Hall-Petch relationship and corrosion behavior of cold-rolled CoNiFe medium entropy alloy


Abstract

CoNiFe medium entropy alloy samples are synthesized by vacuum arc melting and subsequent thermomechanical processing. The fully-recrystallized face-centered-cubic (FCC) single phase microstructures with grain sizes ranging from 10 to 100 μm are obtained by annealing processes and the grain growth kinetics and Hall-Petch relationship are investigated. The activation energy for grain growth is 153.9 kJ mol⁻¹ and the recrystallized sample processed at 700 °C possesses superior mechanical properties including high strength and ductility. The lattice friction stress is 168.4 MPa which is larger than that of the CoNiCrFeMn high entropy but less than that of the CoNi medium entropy alloy. In addition, in order to investigate the effect of solution temperature on corrosion behaviors of CoNiFe MEA, electrochemical tests in NaCl/H₂SO₄ solution with different temperature are carried out. The electrochemical experiments show corrosion current density increases and corrosion potential decreases, indicating the corrosion resistance of CoNiFe MEAs in NaCl and H₂SO₄ solution is weaken with increasing solution temperature.

Keywords:
CoNiFe
MEAs
Hall-Petch relationship
Grain growth kinetics
Corrosion behavior

1. Introduction

Multi-component alloys (MCAs) have attracted much attention [1,2] as they represent a conceptual breakthrough compared to traditional alloys. MCAs often form a random solid solution rather than intermetallic compounds during solidification due to the high entropy effect [3–5]. According to the mixing entropy (ΔS_mix), multi-component alloys can be classified as low entropy alloys (LEAs: ΔS_mix < 1 R), medium entropy alloys (MEAs: 1 R < ΔS_mix < 1.5 R), and high entropy alloys (HEA: ΔS_mix > 1.5 R), where R is the ideal gas constant, 8.314 J/K/mol. HEAs with a high mixing entropy and at least five principal elements in equimolar to near-equimolar ratios [3,5] possess outstanding properties such as excellent cryogenic strength and toughness [5,6], high-temperature properties [7], thermal stability [8], wear resistance [2], and so on. It has been found that the composition of the principal elements instead of the number of elements plays the more important role in the improved properties of multi-component alloys [10–12]. Medium entropy alloys (MEAs) composed of two to four principal elements with the mixing entropy between 1 R and 1.5 R have also been studied [9,10].

MEAs have excellent mechanical properties [11,12] and better industrial potential than HEAs and traditional alloys [13]. In addition, owing to the excellent magnetic and mechanical properties, CoNiFe MEAs with the fcc structure has aroused much interest [14–17]. MEAs with the ultra-fine grain size (UFG; grain size d < 1 μm) and nanotwins possess the desirable combination of strength and ductility [21,22]. In order to produce a microstructure with UFG, severe plastic deformation such as high pressure torsion (HPT) is usually adopted [18,19], but it is not a suitable production method due to the complex process and high manufacturing cost. Cold working (e.g. by forging, rolling) followed by recrystallization is one of the simplest conventional thermal mechanical processes (TMPs) to control the grain size and the Hall-Petch relationship can reveal the strengthening mechanism to improve the mechanical properties. The grain size dependence of the yield stress (Hall-Petch relationship) in traditional materials such as Ni [20], Al [21], and Mg alloys [22] has been investigated and the Hall-Petch relationship of HEAs with low stacking fault energy (SFE) has also been studied [28,29]. Stacking fault energy (SFE) is one of the most important parameters that determines the degree of recovery [23] and the formation of deformation twins [24]. Previous researches show that the SFE of FeNiCoCr systems alloys increase in the order: NiCoCr(18 ± 4 m²) < FeNiCoCr (27 ± 4 m²) < NiCo < FeNiCo.
(70 mJ m^{-2})< \text{FeNi}< \text{Ni} (125 mJ m^{-2}) [23,25]. Shuhei Yoshida [18], et al., have investigated the friction stress an Hall-Petch relationship in CoCrNi equi-atomic medium entropy alloy with low SFE. Besides, R.W Armstrong [26] have studied the Hall-Petch relationship of pure metal Ni with high SFE. Compared to both results, the friction stress of CoCrNi MEA with low SFE was much higher than pure metals with high SFE. Although low SFE alloys can produce fine grains, even nano-grains, during deformation [27], the Hall-Petch relationship of medium SFE MEAs such as CoNiFe have not been reported. Besides, The CoFeNi MEA, as an important alloy with application potential, its corrosion behavior have been investigated [28,29]. However, those studies are mainly focusing on as-cast or film CoFeNi MEA.

