation of Hot Deformation Parameters

During hot compression, the flow stress (σ) is influenced by the deformation temperature (*T*), strain rate ($\dot{\varepsilon}$), and strain (ε). The relationship of those parameters can be expressed by a favorable constitutive equation, where the low stress relationship is given as [27,28]

$$\dot{\varepsilon} = A_1 \sigma^{n_1},\tag{1}$$

and the high stress relationship is

$$\dot{\varepsilon} = A_2 \exp(\beta \sigma). \tag{2}$$

 A_1 , A_2 , n_1 , β are material constants. The relationship at different stress can be concluded into a hyperbolic-sine relationship [29], which is given as

$$\dot{\varepsilon} = A_3 [sinh(\alpha\sigma)]^n exp(-Q_{def}/RT).$$
(3)

 A_3 , α (= β/n_1), n are material constants, Q_{def} is the apparent activation energy (J·mol⁻¹), and R is the gas constant (8.314 J·K⁻¹mol⁻¹).

The experimental results displayed in Figure 2 were used to determine the constants for CoCrNi alloy. Taking the log function on both sides of Equations (1) and (2), α value can be obtained as 0.0043585. Taking the log function on both sides of Equation (3),

$$n = \langle \partial ln\dot{\varepsilon} / \partial \left(\sinh(\alpha\sigma) \right) \rangle_{\mathrm{T}},\tag{4}$$

$$Q_{def} = nR \left\{ \partial(\sinh(\alpha\sigma)) / \partial(1/T) \right\}_{\varepsilon}.$$
(5)

For calculating the exponent n, the relationship of ln(strain rate) and lnsinh($\alpha\sigma$) at different temperatures is plotted in Figure 4a. The average value of slopes is 5.456, i.e., the value of n. For calculating the apparent activation energy Q, the relationship between lnsinh($\alpha\sigma$) and 1000/T at different strain rates is plotted in Figure 4b. The average value of slopes 8.8419, i.e., the value of $Q_{def}/1000$ nR. Q_{def} value is, therefore, 401080 J/mol.



Figure 4. The relationship and linear fitting between (**a**) $\ln \dot{\epsilon}$ vs. $\ln[\sin(\alpha\sigma)]$, (**b**) $\ln[\sinh(\alpha\sigma)]$ vs. (1/T), and (**c**) $\ln Z$ vs. $\ln[\sinh(\alpha\sigma)]$ of the CoCrNi alloy. The hot-compression was carried out at 900, 1000, and 1100 °C with a strain rate of 0.1, 0.01, and 0.001 s⁻¹.

As is widely known, strain rate and deformation temperature can be expressed through Zener–Hollomon parameter (Z) [30,31],

$$Z = \dot{\varepsilon} exp(Q_{def}/RT). \tag{6}$$

Comparing Equations (3) and (6),

$$lnZ = lnA_3 + nln(sinh(\alpha\sigma)).$$
⁽⁷⁾

Linear fitting between $lnsinh(\alpha\sigma)$ versus lnZ is shown in Figure 4c. The coefficient of determination is 0.985, indicating a significant linear dependence. A₃ is obtained as 2.9779 × 10¹⁵.

Therefore, the constitutive equation of CoCrNi alloy is

$$\dot{\varepsilon} = 2.9779 \times 10^{15} [\sinh(0.0043585\sigma)]^{5.456} exp(-401080/RT).$$
(8)

Experimental results displayed in Figure 3 are used to determine the constants for $(\text{CoCrNi})_{94}\text{Ti}_3\text{Al}_3$ alloy. Taking the log function on both sides of Equations (1) and (2), α value can be obtained as 0.00646. The relationship between ln(strain rate) and lnsinh($\alpha\sigma$) at different deformation temperatures is plotted in Figure 5a. According to Equation (4), n value is 4.4838, which equals the average value of slopes. The relationship between lnsinh($\alpha\sigma$) and 1000/T at different strain rates is plotted in Figure 5b. The average value of slopes, which equals $Q_{def}/1000$ nR, is 15.1865. Q_{def} is obtained as 566128 J/mol. Linear fitting between lnsinh($\alpha\sigma$) versus lnZ is shown in Figure 5c. The coefficient of determination is 0.981, indicating a significant linear dependence. A_3 is obtained as 6.8997 × 10²⁰.



