Effects of Iron on Microstructure and Properties of $CoCrFe_xNi$ Multi-principal Element Alloys

Linge Han, Hui Jiang, Dongxu Qiao, Yiping Lu and Tongmin Wang

Abstract In this work, $CoCrFe_xNi$ (x = 2, 3, 4) multi-principal element alloys were designed and synthesized by vacuum arc melting technique, and effects of Fe on microstructure and properties of $CoCrFe_xNi$ alloys were investigated. The crystal phase and microstructure of these alloys were studied by X-ray diffraction and scanning electron microscopy, while mechanical properties were measured by Vickers hardness and compressive tests, respectively. The $CoCrFe_xNi$ alloys presented a single face-centered cubic (FCC) structure with columnar crystal morphology, indicating that the Fe content doesn't change the microstructure of $CoCrFe_xNi$ alloys. However, the lattice parameters of FCC phases decreased with the addition of Fe element. It was found that all the alloys exhibited excellent ductility without fracture. In addition, the yield strength decreased, and the Vickers hardness varied from 124 HV for $CoCrFe_2Ni$ to 109 HV for $CoCrFe_4Ni$.

Keywords Multi-principal element alloys · Microstructure · Crystal phase Mechanical properties

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Introduction

Traditional alloys have been developing for thousands years, which usually have one principal element as the matrix. A new sort of alloys were researched, called multi-principal element alloys (MPEAs) or high entropy alloys (HEAs) [1, 2], which broke through the traditional alloy design concept. In traditional research of physical metallurgy and phase diagrams, intermetallic compounds which caused brittleness would be generated in multiple principal alloys. However, these MPEAs could simplify the microstructure due to the high entropy effect, and form solid solution such as face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal close-packed (HCP) phases [3–7]. These alloys have good comprehensive properties, such as excellent corrosion resistance, wear resistance, thermal stability, etc. [8–10].

The typical CoCrFeNi MPEA has attracted extensive research attention because of its good ductility with a single FCC structure. Many CoCrFeNi-based MPEAs were investigated, such as $CoCrFeNiTi_x$ alloys, $CoCrFeMo_xNi$ alloys, $CoCrFeNb_xNi$ alloys, and so on [11–13]. Above referred research is an efficient strengthening method through addition of larger-atomic size elements (Ti, Mo and Nb). However, the effects of inherent elements on CoCrFeNi alloy also have been rarely researched. In addition, the research has important significance for practical industrial applications. Therefore, effects of Fe element on the microstructure and properties of $CoCrFe_xNi$ MPEAs were investigated in this study.

Experimental Procedures

The purity of master elements is higher than 99.9 wt%. Table 1 shows the nominal atomic percent of $CoCrFe_xNi$ alloys. Alloys ingots were prepared by vacuum arc furnace with re-melting 4–5 times in a Ti-gettered high purity argon atmosphere with the pressure of 0.05 MPa and casted in a water-cooling copper crucible. Alloys ingots were the fastener-like shape with 30 mm in diameter and 10 mm in length. The crystal structures of alloys were analyzed by X-ray diffractometer (Empyrean) with CuKα radiation and a 2θ range from 20° to 100°. Microstructures of alloys were measured through Scanning Electron Microscope (SEM). Moreover, chemical compositions were determined by Energy dispersive spectrometry (EDS). And pure aqua regia was chose (HCL: HNO3 = 3:1) as the corrosive liquid to etch samples before observing microstructures. Universal testing machine tested compressive

Table 1 Nominal composition of $CoCrFe_xNi$ alloys

Alloys	Co (at.%)	Cr (at.%)	Fe (at.%)	Ni (at.%)
$CoCrFe_2Ni$	20	20	40	20
$CoCrFe_3Ni$	16.7	16.7	50	16.7
$CoCrFe_4Ni$	14.3	14.3	57.1	14.3

yield strength and ductility at a strain rate of 1×10^{-3} s^{-1}. The experimental samples of compressive test were cut from ingots with a size of $\Phi 5 \times 10$ mm. Every alloy prepared two samples to assure the accuracy of experimental results. The hardness was carried out by Vickers hardness tester under the load of 500 g applied for 15 s. Every ingot selected at least 5 points to take experiment and calculated the average value as the final results.

