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The microstructural evolution and hardness of the equiatomic CoCrCuFeNi high-entropy alloy in the semi-solid state

L.J. Zhang [a], J.T. Fan [a], D.J. Liu [a], M.D. Zhang [a], P.F. Yu [a], Q. Jing [a], M.Z. Ma [a], P.K. Liaw [b], G. Li [a, b, *], R.P. Liu [a, **]

[a] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, 066004, China
[b] Department of Materials Science and Engineering, The University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

The semi-solid slurries of the CoCrCuFeNi high entropy alloy (HEA) were fabricated through the recrystallization and partial melting (RAP) process by cold-rolling and partial remelting. Based on Kim's theory, the solidus-liquidus temperature range and the fraction of the liquid phase as a function of temperature were examined from the Differential Scanning Calorimetry (DSC) curve. The effect of isothermal temperature and soaking time on the microstructural evolution of the CoCrCuFeNi HEA in a semi-solid state were analyzed. The results showed that the globular structure was obtained without the new phase formed for the semi-solid slurries, containing two face-centered-cubic (FCC) solid-solution phases. The average grain size of the globular grain and the globular degree increased with increasing the isothermal temperature and soaking time. The study of the coarsening kinetics indicated that the coarsening process could be described by the modified liquid film migration model. The sluggish diffusion effect of the current HEA leaded to the low coarsening rate, compared with other conventional alloys. However, the existence of the liquid phase in the semi-solid state resulted in a higher grain growth rate for the CoCrCuFeNi HEA with a lower activation energy of 206.9 kJ/mol, compared with the diffusion couple and the grain growth process for the other HEAs at low temperatures. To evaluate the mechanical properties, Vickers hardness was measured to represent the strength of the CoCrCuFeNi HEA. The CoCrCuFeNi semi-solid slurries showed a Hall-Petch type relationship of the average grain size dependence on Vickers hardness.

1. Introduction

High entropy alloys (HEAs), as a new alloy design concept, have attracted much attention in recent years. Unlike the traditional "single-element" base idea, HEAs are the multi-component alloys with equimolar or near-equimolar compositions [1,2]. Due to the excellent cryogenic mechanical properties [3,4] and outstanding thermal stability [5], HEAs were treated as a promising structural material. Many researchers have carried out various methods to tailor the structure to further improve the mechanical properties of the HEAs. For example, the nanocrystalline HEAs with high strength were fabricated by mechanical alloying followed via spark plasma sintering [6], high-pressure torsion [7], and equal-channel angular pressing [8]. The $AlCoCrFeNi_{2.1}$ eutectic HEA was prepared with modulated lamellar structures and high strength and high ductility [9,10]. The precipitation-strengthened HEAs being alloyed with Al [11], Al/Ti [12], Nb [13], Mo [14], and Gd [15] additions were designed. The semi-solid forming technology was a simple and practical method to control the structure of the alloys, which might be used in the HEAs to obtain superior mechanical properties.

The semi-solid metal process (SSM), as the most promising material-forming process in the 21st century, combined with the advantages of solidification and plastic processing, such as the good flowing ability, low resistance to deformation, and easy formation of complex and high precision parts [16,17]. The most critical stage in the SSM process is to obtain the semi-solid slurry with a uniform, small non-dendritic structure. The required globular microstructure

* Corresponding author. State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, 066004, China.
** Corresponding author.
E-mail addresses: gli25@utk.edu, gongli@ysu.edu.cn (G. Li), riping@ysu.edu.cn (R.P. Liu).

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can be produced by either a liquid state route or a solid-state route. The solid-state route included the strain-induced melt activated (SIMA) method and recrystallization and partial melting (RAP) method [18]. Many researchers have been devoted to studying the microstructural evolution of different materials by the solid-state route, due to the advantages of the high density, non-polluting, and wide range of applications, especially for the preparation of high melting point non-dendritic alloys [18–22]. The effects of plastic deformation, isothermal temperature, and soaking time in the appropriate semi-solid temperature range on the microstructural evolution and tensile properties of the A380 aluminum alloy have been investigated by the SIMA and RAP method [20]. Chen et al. [21] pointed out that SIMA process could produce the ideal, fine semi-solid microstructure, in which spheroidal α-Mg grains have a little of entrapped liquid. The relationship among the degree of grain spheroidization, holding time, and liquid fraction during isothermal treatment was also discussed. However, the research focuses on the low melting points of the aluminum alloy and magnesium alloy. There are few reports about the high melting point alloys, especially for the HEAs. Recently, Rogal [22] has obtained the globular microstructure of the CoCrCuFeNi HEA required for the thixoforming process by the RAP method. But the author had not given out the effect of semi-solid conditions (isothermal temperature and time) on the microstructural evolution, mechanical properties, and the coarsening mechanism during the semi-solid process. These explorations will be very interesting and meaningful and expand the understanding and application of HEAs.

The objective of the present paper was to select a dual-phase FCC CoCrCuFeNi HEA. The semi-solid slurry was fabricated, through the RAP process by cold-rolling and partial remelting. The purpose of the present work is to investigate the effect of isothermal temperature and soaking time on the microstructural evolution and hardness of the CoCrCuFeNi HEA in the semi-solid state process. What's more, the coarsening kinetics of the CoCrCuFeNi HEA in a semi-solid state is also studied. The results of this investigation can provide a guide for the fabrication of the HEA semi-solid slurry and the application of the SSM technology in HEAs.