Figure 5. The relationship and linear fitting between (**a**) $\ln \dot{\epsilon}$ vs. $\ln[\sin(\alpha\sigma)]$, (**b**) $\ln[\sinh(\alpha\sigma)]$ vs. (1/T), and (**c**) $\ln Z$ vs. $\ln[\sinh(\alpha\sigma)]$ of the (CoCrNi)₉₄Ti₃Al₃ alloy. The hot-compression was carried out at 900, 1000, and 1100 °C with a strain rate of 0.1, 0.01, and 0.001 s⁻¹.

Therefore, the constitutive equation of (CoCrNi)₉₄Ti₃Al₃ alloy is

$$\dot{\varepsilon} = 6.8997 \times 10^{20} [sinh(0.00646\sigma)]^{4.4838} exp(-566128/RT).$$
(9)

In contrast to CoCrNi alloy, $(CoCrNi)_{94}Ti_3Al_3$ alloy has a relatively lower n value but higher apparent activation energy. Equations (8) and (9) make it possible to predict the flow stress at any temperature and strain rate within the range of considered Zener–Hollomon parameters.

3.3. Microstructure After Hot Deformation

Figure 6 shows the electron backscatter diffraction (EBSD)image quality (IQ) maps of the CoCrNi alloy hot-compressed to a true strain of 1.0 at (a–d) 850 °C, (e–h) 900 °C, (i–l) 950 °C, and (m–p) 1000 °C with a strain rate of (a,e,i,m) 0.001 s⁻¹, (b,f,j,n) 0.01 s⁻¹, (c,g,k,o) 0.1 s⁻¹, and (d,h,l,p) 1 s⁻¹, respectively. High angle grain boundaries (HAGBs) with misorientation angles higher than 15 ° ($\theta \ge 15$ °) are indicated by blue lines meanwhile low angle grain boundaries (LAGBs) with misorientation angles 12 ≤ $\theta < 15$ ° are indicated by red lines in the image quality (IQ) maps. Fine- and coarse- grains forming a necklace structure is observed in the samples hot-compressed at relatively low temperatures and high strain rate. The fine grains surrounded by HAGBs are the discontinuous dynamic recrystallized (dDRXed) grains, whereas the coarse grains are those plastic-deformed grains containing a high density of sub-grain boundaries and LAGBs. The occurrence of dDRX is consistent with the flow softening behavior during compression as demonstrated in the σ - ε curves in Figure 2. According to the IQ maps, a larger amount of necklace structure is observed in Figure 6a,b,f–h,j–l,o,p, which indicates a higher fraction of dDRX proceeded when the alloy is compressed under those conditions. On the other hand, a higher fraction of LAGBs is observed when the alloy was hot-compressed at a high strain rate and/or low temperature, which indicates that the initial grains were severely plastic deformed but

few dDRX proceeded under those conditions. It is noteworthy that the grains in Figure 6i,m,n are mainly equiaxed grains containing an extremely low density of LAGBs, which indicates the formation of a completely recrystallized structure. It can be concluded that relatively high temperatures and low strain rates are the prerequisites for obtaining fully recrystallized grain structures by hot-compression.



Figure 6. Electron backscatter diffraction (EBSD) image quality (IQ) maps of the CoCrNi alloy hot-compressed at (**a**–**d**) 850 °C, (**e**–**h**) 900 °C, (**i**–**l**) 950 °C, and (**m**–**p**) 1000 °C with a strain rate of (**a**,**e**,**i**,**m**) 0.001 s⁻¹, (**b**,**f**,**j**,**n**) 0.01 s⁻¹, (**c**,**g**,**k**,**o**) 0.1 s⁻¹, and (**d**,**h**,**l**,**p**) 1 s⁻¹, respectively.

Figure 7 shows the EBSD inverse pole figure (IPF) maps corresponding to the IQ maps in Figure 6, where the CoCrNi alloy was hot-compressed to a true strain of 1.0 at (a–d) 850 °C, (e–h) 900 °C, (i–l) 950 °C, and (m–p) 1000 °C with a strain rate of (a,e,i,m) 0.001 s^{-1} , (b,f,j,n) 0.01 s^{-1} , (c,g,k,o) 0.1 s^{-1} , and (d,h,l,p) 1 s^{-1} , respectively. The color in the IPF maps represents the crystallographic orientation. It can be seen that the fine dDRXed grains exhibit orientations different from the initial coarse grains, and no preferential orientation (texture) is observed in the dDRXed grains. On the other hand, bands were formed in coarse grains, when the alloy was compressed at relatively low temperatures and high strain rate. For instance, many bands can be observed in Figures 7b–d and 6b–d as indicated by the arrowheads. These bands subdivide the coarse-grains into regions of different orientations. As temperature increases and strain rate decreases, bands become inapparent. In Figure 7m, annealing twins are observed in those equiaxed recrystallized grains. Different from the deformation band structure in the un-recrystallized grains, annealing twins are simply associated with HAGBs.