In this work, CoNiFe MEA samples with a single fcc structure are produced by cold forging and rolling and the grain growth kinetics and Hall-Petch relationship are studied for an expanded annealing temperature range from 600 to 1000 °C for 1 h. To investigate the relationship between environment condition and corrosion behaviors of roll-CoNiFe MEA, electrochemical tests in NaCl/H\textsubscript{2}SO\textsubscript{4} solution with variation temperature are carried out.

2. Experimental procedure and methods

Co, Ni and Fe metals with >99.9% purity were the raw materials and the CoNiFe MEAs ingots were produced by vacuum arc melting under argon. The ingots were re-melted under electromagnetic stirring at least five times to enhance the uniformity of the chemical composition. The as-cast ingots were cut to expose four flat faces and homogenized at 1000 °C for 12 h in an air furnace, cold-forged, and cross-rolled at room temperature along the side. The thickness was reduced by 90% from 10 mm to 1 mm and the rolled samples were then annealed in a furnace in air at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C for 1 h are depicted in Fig. 1(a–f). The microstructure of the cold-rolled samples show deformation bands stretched along the rolling direction (Fig. 1a). Fig. 1b shows that the structure does not change obviously and most grains remain elongated. However, some small grains are produced at the junction of the grain boundaries. When the annealing temperature is increased to 700 °C, uniform and fine equiaxed grains replace the deformed structure indicating that recrystallization is basically complete (Fig. 1c) and this phenomenon is consistent with that observed by Satiaraj et al. [27]. Besides, annealing twins appear and with increasing annealing temperature, the grain size increases. It has been reported that the CoNiFe MEA has a wider grain size distribution and higher homologous temperature than the CoNiFeCr and CoNiFeCrMn HEAs, indicating that CoNiFe MEAs offer weaker resistance to grain growth as the temperature goes up. Our experimental results are consistent.

Grain boundary character distribution (GBCD), namely as grain boundary engineering (GBE), were proposed for a aim to improve the properties of polycrystalline material by increasing dramatically especial boundaries. Special boundaries are characterized by a low reciprocal density of coinciding sites, Σ, of the coincident site lattice (CSL). The Σ3 boundary is one of the most important and common of CSL boundaries, which are classified as coherent and incoherent Σ3 boundary. In practice, the Σ3 boundaries are inherently associated with the deformation and subsequent annealing.

scan rate of 0.1 mV s^{-1} from −1 to 2 V. Moreover, the measurement was conducted 5 times at least to ensure the credibility of the data.

3. Results and discussion

3.1. Hall-Petch relationship of cold-rolled CoNiFe MEAs

The EBSD micrographs exhibiting the grain evolution in the samples annealed at 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C are depicted in Fig. 1(a–f). The microstructure of the cold-rolled samples show deformation bands stretched along the rolling direction (Fig. 1a). Fig. 1b shows that the structure does not change obviously and most grains remain elongated. However, some small grains are produced at the junction of the grain boundaries. When the annealing temperature is increased to 700 °C, uniform and fine equiaxed grains replace the deformed structure indicating that recrystallization is basically complete (Fig. 1c) and this phenomenon is consistent with that observed by Satiaraj et al. [27]. Besides, annealing twins appear and with increasing annealing temperature, the grain size increases. It has been reported that the CoNiFe MEA has a wider grain size distribution and higher homologous temperature than the CoNiFeCr and CoNiFeCrMn HEAs, indicating that CoNiFe MEAs offer weaker resistance to grain growth as the temperature goes up. Our experimental results are consistent.

