Scripta Materialia 126 (2017) 15–19

Contents lists available at ScienceDirect

Scripta Materialia

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

Regular Article

Phase separation of metastable CoCrFeNi high entropy alloy at intermediate temperatures

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ARTICLE INFO

Article history:
Received 3 July 2016
Received in revised form 12 August 2016
Accepted 12 August 2016
Available online xxxx

Keywords:
Phase separation
High entropy alloys
Annealing

ABSTRACT

CoCrFeNi alloy is an exemplary stable base for high entropy alloys (HEAs), but its phase stability is still suspicious. Here, the CoCrFeNi HEA was firstly identified to be thermally metastable at 750 °C. Composition decomposition occurred after annealed at 750 °C for 800 h. The minor addition of Al accelerated the composition decomposition and a second fcc phase with a different lattice constant occurred in the long time annealed CoCrFeNiAl$_{0.1}$ HEA. The CoCrFeNi HEA cannot be seen as stable alloys anymore and researchers should be very careful when using the current phase selection models to predict stability of HEAs at intermediate temperatures.

The equal-atomic alloy of CoCrFeNi is widely accepted as a thermally stable single-phase solid-solution HEA for its high mixing entropy [1–14]. The CoCrFeNi HEA has face-centered cubic (fcc) crystal structure and high toughness even at cryogenic temperatures [15–17]. However, its strength is far from industrial applications [18], and consequently many researchers treated it as a base alloy. Different from traditional single-based alloys, the CoCrFeNi alloy, as a high entropy base of a new catalog of alloys, has aroused much attention since the concept of HEAs was proposed [19–22]. On the one hand, the equal-atomic CoCrFeNi base is strengthened through solid solution by the mixing of alloying elements with different atomic size. On the other hand, the thermodynamic and kinetic behaviors of the single-phase solid-solution CoCrFeNi alloy will extend the current theory of physical metallurgy.

In the past decade, many researchers took the CoCrFeNi HEA as a base alloy and designed lots of new alloys by adding alloying elements. Many of those CoCrFeNi based alloys showed great potential application prospect [9,10,23–31]. As the base alloy, the physical properties of CoCrFeNi matrix are of great significance from both scientific and industrial aspects. One of the central issues is the phase stability. Lots of efforts have been made to confirm the stable single solid solution of CoCrFeNi HEA. With XRD and neutron diffraction measurements, Lucas et al. [6] found that there is no chemical ordering in the CoCrFeNi HEA. Through TEM and atom probe tomography (APT) characterizations, Cornide et al. [14] also suggested one single fcc solid-solution phase in CoCrFeNi HEA. It was also found that the single fcc solid solution phase in CoCrFeNi was thermally stable after annealed at different temperatures [5–7,9–14,32]. Besides the experimental results, all the present phase selection models, CALPHAD and first principle calculations indicated that the CoCrFeNi HEA should be a stable single fcc solid-solution phase [33–37]. Moreover, plenty of investigations also indicate that minor additions of alloying elements would not affect the phase stability of the CoCrFeNi base [9,10,36,38,39].

Recently, Pickering and Otto reported that the CoCrFeMnNi HEA is unstable at intermediate temperatures [40,41], which brings great challenges to the HEA community. Almost at the same time, by using XRD and neutron diffraction, Dahlborg et al. [42] claimed that the CoCrFeNi alloy should have two fcc phases with a discrepancy of 0.001 Å in lattice parameter. These clues suggest the instability or meta-stability of the CoCrFeNi base. Considering the wide acceptance of the stable CoCrFeNi and CoCrFeNi based HEAs, it is intriguing and urgent to demonstrate whether the CoCrFeNi base is stable or not with clear experiment evidence.

Accordingly, in the present work, we report the metastable state of CoCrFeNi at intermediate temperatures for the first time. The separation of composition is identified, and the decomposition of the matrix into two phases is confirmed with minor additions of Al element.