Figure 7. EBSD inverse pole figure (IPF) maps of the CoCrNi alloy hot-compressed at (**a**–**d**) 850 °C, (**e**–**h**) 900 °C, (**i**–**l**) 950 °C, and (**m**–**p**) 1000 °C with a strain rate of (**a**,**e**,**i**,**m**) 0.001 s⁻¹, (**b**,**f**,**j**,**n**) 0.01 s⁻¹, (**c**,**g**,**k**,**o**) 0.1 s⁻¹, and (**d**,**h**,**l**,**p**) 1 s⁻¹, respectively.

Figure 8 shows the EBSD IQ maps of the (CoCrNi)₉₄Ti₃Al₃ alloy after hot compression to a true strain of 1.0 at (a–c) 900 °C, (e–g) 1000 °C, and (i–k) 1100 °C with a strain rate of (a,d,g) 0.001 s⁻¹, (b,e,h) 0.01 s⁻¹, and (c,f,i) 0.1 s⁻¹, respectively. HAGBs are indicated by blue lines and LAGBs are indicated in red lines. The necklace structure is also observed at 900 °C and 1000 °C, which is similar to that shown in Figure 7. The LAGBs are mainly observed in the plastic deformed coarse grains, and no aggregation distribution in grain interior is confirmed. The amount of LAGBs decreased significantly when the temperature is increased to 1000 °C, indicating the dynamic recovery of dislocations proceeded rapidly. Moreover, fully equiaxed grains are formed at a strain rate of 0.001 s⁻¹, but the necklace structure is observed, and the grains are completely recrystallized resulting in relatively homogeneous grain morphologies. The CoCrNi and (CoCrNi)₉₄Ti₃Al₃ alloys show a similarity microstructural evolution under hot compression. However, a difference is found when the alloys were hot compressed at 900 °C with 0.001 s⁻¹ (Figure 6e vs. Figure 8a) and 1000 °C with 0.01 s⁻¹ (Figure 6n vs. Figure 8f), where near fully-recrystallized grains are formed in the CoCrNi alloy but the neckless structure is observed in the (CoCrNi)₉₄Ti₃Al₃ alloy.

Figure 9 shows the EBSD IPF maps corresponding to the IQ maps in Figure 8, where the alloy was compressed to a true strain of 1.0 at (a–c) 900 °C, (e–g) 1000 °C, and (i–k) 1100 °C with a strain rate of (a,d,g) 0.001 s^{-1} , (b,e,h) 0.01 s^{-1} , and (c,f,i) 0.1 s^{-1} , respectively. The necklace grains exhibit crystallographic orientations different from those initial coarse grains, and necklace grains do not show a texture. Bands surrounded by LAGBs are observed in Figure 9c. With higher temperatures and lower strain rates, bands are replaced by a thick necklace structure. After high degree recrystallization,

annealing twins are typical features in equiaxed grains (Figure 9d,h). During the further grain growth process, annealing twins stably exist and achieve larger sizes.



Figure 8. EBSD IQ maps of the (CoCrNi)₉₄Ti₃Al₃ alloy hot-compressed at (**a**–**c**) 900 °C, (**d**–**f**) 1000 °C, and (**g**–**i**) 1100 °C with a strain rate of (**a**,**d**,**g**) 0.001 s⁻¹, (**b**,**e**,**h**) 0.01 s⁻¹, and (**c**,**f**,**i**) 0.1 s⁻¹, respectively.



Figure 9. EBSD IQ maps of the (CoCrNi)₉₄Ti₃Al₃ alloy hot-compressed at (**a**–**c**) 900 °C, (**d**–**f**) 1000 °C, and (**g**–**i**) 1100 °C with a strain rate of (**a**,**d**,**g**) 0.001 s⁻¹, (**b**,**e**,**h**) 0.01 s⁻¹, and (**c**,**f**,**i**) 0.1 s⁻¹, respectively.