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processes [30,31]. The \( \Sigma 3 \) boundaries have greatly influence on materials properties due to its low energy. Therefore, it is significant to understand the properties variation of alloys by investigating the relationship between CSL boundaries, especially \( \Sigma 3 \) boundaries and heat treatment condition.

The mean grain sizes of the samples annealed at different temperature are shown in Fig. 2a. During annealing at 800 °C and 900 °C, grain coarsening is weaker leading to mean grain sizes of 19 ± 0.2 \( \mu \)m and 32 ± 0.3 \( \mu \)m, respectively. Obvious grain coarsening is observed after annealing at 1000 °C and a mean grain size of 72 ± 0.1 \( \mu \)m is observed. Fig. 2b exhibits the change in the misorientation distribution with annealing temperature. The strong peak at -6° indicates formation of annealing twins during recrystallization and grain growth. The grain boundary characteristic distributions (GBCDs) of the rolled CoNiFe MEA samples annealed at different temperature indicate that the fraction of low angle grain boundaries (LAGBs) is larger than those of the coincidence site lattice (CSL) and high angle grain boundaries (HAGBs) when the temperature is below 600 °C (Fig. 2c). As the annealing temperature is increased from 700 °C to 900 °C, the fraction of CSL is quite high and Fig. 2d shows that most of the CSL boundaries belong to the \( \Sigma 3 \) category. The highest fraction of \( \Sigma 3 \) is observed from the recrystallized samples at 700 °C. When the annealing temperature is increased from 800 °C to 1000 °C, the fraction of CSL TBs and HAGBs decrease markedly while that of \( \Sigma 3 \) TBs increases. The reason is that the \( \Sigma 1 \) boundaries belong to the low angle grain boundaries (LAGBs) and have relatively low energies. Higher-energy grain boundaries are preferentially eliminated from the network compared to the lower-energy grain boundaries during grain growth as observed by Dillon et al. [32], thus leading to a higher relative population of low energy grain boundaries at the high annealing temperature.

After annealing at 700 °C, fully recrystallized fine grains are observed. Fig. 3a shows the room-temperature tensile stress-strain curves of the rolled-CoNiFe MEAs annealed at different temperature for 1 h. Both the yield strength (\( \sigma_y \)) and ultimate tensile strength (UTS) decrease in conjunction with increased tensile ductility (Elongation, \( \varepsilon \)) as the annealing temperature goes up. The rolled-CoNiFe MEA annealed at 700 °C for 1 h possesses superior mechanical properties including high strength (590 ± 7 MPa) and ductility (50%), which can be explained by coarsening of grains and variation of the \( \Sigma 3 \) grain boundary. When the annealing temperature is increased from 800 °C to 1000 °C, the strength decreases but ductility increases. The similar results can be seen in CR-CoNiCr MEAs [32]. The CR-CoNiCr MEAs annealed at 700 °C have been shown to possess a combination of high ultimate tensile strength of 946 MPa and ductility of 66% due to nanometer grains and annealing twins. Z Wu et al. [33] have investigated the tensile properties at temperature in the range 77–673 K. The UTS and uniform elongation to fracture of FeCoNi alloy increase with decreasing temperature. The UTS and elongation at room temperature are about 400 MPa and 25% respectively. T. Yang et al. [34] have designed a (FeCoNi)_{86}Al_{17}Ti{7} (Al_{7}Ti_{7}) multi-component alloys by highly alloying with Ti and Al additions. The ultimate tensile strength of the Al_{7}Ti_{7} alloy had a tensile yield strength as high as 1 GPa and an ultimate tensile strength of 1.5 GPa, which was five times higher than that of FeCoNi medium entropy alloys. Besides,
T.T Zuo et al. [35] have found that the amounts of Al and Si additions strongly influence the phase structures and mechanical properties, both Al and Si addition can increase the yield strength with the sacrifice of plasticity. To investigate the mechanism and Hall-Petch behavior, TEM images are acquired from the rolled-MEA annealed at 700 °C. Dislocations are present in the grain boundaries (GBs) as shown in Fig. 3b and c and dislocations accumulate at the grain boundaries. It is because the lattice mismatch is most pronounced in the grain boundary regions [36] and furthermore, since dislocations accumulate continuously, the resistance to dislocation glide is presumably due to dislocation-dislocation interactions [37]. Severe plastic deformation (SPD) and phase transformation generate high dislocation densities in metals giving rise to large ductility and high strength [38]. The X-ray diffraction patterns of the cold-rolled samples annealed at different temperature are displayed in Fig. 3d. An fcc single phase with a lattice parameter of 3.59 Å is revealed implying that no phase transformation occurs as the annealing temperature is increased.