2. Experimental procedure

The equiatomic CoCrCuFeNi HEA was synthesized in a vacuum arc melting furnace with a water-cooled Cu crucible under a Ti-gettered high-purity argon atmosphere by arc-melting a mixture of pure metals (purity > 99 wt%). The alloy was re-melted six times in order to obtain good chemical homogeneity. The rectangular sample with a dimension of 30 mm × 30 mm × 7 mm was cut from the as-cast button. The sample was subjected to multi-pass cold-rolling to ~50% reduction in thickness using a two-high rolling machine with 140 mm diameter rolls. The Differential Scanning Calorimetry (DSC) curve was measured, using a Netzsch STA 449C at the rate of 10 °C/min, up to 1500 °C in an argon atmosphere. The solidus-liquidus temperature range and liquid phase fraction were determined from the DSC curve. According to the DSC curve, the isothermal temperature was selected as 1160 °C, 1200 °C, and 1250 °C, and the soaking time was selected as 5 min, 20 min, 60 min, and 120 min respectively. The pre-deformed samples were partial remelted in the high-temperature vacuum tube furnace at the heating rate of 10 °C/min, followed by water quenching.

The X-ray diffraction (XRD) measurements of the crystal structure were identified using a D/MAX-2500/PC diffractometer with Cu Ka radiation (λ = 1.54 Å). The Hitachi S-3400 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) detector was performed to characterize the microstructure and phase distribution. The chemical compositions of different phases were determined through the SEM energy dispersive spectrometer (EDS). The EDX maps were acquired to check for the elemental distribution. Statistical analysis of the average grain size and shape factor was performed, using the Image-Pro Plus software. Vickers hardness measurements were conducted, using a hardness tester (HVS-1000) under a load of 300 g for 10 s, and for each specimen, at least 20 measurements were carried out to obtain an average value.

3. Results

3.1. Starting materials and calorimetric results analysis

The microstructure of the as-cast CoCrCuFeNi HEA was the typical dendrite (DR) and interdendrite (ID) structures, as shown in Fig. 1(a). The dual-phase FCC structure was identified with the XRD in Fig. 2. The DR structure is the FCC2 matrix phase with a high volume fraction. Among the DR area, the ID phase with the low volume fraction is the FCC1 phase. The chemical composition of the FCC1 and FCC2 phases revealed that the FCC1 phase was a Cu-rich phase, and the FCC2 phase was a near-equiatomic concentration of Co, Cr, Fe, and Ni phase (see Table 1). The reason leading to a strong segregation of Cu in the FCC1 phase from the EDS results is the positive mixing enthalpy of Cu-Cr, Cu-Co, Cu-Fe, and Cu-Ni [23]. The average grain size of the FCC2 phase was ~30 μm (in width). The Cu-enriched FCC1 phase with the thickness of 0.8–4.5 μm and the length of 3–50 μm occurred among the FCC2 phase. The volume fraction of the FCC2 phase was estimated to be ~85%, using the Image-Pro Plus software. The pre-deformed specimen after cold-rolling to ~50% reduction in thickness showed a severe grain flow, as shown in Fig. 1(b). The average grain size and volume fraction of the FCC2 phase became ~22 μm (in width) and ~86%. The pre-

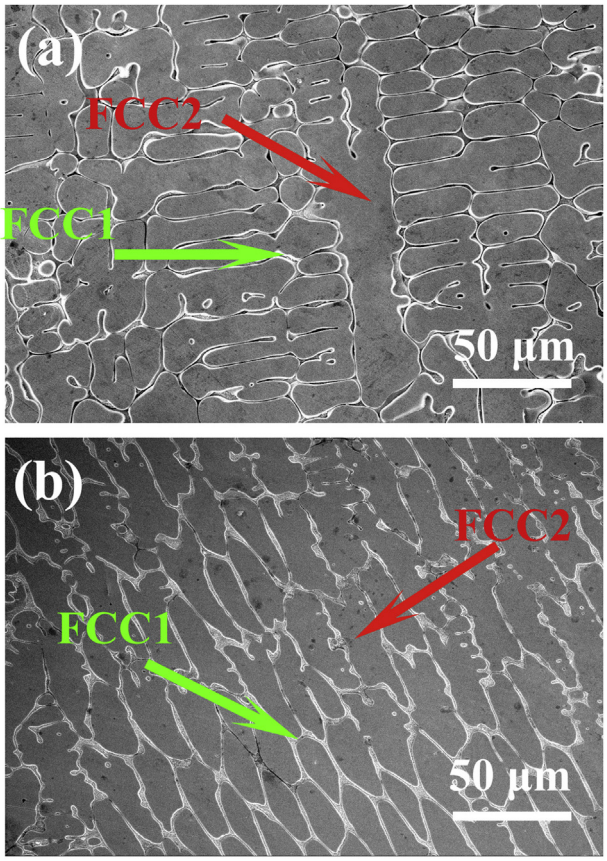

Fig. 1. SEM microstructure of the as-cast (a) and cold-rolled (b) CoCrCuFeNi HEA.