Intermetallics 79 (2016) 1–11

Contents lists available at ScienceDirect

Intermetallics

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

Compositional dependence of phase formation and mechanical properties in three CoCrFeNi-(Mn/Al/Cu) high entropy alloys

Z.G. Zhu [a], K.H. Ma [a], Q. Wang [b], C.H. Shek [a, *]

[a] Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China
[b] Department of Mechanical and Biomedical Engineering, City University of Hong Kong, Hong Kong, China

ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form
27 June 2016
Accepted 14 September 2016

Keywords:
High entropy alloys
Phase formation
Microstructure
Mechanical property

ABSTRACT

Starting from three typical equiatomic CoCrFeNiMn, CoCrFeNiAl and CoCrFeNiCu high entropy alloys (HEAs), we systematically investigated the compositional dependence of phase formation and mechanical properties of 78 alloys by varying the atomic ratio of the constituent elements. It was found that the simple phase structures, including a single face-centered cubic (FCC) or body-centered cubic (BCC) phase, duplex FCC phases, duplex BCC phases, instead of intermetallics, could form within a broad compositional landscape in 68 out of the 78 alloys not limited to the equiatomic composition where the configurational mixing entropy is maximum. This fact indicates that it may be the nature of the constituent elements that leads to simple phase structure formation. With compositional variation, the microstructure and mechanical properties including hardness and tensile properties show corresponding changes. It was found that the hardness variation of samples within the same structure is smaller for the FCC than that of the BCC. Tensile results indicated that the tensile elongation of $(CoCrFeMn)_{(100-x)}Ni_x$ ($x = 0$, 10 and 20) alloys increases with Ni addition due to the decreasing volume fraction of sigma phase. For the $(CoCrFeAl)_{(100-x)}Ni_x$ (x = 27.3, 33.3, 38.5, 42.9 and 50) alloys, the yield strength decreases and tensile elongation increases with Ni addition due to decreasing volume fraction of BCC phase which is hard yet brittle. The present results are important to understand the phase formation and relationship between microstructure and mechanical properties in HEAs.

1. Introduction

High entropy alloys (HEAs), which usually contain five or more elements with equal or near equal atomic ratio, have attracted significant attention from both scientific and technological viewpoints in the past decade [1–4]. Though its definition is still under discussion, for example, some quaternary medium entropy alloys have also been termed as HEAs [5], this does not affect the exploration of this new class of materials [6]. From the technological perspective, HEAs exhibit outstanding properties, such as the extremely high fracture toughness [7,8], exceptionally high temperature strength [9], good wear resistance [10], etc., which make them potential candidates for high temperature applications [11]. Due to their complex compositional design and relatively simple phase structure, HEAs could serve as model systems to investigate the scientific problem of phase formation of multicomponent alloys, which is not covered in currently available phase diagrams.

As far as the phase formation of HEAs is concerned, the high configurational mixing entropy (ΔS_{mix}) of alloys containing multiple elements has been proposed to stabilize the single phase by Yeh et al. [12] since its advent. However not all the multicomponent alloys would form a single phase structure, which is in fact quite rare [13]. Intermetallics [14] or even metallic glasses (MGs) [15,16] form for some multicomponent alloys, and this makes the role of configurational mixing entropy questionable. Recently, the role of mixing entropy was further challenged both theoretically and experimentally [17,18]. Ma et al. [17] found that the vibrational, electronic and magnetic entropy are on an equal footing to predict the phase formation through *ab initio* methods. Experimentally Otto et al. [18] found that when each constituent element of CoCrFeNiMn was substituted by another element with the same room temperature crystal structure and comparable size/electronegativity while keeping the mixing entropy the same, multiple phases were observed in all but the base CoCrFeNiMn alloy. This gave direct evidence that the mixing entropy may not be the dominating factor of phase formation for multicomponent alloys.