For quantitatively calculating the volume fraction of recrystallized grains and their average size, the grains were distinguished by a grain orientation spread (GOS) method [32]. The grains with GOS $\leq 2^{\circ}$ are determined as recrystallized grains, and grains with GOS $> 2^{\circ}$ are un-recrystallized ones. Figure 10a,b, respectively, show the fraction of recrystallization and the average size of the recrystallized grains of the CoCrNi hot compressed to a true strain of 1.0. It can be concluded from Figure 10a that the fraction of recrystallization has a notable positive correlation with temperature but a negative correlation with strain rate, where a higher fraction of DRXed grains is obtained at a higher temperature but low strain rate. On the other hand, the average size of the DRXed grains also has a positive correlation with temperature but a negative correlation with temperature but a negative correlation with strain rate, where a higher fraction with strain rate, which demonstrates a more rapid grain growth at higher temperatures. For instance, the fraction of recrystallized grains is 6.3% and 90.3%, meanwhile, the average grain size is 2.8 µm and 16.99 µm, when the alloys were compressed at 850 °C with 0.1 s⁻¹ and 1000 °C with 0.001 s⁻¹ is an appropriate condition for obtaining fully recrystallized grain structures.



Figure 10. The volume fraction (**a**) and average grain size (**b**) of the recrystallized grains in the CoCrNi alloy hot-compressed to a true strain of 1.0. The compression temperature is 850, 900, 950, and 1000 °C, and the strain rate is 0.001, 0.01, and 0.1 s^{-1} .

Figure 11a,b, respectively, show the fraction of recrystallization and the average size of the recrystallized grains of the $(CoCrNi)_{94}Ti_3Al_3$ hot compressed to a true strain of 1.0. As compression temperature increases, specimens deformed at a strain rate of 0.001/s achieve high recrystallization fraction. On the other hand, the two-stage dependence of recrystallized grain size on compression temperature is observed in all three strain rates. Increment of grain size is smooth from 900 to 1000 °C and becomes significant from 1000 to 1100 °C. The grain growth of specimen deformed at 0.001/s and 1100 °C is even more remarkable (to 42 μ m), which corresponds to grain coarsening after complete recrystallization.



Figure 11. The volume fraction (**a**) and average grain size (**b**) of the dynamically recrystallized grains in the $(CoCrNi)_{94}Ti_3Al_3$ alloy hot-compressed to a true strain of 1.0. The compression temperature is 850, 900, 950, and 1000 °C, and the strain rate is 0.001, 0.01, and 0.1 s⁻¹.

4. Discussion

4.1. Flow Behavior Analysis

The flow behaviors of the MEAs during hot-compression is associated with the established constitutive equations. The addition of Ti and Al increases the activation energy of CoCrNi alloy, due to the impediment of plastic deformation and recrystallization by solid solution strengthening. According to Equations (4) and (5), the flow stress of the (CoCrNi)₉₄Ti₃Al₃ alloy decreases more rapidly than that of the CoCrNi alloy, when the temperature changes from 900 to 1000 °C as shown in the σ - ε curves in Figures 2 and 3. It indicates that the addition of Ti and Al enhances the temperature-sensitivity of flow behaviors of the alloys. On the other hand, the two alloys exhibit nearly equivalent flow stress at 1000 °C. Therefore, it can be concluded that the flow stress of (CoCrNi)₉₄Ti₃Al₃ alloy will be relatively higher (temperature < 1000 °C) but lower (temperature > 1000 °C) than that of the CoCrNi alloy.

The slope of σ - ε curves before reaching peak stresses represents the work hardening rate, which indicates the deformation mechanism. Based on Senkov's study on the hot compression process, deformation twins and shear bands were found at a relatively lower temperature but annealing twin occurs in the recrystallized equiaxed grains at higher temperatures [33]. In the present study, the CoCrNi alloy deformed at 0.001/s and temperature ≥ 900 °C shows smaller hardening slopes, in which a high degree of recrystallization and annealing twins are observed in Figure 7. When the alloy was deformed under other conditions, the work hardening rates are relatively high, in which low degree of recrystallization, deformation bands, and local-distorted coarse grains are observed. As confirmed by Alexei's model, the concave-upward trend in the σ - ε curves is commonly associated with the propagation of deformation bands [34]. Hence, a resembling plastic-deformation mechanism will result in the same concave, leading to good overlapping of the slops in the initial stages of the σ - ε curves. In contrast, no apparent deformation band is observed in the (CoCrNi)₉₄Ti₃Al₃ alloy after hot compression (Figure 9). The softening effect is more significant; hardly can typical high hardening slope be achieved.

The plateau in σ - ε curves indicates a steady flow behavior, which is a balance of work hardening by further deformation and softening by dislocation recovery, DRX, and grain growth. The alloys deformed at relatively high temperatures and low strain rates undergo high degree recrystallization; therefore, the plateaus are formed under those conditions as shown in Figures 2 and 3. The continuous stress decreasing after peak stress indicates the progress of further recrystallization as indicated in Figures 10 and 11. The stress drop is easier to occur at a higher temperature and lower strain rate, which represents the completion of recrystallization [33]. After the stress drop, the grains coarsened rapidly in the following deformation, resulting in large grains shown in Figures 9 and 11.

