Intermetallics 77 (2016) 23–33

Contents lists available at ScienceDirect

Intermetallics

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

Affordable FeCrNiMnCu high entropy alloys with excellent comprehensive tensile properties

Z.Y. Rao, X. Wang, J. Zhu, X.H. Chen, L. Wang, J.J. Si, Y.D. Wu, X.D. Hui*

State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form
20 June 2016
Accepted 21 June 2016
Available online 16 July 2016

Keywords:
High entropy alloys
Mechanical properties
Microstructure
Solid solution strengthening

ABSTRACT

$Fe_{0.4}Cr_{0.4}NiMn_xCu$ ($0 \leq x \leq 1.4$) high entropy alloys (HEAs) were prepared by copper-mold casting. The phase selection, microstructure, tensile properties and fracture morphologies were investigated. The microstructure with dual FCC phases was formed in the as-cast HEAs with $x \leq 1$, and BCC phase was crystallized from the central FCC dendrites of HEAs with $x = 1.2$ and 1.4. In homogenized $Fe_{0.4}Cr_{0.4}NiMnCu$ HEA, needle-like shaped BCC phase was formed resulting in a slight enhancement of yield strength. Compositional heterogeneity was detected in both FCC and BCC dendrites. These HEAs exhibit excellent comprehensive tensile properties, *e.g.* the yield strength, ultimate strength and elongation of the HEA with $x = 1$ reaches 439 MPa, 884 MPa and 23.4%, respectively. High density of dislocations in FCC matrix was formed after tensile deformation. FCC type of fine polyhedra, which is mainly composed of Cr, Mn and O, is formed in dendrites. In this work, the phase selection and strengthening mechanism were evaluated based on atomic size factor. It was found that two criteria can be employed to predict the phase regions of current alloys. The solid solution strengthening for this HEA system is the most important among the four kinds of strengthening mechanisms.

\

1. Introduction

For thousands of years, the conventional strategy of alloys design is based on one or two principal elements and mediated with other minor elements. This kind of design logos has brought us a plenty of engineering alloy systems such as Fe-, Al-, Cu- and Ni-based alloys, *etc*. Recently, a new kind of alloys, named high entropy alloys (HEAs) has been developed by using a subversive design strategy. In contrast to classical engineering alloys, HEAs contain 5–13 kinds of elements with equimolar or near equimolar compositions. The atomic fraction of each element is between 5 and 35 at.% [1,2]. According to traditional point of view, high concentration of alloying elements may cause the formation of intermetallic compounds, but not terminal solid solution phases (SS). This rule has been cracked with the discovery of HEAs due to the formation of high configurational entropy [1–8]. Simple SS phases, such as face centered cubic (FCC) or body centered cubic (BCC) *etc*, have been formed in some HEAs. These HEAs have been found to possess unique mechanical, physical and chemical properties. For example, FCC structured HEAs exhibit low strength and high plasticity, whereas BCC structured HEAs show the opposite trend in the strength and plasticity [9].

Of all kinds of HEAs, FCC structured HEAs have been widely researched to date. Most elements in FCC HEAs are transition metals in the forth period in the periodic table of elements. For instance, FCC structured FeCoCrNiMn HEA exhibits exceptional mechanical properties with fracture strength and tensile elongation reaching to 496 MPa and 61.7%, respectively, at room temperature. With the addition of Al, the fracture strength of this kind of HEAs is improved to 529 MPa and the elongation is reduced to 47.2%. Bernd Gludovatz et al. found that FeCoCrNiMn HEA has much higher fracture toughness at cryogenic temperature due to the strengthening mechanism similar to that of high Mn bearing austenitic TWIP steels. He et al. proposed a further strengthening method to improve the toughness of FeCoNiCr HEA by adding Al and Ti to induce the precipitation of nano-size precipitates [10–14]. Taking cost into account, however, these HEAs are comparable to some Ni-base superalloys, and much higher than most of steels due to the addition of Co. The high cost has become one of the problems to restrict the engineering application of Co-

* Corresponding author. Tel.: +86 10 62333066; fax: +86 10 62333447.
E-mail address: xdhui@ustb.edu.cn (X.D. Hui).

http://dx.doi.org/10.1016/j.intermet.2016.06.011
0966-9795/

containing HEAs [9].