Results and Discussion

Crystal Structure. Table 2 shows the values of valence electron concentration (VEC), electro-negativity difference (χ), atomic radius difference (δ), and mixing enthalpy (ΔH). For $CoCrFe_xNi$ alloys, the values of VEC > 8.0, $\delta < 4.72\%$, and 7.27 kJ mol^{-1} < ΔH < 4 kJ mol^{-1} indicate that these alloys should be possessed a simple FCC solid solution structure according to the reports in Refs. [4, 14]. Moreover, the value of χ is below 0.117 in $CoCrFe_xNi$ alloys indicating inexistence of topological close-packed (TCP) phase [15]. The XRD patterns of $CoCrFe_xNi$ alloys are presented in Fig. 1. The XRD peaks are indexed as a single FCC solid solution structure, which consisted with above theoretical prediction. Figure 1b is the magnifying pattern of $(111)_{FCC}$ peak. The peak of $(111)_{FCC}$ moves right gradually with the addition of Fe element. The lattice parameters of CoCrFeNi alloy [16] and $CoCrFe_xNi$ are 3.5752, 3.5709, 3.5543, 3.5473 Å, respectively. The results are in agree with the change of $(111)_{FCC}$ peak in the Fig. 1b.

Table 2 Values of VEC, χ, δ and ΔH for $CoCrFe_xNi$ (x = 2, 3, 4) alloys

Alloys	VEC	χ	δ (%)	ΔH (kJ mol^{-1})
Fe_2	8.200	0.107	1.055	−3.040
Fe_3	8.170	0.079	0.964	−2.560
Fe_4	8.143	0.073	0.894	−2.204

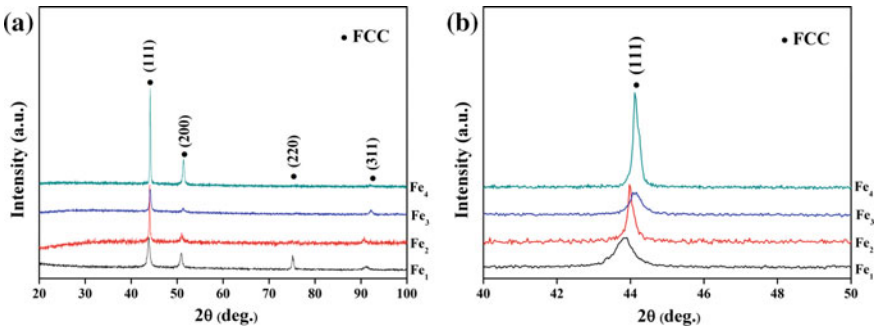

Fig. 1 XRD patterns of $CoCrFe_xNi$ alloys, **a** XRD pattern; **b** magnifying peak of $(111)_{FCC}$

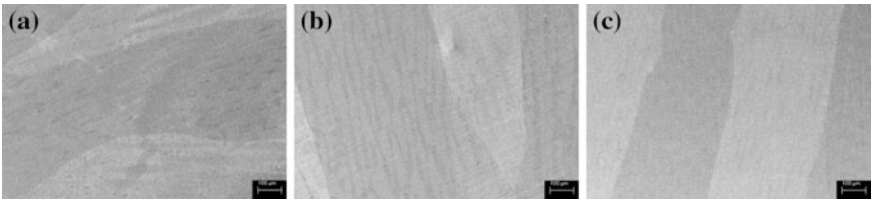

Fig. 2 Microstructure of $CoCrFe_xNi$ alloys, **a** x = 2, **b** x = 3, **c** x = 4