According to the classical theory on grain growth, the kinetics of grain growth can be deduced by analyzing the grain size as a function of time. Based on the theory proposed by Cahn [39] and Brook [40], the velocity, \( v \), of a slowly moving grain boundary and instantaneous grain size (D) have the following relationship:

\[ v \propto \frac{1}{D^2} \]

(1)

The grain-growth constant, \( D \), in Eq. (1) follows the Arrhenius relationship:

\[ D^2 = A \exp\left(-\frac{Q}{RT}\right) \text{ or } \ln D = \frac{1}{2} \ln A - \frac{Q}{2RT} \]

(2)

where \( T \) is the absolute temperature, \( Q \) is the activation energy for grain growth, \( A \) is a constant, and \( R \) is the gas constant. The activation energies of grain growth obtained from the slope of the \( \ln(D) \) versus \( 1/T \) plot shown in Fig. 4a is 153.9 kJ mol\(^{-1}\) revealing that grain growth is temperature sensitivity.

The effects of the grain size on yield strength are described by the Hall-Petch relationship:

\[ \sigma_y = \sigma_0 + k_y d^{-1/2} \]

(3)

where \( \sigma_y \) is the intrinsic lattice strength of CoNiFe MEA, \( d \) is the mean grain size, and \( k_y \) is the Hall-Petch coefficient. The Hall-Petch curves of the rolled-CoNiFe MEAs are prepared using the mean grain size (Fig. 4b) and \( \sigma_0 \) and \( k_y \) obtained by fitting Eq. (3) are 168.4 MPa and 288.5 MPa, respectively. \( \sigma_0 \) is the friction stress and CoCrNi has a high lattice friction \( \sigma_0 \) (218 MPa) [23]. Comparing to
other materials, $\sigma_0$ of CoNiFe MEA is less than that of the CoCrNi MEA but more than those of pure fcc (4–14 MPa) metals [41] and CoCrFeMnNi HEAs (125 MPa) [42]. The CoCrNi MEA has high lattice friction because Cr atoms are larger than Fe atoms leading to local severe lattice distortion in CoNiCr and there is fluctuation in the Peierls potential for the dislocation motion [18].

The yield stress increases with decreasing mean grain size and it is defined as Hall-Petch strengthening. The number of grain boundaries increases as the grain becomes finer but grain boundaries act as pinning points impeding further dislocation propagation in Hall-Petch strengthening. Theoretically, grain sizes between 10 nm and 100 µm are effective for this type of strengthening. Schuh et al. [8] have studied the CoCrFeMnNi high entropy alloy (HEA) with a grain size of approximately 50 nm produced by severe plastic deformation (SPD) using high-pressure torsion and the strength and hardness of the alloys with nanocrystallinity increase significantly compared coarse-grain ones. Otto et al. [42] have found that the yield strength increases as the grain size decreases from 155 to 4.4 µm but increases slightly when it decreases from 155 to 50 µm. To investigate the Hall-Petch relationship of alloys with small grains, Yoshida et al. [18] have been adopted pressure torsion (HTP) which is a severe plastic deformation process to obtain nanoscale grains and their conclusion is similar to that inferred from our experimental data.