Recently, Co-free (or low content of Co bearing) HEAs have been investigated. Chen et al. substituted Co element by Mn in AlCrCuFeCoNi HEA. They found that AlCrCuFeMnNi is composed of both FCC and BCC phase, and the addition of Mn enhances the formation of BCC phase, leading to an improvement of hardness and decrease of plasticity [23]. Ren et al. designed CuCrFeNiMn HEA alloy based on the concept of Ni- and Cr-equivalent. It is shown that the HEAs with higher Ni_{eq} consist of a single FCC solid solution phase, and those with higher Cr_{eq} have FCC + BCC structure [24]. They prepared three kinds of Co-free HEAs with single FCC phase. However, the tensile properties of these HEAs have not been reported. Very recently, Chun Ng et al. [25] prepared $Al_{0.5}CrCuFeNi_2$ HEA with a fracture stress of 500 MPa and an elongation of 16.1%, respectively. Ma et al. [26] performed cold rolling and subsequent annealing for $Al_{0.5}CrCuFeNi_2$ HEA. It was found that cold-rolled alloy demonstrates a large yielding strength of 1132 MPa but a very limited tensile elongation of 1.6%. All these Co-free HEAs are much cheaper, but show relatively lower elongation, than FeCoNiCrX HEAs.

In this study, Co-free $Fe_{0.4}Cr_{0.4}NiMn_xCu$ HEAs with Mn content changing from $x = 0$ to $x = 1.4$ are investigated. This alloy system is designed as nonequiatomic HEAs in order to form FCC or FCC + BCC phase. The microstructure and tensile properties of these HEAs are characterized at room temperature. And the phase selection and strengthening mechanism were studied by TEM technology and evaluated based on atomic size factor.

2. Experimental methods

In this work, $Fe_{0.4}Cr_{0.4}NiMn_xCu$ HEAs with $x = 0$, 0.2, 0.4, 0.6, 0.8, 1, 1.2, and 1.4 (denoted as Mn0, Mn0.2, Mn0.4, Mn0.6, Mn0.8, Mn1, Mn1.2 and Mn1.4, respectively, in the following context) were designed. The alloy ingots were prepared by arc-melting elements with the purity higher than 99 wt% in vacuum arc furnace in a water-cooled copper hearth under a Ti-gettered argon atmosphere. To ensure the chemical homogeneity, the alloys were remelted at least four times. Then the specimens with the dimension of $10 \times 10 \times 60$ mm^3 were prepared by using a water-cooled cooper mold cast. At last, the sample was homogenized at 1000 °C for 24 h, followed by water quenching.

The tensile properties were measured at room temperature by CMT4105 universal electronic tensile testing machine with a nominal strain rate of 1×10^{-3} s^{-1}. The tensile samples were artificially machined to plate shaped specimens with gauge geometry of 1 mm × 5 mm × 10 mm. To ensure the facticity of tensile properties, at least four samples were prepared for each nominal composition of HEA.

The phase structure was characterized by X-ray diffraction (XRD) using a PHILIPS APD-10 diffractometer (Philips, Amsterdam, the Netherlands) with Cu Kα radiation. The XRD scanning angles are ranged from 20° to 100° and the scanning rate is 5° per min. The microstructure and fracture morphologies were investigated by ZEISS SUPRA 55 scanning electron microscope (SEM) with energy-dispersive spectrometry (EDS). The proportion of dendrite region and interdendrite region is computed by Adobe Photohop CS4 using at least three SEM micrographs for each alloy. The refined microstructures were studied by FEI G^2F20 type of transmission electron microscope (TEM). The TEM samples were primarily punched to Φ3 mm of circular sheets and then ground to about 50 μm in thickness, followed by twin-jet electro-polishing using a solution of HNO_3:CH_4O = 1:4 with a voltage of 25 V and a current of 80 mA at the temperature of 230 K.