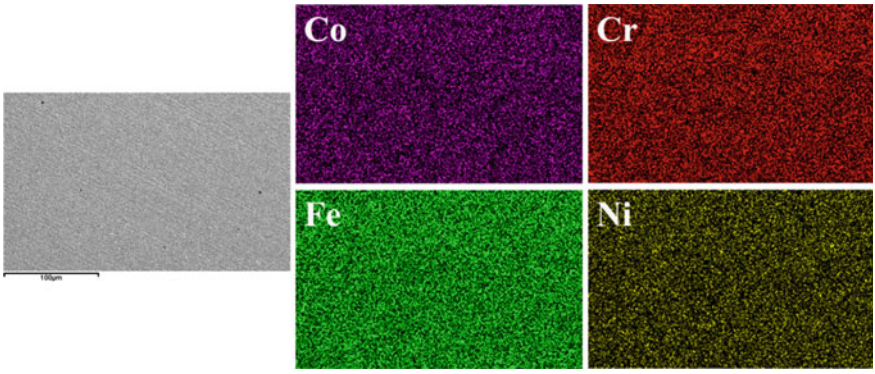

Fig. 3 EDS mappings of $CoCrFe_2Ni$ alloys

Microstructure. Figure 2 exhibits the low magnification SEM images of $CoCrFe_xNi$ alloys. Because water-cooling copper crucible had rather fast cooling rate and ingots weren't thick enough. Grains grew up from bottom to top figuring columnar crystal morphology with a size of 400–500 μm. From EDS mappings of $CoCrFe_2Ni$ alloy shown in Fig. 3, the elements distribution were uniform which was in accord with the microstructure identified the single phase structure. Other alloys were same as $CoCrFe_2Ni$ alloy, and the results weren't put on the article to avoid repetition.

Mechanical Properties. The compressive engineering stress-strain curves of $CoCrFe_xNi$ alloys are showed in Fig. 4. Three alloys exhibit excellent plastic with 50% compressive strain no fracture and the yield strength of 142, 132 and 103 MPa for $CoCrFe_2Ni$, $CoCrFe_3Ni$ and $CoCrFe_4Ni$, respectively. The excellent plastic of the alloys results from the single FCC phase which has multiple easy slip systems.

Figure 5 shows the relationship between Vickers hardness and the Fe content in $CoCrFe_xNi$ alloys. The Vickers hardness decrease from 124 HV for $CoCrFe_2Ni$ to 109 HV for $CoCrFe_4Ni$. With the increase of Fe content, both the Vickers hardness and yield strength decrease. This can be due to the decreased atomic radius difference (see Table 2) which leads to the lower lattice distortion.

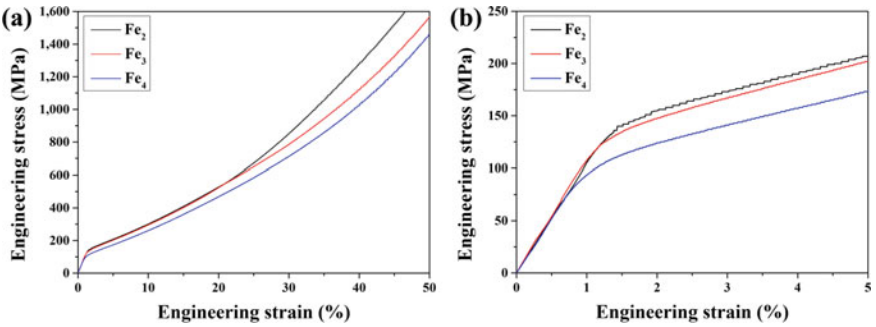

Fig. 4 Compressive engineering stress-strain curves of $CoCrFe_xNi$ alloys, **a** the integral map, **b** the local zoom picture

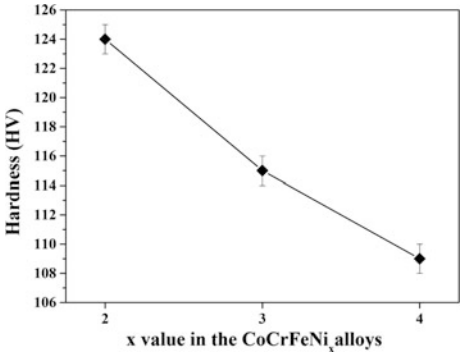

Fig. 5 Vickers hardness of $CoCrFe_xNi$ alloys

Conclusions

In this study, effects of Fe element on microstructure and mechanical properties of $CoCrFe_xNi$ MPEAs were investigated. And conclusions can be drawn as follows:

(1) $CoCrFe_xNi$ alloys present a single FCC structure and the lattice parameters decrease with the addition of Fe element. All the alloys exhibit large columnar crystal morphology with a size of 400–500 μm.
(2) $CoCrFe_xNi$ alloys possessed good ductility without fracture in compressive test. With Fe content increased, both the Vickers hardness and yield strength decrease which can be due to the decreased atomic radius difference.

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