### 3.2. Corrosion behavior of cold-rolled CoNiFe MEAs

Metal corrosion is intensified by the conjoint action of the physical process and the chemical environment. The electrochemical techniques including polarization curve and AC (alternating current) impedance are the important methods to predict the lifetime of alloys from short term experimental corrosion data. AC impedance techniques which also called electrochemical impedance spectroscopy (EIS) has been used to study the alloy interface. Fig. 5 shows the schematic illustration of active-passive curves and ESI spectra. The polarization curve can be divided three region: active region, passive region and transpassive region (Fig. 5a). $I_{\text{crit}}$ and $E_{\text{pp}}$ represent the critical current density and the potential for passivation, respectively, revealing a passive film is being formed on the alloy surface. Besides, $\Delta E$ shows the passivation/protection range. And $E_b$ represents the breaking potential, indicating the passive film is destroyed. The plots of $Z'$ vs. $Z''$ are formed depressed semi-circles, $R_p$ is the resistance to charge transfer (Fig. 5b). It is obvious that the semi-circles radius ($R_p$) are more larger, the ability of resistance to charge transfer for alloy is more intensity.

![Fig. 4](image1.png)

![Fig. 5](image2.png)

*Fig. 4.* (a) Grain growth constant, $D$, as a function of the reciprocal of absolute temperature; (b) Hall-Petch relationship of CoNiFe MEAs: Yield strength as a function of grain size.

*Fig. 5.* (a) The schematic polarization curve including three region: active region, passive region and transpassive region; (b) Schematic diagram of alternating current (AC) impedance. $C$ is the double layer capacitance, $R_p$ is the resistance to charge transfer, and $R_s$ is the ohmic resistance of the solution.
Temperature have a significant influence on the corrosion process. Fig. 6 shows electrochemical behavior of CoNiFe MEAs in NaCl and H$_2$SO$_4$ solution for 30°C, 40°C, 50°C, 60°C. The data calculated from polarization curves are listed in Table 1. It can be found that corrosion potential ($E_{corr}$) decrease from −0.36 to −0.46 V while corrosion current density ($i_{corr}$) increase from 0.21 to 2.7 $\mu$m/cm$^2$ with increasing NaCl solution temperature. A reasonable explanation is that the solution viscosity decrease while the ion thermal motion and diffusion accelerate, leading to aggravate the reactions of anodic and cathodic. Overall, the corrosion resistance of CoNiFe MEAs in NaCl solution was weakened with increasing solution temperature, which consistent with the results of previous researches [43].

Besides, the electrochemical characteristics of CoNiFe MEAs in H$_2$SO$_4$ solution have been presented at Fig. 6b and Table 2, the $E_{corr}$ decrease slightly while the $i_{corr}$ increase obviously. The $i_{corr}$ of CoNiFe MEAs in H$_2$SO$_4$ solution increase from 7.94 $\mu$m/cm$^2$ to 56.2 $\mu$m/cm$^2$ as solution temperature increasing from 50°C to 60°C. Moreover, due to the active-passive character can be seen in polarization curves (Fig. 6b), meaning that the passive films are formed in CoNiFe MEAs surface. The $i_{corr}$ tends to be stable with the $E_{corr}$ increasing constantly, resulting from the protective effect of the films. Balyanov et al. [44] have proposed that the crystal lattice defects are the place where the formation of passive films. From Table 2, there are nearly the same pitting potential ($E_p$) value while the passivation/protection range ($\Delta E$) are reduced gradually with increasing H$_2$SO$_4$ solution temperature. It indicates that the passive films deteriorates and dissolves with increasing temperature.