* Corresponding author.
E-mail address: apchshek@cityu.edu.hk (C.H. Shek).

http://dx.doi.org/10.1016/j.intermet.2016.09.003
0966-9795/

Thus the prediction of phase formation and alloy design of HEAs still need to be clarified. Generalizing from the role of atomic size difference in Hume-Rothery rule [19] to understand the phase formation of binary alloys, Zhang et al. [14] found that the atomic size mismatch (δ) also plays an important role besides the mixing enthalpy (ΔH_{mix}) for the phase formation of HEAs. The single phase usually forms in the composition range where δ is small and ΔH_{mix} is near zero. The single solid solution was predicted, but it still could not predict when the body-centered cubic (BCC) or face-centered cubic (FCC) structure forms. To solve this problem, Guo et al. [20] found that FCC phases are stable at higher valence electron concentration (VEC, VEC $\geq$ 8) while BCC phases are stable at lower VEC (VEC < 6.87). Besides δ, ΔH_{mix} and VEC, several other parameters [21–32] have been proposed aiming at understanding what factors dominate the phase formation of the HEAs. For example, from the residual strain perspective, Ye et al. [21] found that the transition from single phase to multi-phase is observed at the root-mean-square residual strain of 5%. However the proposed parameters are mainly based on the statistics of the reported HEAs hitherto, newly developed alloys may violate the proposed parameters [33], and thus phase formation of more HEA systems are needed to verify and amend the present proposed parameters.

In spite of the unsolved scientific problems, many novel HEAs have been developed [34–43] from technological perspective due to their promising characteristics. Among them three CoCrFeNi-(Mn/Al/Cu) multicomponent alloys forming simple FCC or/and BCC phase instead of intermetallic compounds have been investigated thoroughly [7,33,44–51], including the mechanical properties [7], phase formation [44–46], phase stability [33], phase separation [47–50], etc. CoCrFeNiMn [44] with single FCC phase is a model HEA system which shows extremely high fracture toughness [7], high thermal stability [33]. CoCrFeNiAl with two BCC phases which include Ni–Al-rich and Ni–Al-depleted regions is a typical HEA system [49–51]. Its microstructure and mechanical properties are dependent on the Al content [51]. CoCrFeNiCu HEA with two FCC phases is a model system to investigate the phase separation in HEAs [46–49]. The microstructure and mechanical properties of materials are well known to be sensitive to the composition [52,53]. With composition variation, microstructure and properties of alloys show corresponding changes. This also works for the HEAs [51], however, systematic study on the "composition-phase formation-microstructure-mechanical properties" is rare for the above three HEA systems [51,54]. As a result, outstanding questions still remain relating to these three typical CoCrFeNi-(Mn/Al/Cu) HEA systems, namely, (1) to what compositional extent could the simple phase structure still remain stable for the these alloys; (2) How do the mechanical properties evolve with the composition and microstructure, especially on the hardness and tensile properties [54–56]. Investigations focusing on the 1st question could help to test and amend the role of reported phase formation criteria. Study on the 2nd question could help to understand the "microstructure-property" relationship and help to design materials with optimized properties.

In the present research, starting from the three typical CoCrFeNi-(Mn/Al/Cu) HEAs as model systems, we intended to answer the above questions by investigating the phase formation of 78 alloys based on Co–Cr–Fe–Ni-(Mn/Al/Cu) in a broad compositional landscape, and the "composition-phase formation-structure-mechanical properties" relationship in part of the alloys.

2. Experimental

Staring from the three CoCrFeNi-(Mn/Al/Cu) HEAs, 78 alloys listed in Table 1 were prepared and investigated. Alloy ingots were prepared by arc-melting a mixture of high purity metals in a Ti-gettered high purity argon atmosphere. These ingots were flipped and remelted at least five times to ensure the chemical homogeneity. The alloy ingots were then cast in copper mould into rods with diameter of 5 mm or plates with dimension of 2 mm or 1 mm × 10 mm × 70 mm. The rod samples were used for structural characterization while plate samples were used for tensile experiments (For the $(CoCrFeMn)_{(100-x)}Ni_x$ samples, plates with thickness of 2 mm were used while for the $(CoCrFeAl)_{(100-x)}Ni_x$ samples, plates with thickness of 1 mm were used).

Table 1
Alloy systems investigated in the present research.