4.2. Correlation Between Microstructure and Recrystallization

As is known, hot-compression condition affects the microstructure significantly, which is often quantitatively determined by the Z parameter. A high strain rate and low temperature yield a large Z value. When the CoCrNi alloy was hot-compressed with a large Z value, a great quantity of LAGBs were formed (Figure 6c,d,h). On the other hand, continuous dynamic recrystallization (cDRX) occurs preferentially at a large Z value [35], where the evolution of sub-grains proceeds both at initial grain boundaries and in the grain interior [36]. Deformation bands are often formed particularly in coarse grains, as a consequence of either the inhomogeneous stresses transmitted by neighboring grains or the intrinsic instability of the grain during hot-compression [37]. The misorientation difference between the microbands and initial grain is relatively small until LAGBs transform into HAGBs. The transformation of LAGBs to HAGBs consumes the stored energy significantly. Therefore, the microbands are less possible to be the preferential nucleation sites for recrystallization grains compared with the initial grain boundaries, which will result in the formation of necklace structures (Figure 6d). The interaction between dislocations and bands also have an impact on the microstructure evolution [38]. In some regions with a high stress concentration, junctions of original bands and newly formed structures

are more prone to recrystallization. At higher temperatures and lower strain rates (small *Z* value), the dDRX tends to become a major mechanism [35]. As shown in Figure 6i,m,n, equiaxed dDRXed grains with HAGBs and annealing twins are formed, which is a typical dDRXed structure formed by discontinuous formation of recrystallized fine grains at initial grain boundaries [39].

In the case of $(CoCrNi)_{94}Ti_3Al_3$ alloy, the dDRX is the major mechanism during hot-compression. The addition of Ti and Al increases the friction force for dislocation slip due to the solid solution strengthening effect. The movement of dislocations in the $(CoCrNi)_{94}Ti_3Al_3$ alloy needs a larger driving force to overcome the impediment caused by Ti and Al atoms, which corresponds to a larger value of activation energy compared with the CoCrNi alloy. At lower temperatures, the compression flow stress is determined by the activation energy, hence the $(CoCrNi)_{94}Ti_3Al_3$ alloy exhibiting higher flow stresses compared with the CoCrNi alloy when they were compressed at 900 °C. On the other hand, the addition of Ti and Al enhances the accumulation of dislocations and the storage of deformation energy. When the compression temperature increases, the rate of energy storage in the $(CoCrNi)_{94}Ti_3Al_3$ alloy is higher than that in CoCrNi alloy, which corresponds to a smaller pre-exponent *n*. As a result, the reduction in flow stress of $(CoCrNi)_{94}Ti_3Al_3$ alloy is more significant because of the high rate of recrystallization. The stored energy is nearly exhausted after recrystallization, and the grains coarsened rapidly to reduce the interface energy.

5. Conclusions

The hot deformation behaviors and microstructure evolutions of the CoCrNi and $(CoCrNi)_{94}Ti_3Al_3$ MEAs were investigated by uniaxial hot-compression to a height reduction of 63% corresponding to a true strain of 1.0, which was conducted at temperature ranges from 850 to 1100 °C with strain rate ranges from 0.001 to 1 s⁻¹. The main findings are as follows:

- 1. Constitutive equations describing the relationship between flow stress and compression condition were obtained, where the hyperbolic-sine of the flow stress has a linear relationship with the Zener–Hollomon parameter in the two alloys. The apparent activation energy for the hot deformation was evaluated as 401.08 kJ/mol (CoCrNi) and 566.128 kJ/mol ((CoCrNi)₉₄Ti₃Al₃), respectively, which is higher than that of CoCrFeMnNi high entropy alloys.
- 2. In both alloys, the flow curves show peak stress followed by softening caused by the continuous dynamic recrystallization (cDRX) and discontinuous dynamic recrystallization (dDRX). According to the microstructure evolutions, the dDRX prefers to proceed at a small Zener–Hollomon parameter (high temperature and low strain rate).
- 3. The temperature of 1000 °C and strain rate of 0.001 s⁻¹ is the optimum condition for obtaining fully-recrystallized homogeneous grain structures, where the average grain size is 17 μ m and 12 μ m for the CoCrNi and (CoCrNi)₉₄Ti₃Al₃ MEAs after compression to a true strain of 1.0. The recrystallized grains exhibited very weak textures, and the nucleation is without any preferential orientation selection.

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