Table 1

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$E_{corr}$ (V vs.SCE)</th>
<th>$i_{corr}$ ($\mu$m/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>−0.36 ± 0.05</td>
<td>0.21 ± 0.01</td>
</tr>
<tr>
<td>40°C</td>
<td>−0.40 ± 0.03</td>
<td>0.56 ± 0.03</td>
</tr>
<tr>
<td>50°C</td>
<td>−0.42 ± 0.04</td>
<td>1.23 ± 0.01</td>
</tr>
<tr>
<td>60°C</td>
<td>−0.46 ± 0.05</td>
<td>2.7 ± 0.04</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$E_{corr}$ (V vs.SCE)</th>
<th>$i_{corr}$ ($\mu$m/cm$^2$)</th>
<th>$i_{crit}$ (mA/cm$^2$)</th>
<th>$i_{pass}$ (mA/cm$^2$)</th>
<th>$E_p$ (V vs.SCE)</th>
<th>$\Delta E$ (V vs.SCE)</th>
<th>$D_E$ (V vs.SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>−0.12 ± 0.01</td>
<td>1.74 ± 0.2</td>
<td>0.61 ± 0.06</td>
<td>3.42 ± 0.07</td>
<td>1.35 ± 0.04</td>
<td>0.79 ± 0.04</td>
<td>0.43 ± 0.03</td>
</tr>
<tr>
<td>40°C</td>
<td>−0.18 ± 0.02</td>
<td>6.03 ± 0.26</td>
<td>0.44 ± 0.06</td>
<td>3.30 ± 0.09</td>
<td>1.36 ± 0.03</td>
<td>0.67 ± 0.07</td>
<td>0.46 ± 0.02</td>
</tr>
<tr>
<td>50°C</td>
<td>−0.20 ± 0.05</td>
<td>7.94 ± 0.51</td>
<td>0.17 ± 0.04</td>
<td>2.70 ± 0.05</td>
<td>1.39 ± 0.03</td>
<td>0.65 ± 0.03</td>
<td>0.55 ± 0.05</td>
</tr>
<tr>
<td>60°C</td>
<td>−0.25 ± 0.07</td>
<td>56.2 ± 4.89</td>
<td>0.34 ± 0.07</td>
<td>1.83 ± 0.08</td>
<td>1.35 ± 0.04</td>
<td>0.35 ± 0.04</td>
<td>0.78 ± 0.13</td>
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</table>

Fig. 6. Electrochemical behavior of CoNiFe MEAs in NaCl and H$_2$SO$_4$ solution for 30°C, 40°C, 50°C, 60°C. (a) polarization curves in 3.5 wt% NaCl solution; (b) polarization curves in 1 M H$_2$SO$_4$ solution; (c) ESI spectra in 3.5 wt% NaCl solution; (d) ESI spectra in 1 M H$_2$SO$_4$ solution.
The semi-circles radius (Rp) decrease dramatically with increasing solution temperature. It means that the ability of corrosion resistance for CoNiFe MEAs is reducing with increasing temperature in both NaCl solution and H2SO4 solution.

According to the electrochemical parameters from our results, it is easier to find that the CoNiFe MEAs are sensitive to temperature whether in NaCl solution or H2SO4 solution. By contrast, the sensitive for temperature of CoNiFe MEAs in H2SO4 solution are much more than in NaCl solution, which can be proved by the variation of i_{corr} values getting from polarization curves in both solution. There are several reasons for the corrosion accelerate with increasing temperature. As increasing temperature, at first, Oxygen atoms dissolved in solution are easy to reach to cathodes due to the increase of oxygen diffusion coefficient. Secondly, the resistance of electrolyte solution are reducing dramatically, resulting from convection and diffusion of solution. And the conductivity of the solution is increased resulting in corrosion current density increasing. Thirdly, the activity of surface reactions and consequently increases anodic and cathodic reactions, which leads to increase of total current [45].

Fig. 7 exhibits the corrosion morphology of CoNiFe MEAs in 3.5 wt% NaCl solution and 1 M H2SO4 solution at 30 °C and 60 °C. The Cl− and SO4^2− aggressive ion in solution breakdown the passive film, leading to pitting of the alloy. With increasing solution temperature, the motion of these ions were accelerated constantly, resulting in more serious corrosion, meanwhile, the number of pits increase (Fig. 7a and b). Previous studies [46] have found that corrosion pits includes two style: metastable pitting and stable pitting, wherein metastable pitting is considered to be the precursor stage for stable pitting [47,48]. From corrosion morphology, there are a large number of metastable pitting in samples in 30 °C temperature NaCl solution while the metastable pitting have transformed stable pitting with temperature increasing from 30 °C to 60 °C. The Cl− has a especially influence on corrosion pits forming [49]. The main reason is that Cl− is a strong electron donor and tends to interact with electron acceptors, such as metal cations. On the other hand, Cl− is easy to diffusion due to small size, and diffusion rate increase with environment temperature. This is a good explanation why the number of corrosion pits in 60 °C NaCl solution are higher than in 30 °C. The surface patterns of samples in H2SO4 solution differed from ones in NaCl solution, as is shown in Fig. 7c and d. It can be seen that there are many similar mesh structures and larger corrosion pits in Fig. 7c, in comparison, when solution temperature reaches 60 °C, the surface of sample has been destroyed dramatically, which is composed to many small columnar-bulk Fig. 7d.