HEAs ingots were prepared by arc-melting under an argon atmosphere. The purity of raw materials is 99.5%. To achieve a homogeneous distribution of elements in the alloys, each ingot was re-melted for four times. Heat-treatment of the HEA plate samples were performed under air atmosphere at 750 °C for 800 h followed by water-quenching. The phases were characterized by an X-ray diffractometer (XRD, Bruker D8 discover), using Co Kα radiation scanning from 20° to 120° with a scanning rate of 1°/s. The scanning electron microscope (TESCAN VEGA 3) equipped with energy dispersive X-ray spectrometry (EDX) was used to analyze the microstructures and chemical compositions.

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http://dx.doi.org/10.1016/j.scriptamat.2016.08.008
1359-6462/

Standard bright-field images and diffraction patterns were obtained using a transmission electron microscope (TEM TecnaiFG2).

Fig. 1 shows the SEM image, EDX maps and XRD patterns of the long time annealed CoCrFeNi HEA. In the SEM image, a single phase HEA with grain boundaries was observed. Second phase was not found in the whole sample, neither in grain boundaries nor inside the coarse grains. The XRD patterns also showed regular single fcc peaks. The EDX maps confirmed that there was no composition decomposition in the CoCrFeNi HEA in the present resolution. It seems that these preliminary results in Fig. 1 agreed well with previous reports, where the CoCrFeNi HEA was identified to be thermally stable by TEM, APT, high energy X-ray scattering and neutron scattering [6,14].

However, the details in TEM analyses showed distinct evidences of instability in the prolonged annealed CoCrFeNi HEA. The TEM bright field image is presented in Fig. 2(a). A large number of regions with darker fringes were observed. The insets in Fig. 2(a) show selected diffraction patterns of the matrix (inset A) and darker fringes (inset B) regions. The diffraction pattern of the matrix from [001] zone axis shows regular fcc crystal structure. In the darker region, two diffraction patterns from [011] zone axis are presented (marked as red and yellow), indicating a tiny difference of lattice parameters between the two crystals in the selected area. The red diffraction pattern could be identified as the matrix by comparing with the diffraction pattern of the matrix, while the yellow one should be a new separated phase. The elongated diffraction point of the new phase indicates that only very thin slice of new phase decomposed from the matrix.

To further figure out the phase separation, the lattice parameters of the two regions were separately characterized. Fig. 2(b) is the HRTEM image of the darker region and the inset is the corresponding fast Fourier transform (FFT) image. The FFT image shows that the darker region has the same crystal structure with the matrix. A typical atom arrangement with [001] zone axis of fcc single crystal is observed. The lattice parameter of the darker region is 0.355 nm measured from HRTEM image, a little bit different from that of the matrix (0.366 nm measured from diffraction pattern). Even though the bright field TEM image shows a different region with darker contrast, the HRTEM analysis did not found obvious interface of phase boundary across the two different regions and only lattice distortions were observed. The difference of interplanar spacing of (010) planes at different zones in the HRTEM image identified this lattice distortion. Concerning the tiny difference of 0.01 nm in lattice constant between the two phases and the absence of a clear phase interface, the dark fringes in the long time annealed CoCrFeNi HEA can be seen as the composition decomposition, the initial stage of phase separation. The decomposed composition contains atoms with different radii, inducing a difference in lattice constant.

The composition decomposition in the CoCrFeNi annealed at 750 °C is similar to the clustering of GP zones. Usually, precipitates pass through several stages before a final stable structure appears. For example, the first stage in Al-Cu alloys involves local clustering of the solute atoms to form what are commonly called GP zones [43]. GP zones are favored at a low aging temperature, a small atomic size misfit, and a high degree of solute supersaturation. In the CoCrFeNi HEA, the atomic size misfit is small since there is only a small atom size difference among those component elements, but every element could be regarded as supersaturated solute atoms. During the long-term annealing at 750 °C, the supersaturated CoCrFeNi solid solution may decompose into two phases. Besides, Dahlborg et al. [42] reported that the as-cast CoCrFeNi alloy consists two fcc phases with a lattice constant difference of 0.001 Å using diffraction ways. The lattice constant difference in this study is much larger, so it is possible that the two fcc phases in the CoCrFeNi HEA evolved from metastable state to steady state. According to the above results, it is reasonable to deduce that a fcc phase with different lattice parameters can appear in the CoCrFeNi HEA through long time annealing at 750 °C.