3. Results and discussion

3.1. Microstructural characterization

The phase compositions of as-cast $Fe_{0.4}Cr_{0.4}NiMn_xCu$ alloys with different Mn concentrations can be differentiated by XRD patterns. As shown in Fig. 1, there is only one set of FCC phase peaks in the microstructure when the amount of Mn is $0 \leq x \leq 1.2$. Actually, there is some BCC phase in the HEA with $x = 1.2$ when observed by SEM (which will be discussed later). As the amount of Mn is increased to $x = 1.4$, a weak peak arises at the 2 theta of 55°, indicating that a new BCC phase appears. From Fig. 1(b), it is seen that the peaks of FCC phase shift towards lower angle side with the increase of Mn content because of the larger radius of Mn atom than those of other four elements. In addition, the peaks of FCC phase are broadened as Mn is added to this group of alloys. A shoulder emerges on the original (111) peaks of the HEAS with Mn content of x = 0.2–1.2. According US patent 9150945 B2 [27], there are actually two FCC phases with similar lattice parameters in FeCoCrNiCu HEAs, although x-ray shows one sets of FCC peaks. Therefore, the feature of broaden (111) peak together with a shoulder means that Mn containing HEAs are composed of two kinds of FCC phases. This deduction may be further verified by the SEM observation and EDX measurement in the following section.

The SEM backscattering electron micrographs of $Fe_{0.4}Cr_{0.4}NiMn_xCu$ HEAs are shown in Fig. 2. Typical dendritic microstructures can be observed in all of the as-cast alloys. As the amount of Mn is increased in these HEAs, dendrites become thinner and the volume fraction of interdendrite region increases. When the fraction of Mn reaches $x = 1.2$, a new kind of dendritic appears. Combining the SEM image with XRD patterns, it can be inferred that this new kind of dendrites has BCC type of structure. This result is similar to that of Ref. [23]. As shown in Fig. 2 and the EDX results listed in Table 1, there is compositional segregation in both the FCC and BCC phases of as-cast samples. In FCC phase, Fe, Ni and Cr elements are enriched in dendrite and depleted in interdendrite region. On the contrary, Mn and Cu atoms were repelled into interdendrite region. Especially, the atomic ratio of Cu element in dendrite and interdendrite region reaches above 4, reflecting there is indeed a severe heterogeneity in composition distribution in FCC phase. Due to the compositional heterogeneity mentioned above, it can be considered that there are two FCC phases in current alloys. When further analyzing the composition of BCC phase, it is found that the BCC phase is enriched with Fe and Cr but depleted with Ni, Mn and Cu. The concentration of Cr in the BCC phase of Mn1.4 alloy reaches 47.9%, which is about 5 times as the nominal composition. It is also found that with the increase of Mn, the segregation of Fe and Cr between dendrite and interdendrite region is aggravated, whereas the partitioning of Ni is decreased. With the decrease of Ni and increase of Cr and Fe in FCC dendrite, the FCC phase becomes instable. From Fig. 2(g) and (h), it is shown that BCC phase is crystallized in the dendrite of FCC phase but not in the interdendrite region. Therefore, it is reasonable to infer that the formation of BCC phase is due to the redistribution of solutes in FCC dendrites induced by the addition of Mn.

To further explore the structure of these HEAs, we performed TEM investigation of deformed Mn1 HEA. From Fig. 3(a), it is found that there is high density of dislocation lines in the FCC matrix, indicating that strong work hardening has been produced. A polyhedron phase with a side length of 0.5–1 μm can be observed in Fig. 3(b). According to the selected area electron diffraction (SAED) pattern, this polyhedron phase can be calibrated as FCC structure with a lattice parameter of 0.415 nm. From the EDS pattern (Fig. 3(c)), the polyhedron phase contains O, Cr and Mn. This phase has been reported by Gludovatz and Zaddach et al.