Though the corrosion mechanism of multi-component alloys is not clear, the following anodic and cathodic reactions take place in salt and acid solution [50].

At the local anodes

\[ \text{M} \rightarrow \text{M}^{n+}(\text{aq}) + n\text{e}^- \quad (5) \]

Where M stand for Co,Ni,Fe.

At the local cathodes

\[ \text{H}_2\text{SO}_4 \text{ solution} \quad 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \quad (6) \]

\[ \text{NaCl solution} \quad 2\text{H}_2\text{O}(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^- \quad (7) \]

The overall reaction is the sum of these two half-cell reactions

\[ \text{H}_2\text{SO}_4 \text{ solution} \quad \text{M} + n\text{H}^+(\text{aq}) \rightarrow \text{M}^{n+}(\text{aq}) + n/2\text{H}_2(\text{g}) \quad (8) \]

Fig. 7. The corrosion morphology of CoNiFe MEAs in 3.5 wt% NaCl solution and 1 M H2SO4 solution for 30 °C and 60 °C. (a), (b) in 30 °C and 60 °C NaCl solution; (c), (d) in 30 °C and 60 °C H2SO4 solution. a1, b1,c2, d1 images represent the partial enlarge of a, b, c, d images, respectively.
NaCl solution M+ + nH2O(aq) → m/2H2(g) + Mn+(aq)+ nOH− (9)

As we all know, the process of activation polarization involves electrode reaction in anodic and cathodic. Eq. (5) display the principal electrode reactions in the anodic polarization, the surface of alloys react continuously to large a number of metals ion Mn+ produce in solution. And metals ion are slow to diffuse from the alloy surface, result in electrode reaction continue. From Eq. (6), (7), it can be seen that the cathodic reaction is the evolution of hydrogen.

4. Conclusions

CoNiFe MEA samples are prepared by vacuum arc melting and thermo-mechanical processing. The fully-recrystallized FCC single phase microstructures with grain sizes between 10 and 100 μm are selectively produced by rolling and annealing. The grain boundary characteristic distributions (GBCDs) of the rolled CoNiFe MEA samples annealed at different temperature indicate that the fraction of low angle grain boundaries (LAGBs) when the annealing temperature is below 600 °C. The largest fraction of Σ3 is observed from the recrystallized sample processed at 700 °C and this sample possesses superior mechanical properties including high strength and ductility. The Hall-Petch relationship and grain grow kinetics in the CoNiFe MEAs are investigated and the results add to our fundament understanding the coincidence site lattice (CSL) and high angle grain boundaries (HAGBs) when the annealing temperature is below 600 °C.

References

[10] B. Gludovatz, A. Hohenwarter, K.V. Thurston, H. Bei, Z. Wu, E.P. George, R.O. Ritchie, Exceptional coincidence-site lattice (CSL) and high angle grain boundaries (HAGBs) when the annealing temperature is below 600 °C. The largest fraction of Σ3 is observed from the recrystallized sample processed at 700 °C and this sample possesses superior mechanical properties including high strength and ductility.

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References

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References


[50] L. Wei, Y. Liu, Q. Li, Y.F. Cheng, Effect of roughness on general corrosion and pitting of (FeCoCrNi)0.28(WC)0.11 high-entropy alloy composite in 3.5 wt.% NaCl solution, Corros. Sci. 146 (2019) 44–57.