We have confirmed that the single solid solution CoCrFeNi HEA is metastable at 750 °C. However, the long-term annealing is necessary to observe the phase separation. The long-term existence of metastable state is attributed to the large energy barrier or the small driving force for it to evolve to a steady state. From another perspective, increasing the lattice distortion may aggravate the composition decomposition. Moreover, Xu et al. [44] found that nano-scale phase separation can take place to efficiently minimize the lattice distortion caused by atom size difference of the constituent elements. Therefore, minor additions of alloying elements with large atomic radius will greatly accelerate the decomposition process. Here, the stability of CoCrFeNiAl$_{0.1}$ was investigated to confirm this prediction. The limit solubility of Al element in Co, Cr, Fe and Ni at 750 °C are much larger than 3 at.% according to their binary phase diagrams [45], thus minor addition of Al element does not lead to the formation of aluminide. However, the atom radius of Al element is much larger than that of other four elements.

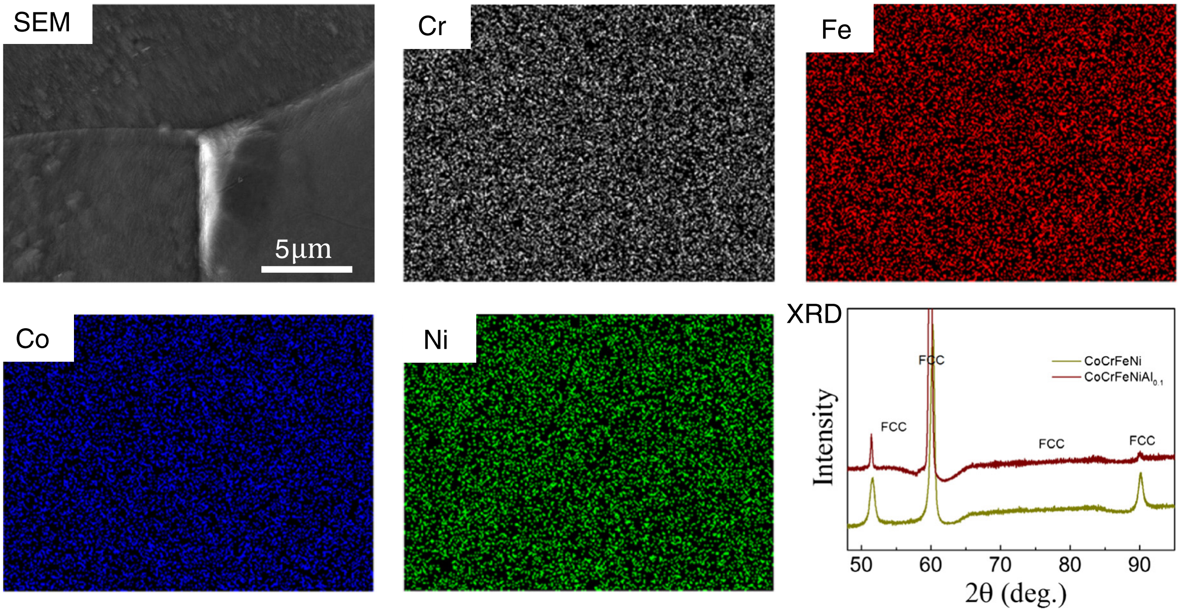

Fig. 1. SEM images and EDX maps of the CoCrFeNi HEA annealed at 750 °C for 800 h. EDX maps illustrated that there is no composition decomposition in the long time annealed CoCrFeNi HEA. The XRD patterns of the CoCrFeNi and CoCrFeNiAl0.1 alloys showed that both the two alloys have fcc crystal structures and the CoCrFeNiAl0.1 HEA has a relative larger distortion.