Alloy system	Alloy composition
Co–Cr–Fe–Ni–Mn	$(CoCrFeMn)_{(100-x)}Ni_x$ (x = 0, 5, 10, 12.5, 15, 20, 27.3, 33.3, 42.9)
	$(CrFeNiMn)_{(100-x)}Co_x$ (x = 0, 5, 10, 15, 20, 33.3)
Co–Cr–Fe–Ni–Al	$(CoCrFeAl)_{(100-x)}Ni_x$ (x = 0, 5, 10, 15, 20, 27.3, 33.3, 38.5, 42.9, 50)
	$(CoNiCrAl)_{(100-x)}Fe_x$ (x = 0, 5, 10, 15, 20, 33.3)
	$(CoFeNiAl)_{(100-x)}Cr_x$ (x = 0, 5, 10, 15, 20, 33.3)
	$(CrFeNiAl)_{(100-x)}Co_x$ (x = 0, 5, 10, 15, 20, 33.3)
Co–Cr–Fe–Ni–Cu	$(CoCrFeCu)_{(100-x)}Ni_x$ (x = 10, 15, 20, 33.3)
	$(CoCrCuNi)_{(100-x)}Fe_x$ (x = 0, 5, 10, 15, 20, 33.3)
	$(CoFeNiCu)_{(100-x)}Cr_x$ (x = 0, 5, 10, 15, 20, 33.3)
	$(CrFeNiCu)_{(100-x)}Co_x$ (x = 0, 5, 10, 15, 20, 33.3)
Quaternary alloys	$(FeCoMn)_{(100-x)}Ni_x$ (x = 0, 5, 10, 15, 20, 25, 40)
	$(FeCoCr)_{(100-x)}Ni_x$ (x = 0, 5, 10, 15, 20, 25, 40)
	$(FeCoCr)_{(100-x)}Al_x$ (x = 0, 5, 10, 15, 20, 25, 40)

Crystal structures of the samples were analyzed by x-ray diffraction (XRD; Rigaku SmartLab) using Cu K_α radiation. The microstructure was examined with an optical microscope (OM; Olympus B061), scanning electron microscope (SEM; JSM-820) equipped with energy dispersive spectroscopy (EDS), and by transmission electron microscopy (TEM; Philips CM-20). The samples for OM were chemically etched in a mixed solution of HNO_3: HCl: H_2O = 1: 3: 6. TEM samples were firstly mechanically ground to ~20 μm followed by ion milling at room temperature.

Flat dog-bone-shaped tensile specimens with a gauge length of 12.5 mm were machined from the as-cast plate samples by electric discharge machine. The tensile specimens were ground on each side to remove scratches, resulting in a final specimen with a thickness of 1.6 mm (or 0.8 mm) and a gauge section of 3.2 mm. Tensile tests were carried out in a screw-driven Instron 5567 test rig at an engineering strain rate of 10^{-3} s^{-1}. Hardness measurements were conducted using a Vickers hardness tester with a load of 500 g, and at least 15 indents were measured to obtain an average value for each sample.

3. Results and discussion

3.1. Phase formation and transition

3.1.1. Phase formation of quinary alloys

3.1.1.1. CoCrFeMnNi. CoCrFeMnNi, first discovered by Cantor et al. [44], is a model HEA with excellent microstructural stability [33] and outstanding fracture toughness [7]. Previous results [57] indicate that the quaternary CoCrFeMn and CrFeNiMn alloys in the as homogenized state exhibit multi-phase structure while other quaternary alloys based on Co–Cr–Fe–Mn–Ni form a single FCC phase. In the present research, $(CoCrFeMn)_{(100-x)}Ni_x$ and $(FeNiCrMn)_{(100-x)}Co_x$ alloys were prepared. Fig. 1(a) shows the XRD patterns of $(CoCrFeMn)_{(100-x)}Ni_x$ alloys. It could be seen that with increasing Ni content, the structure evolves from multi-phase to a single FCC phase. A sigma phase with tetragonal structure forms for the base CoCrFeMn alloy in addition to the primary FCC phase, and this is in accordance with Wu's [57] and Tasan's [58] results. With