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Improved the microstructure and mechanical properties of AlFeCoNi high-entropy alloy by carbon addition

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ABSTRACT

A new set of AlFeCoNiC$_x$ (x = 0, 0.02, 0.04, 0.08, 0.17) high-entropy alloys (HEAs) were designed and fabricated. The microstructure, phase evolution and mechanical behaviors of the alloys were systematically investigated. Results show that the matrix alloy exhibits coarse columnar structure, while the C-doped alloys exhibit typical dendrite microstructure. The dendritic region (DR) is composed of single B2 phase, while the interdendritic region (ID) consists of FCC and E2$_1$ phases and presents an ultrafine cellar structure caused by the coexisting of ordering and spinodal decomposition. Interestingly, both the strength and compressive strain greatly increased with the increase of carbon content. Particularly, the AlFeCoNiC$_{0.08}$ HEA possessed the most excellent mechanical properties, superior to many other HEAs with the yield strength, fracture strength, and fracture strain as high as 1115 MPa, 2517 MPa and 48.8%, respectively. The mechanical properties of the AlFeCoNiC$_{0.17}$ alloy were weakened by the presence of graphite. Further, it is found that there is close relationship between the fracture morphology and alloy properties. Overall, in this study the improved microstructure and mechanical properties of the AlFeCoNi HEA have been accomplished by carbon doping, and our findings could shed light on a new alloy-design route to achieve bulk ultrafine structure materials with desired properties via the direct solidification.

1. Introduction

Over the last decade, high-entropy alloys (HAE), as a new member in the materials family, has attracted intensive attentions due to its novel properties [1–4]. Compared with traditional alloy design, HEAs contain multi-principal components in equal or near-equal atomic ratio. Therefore, the high configuration entropy is usually regarded as the primary actor to promote the formation and stability of solid solutions rather than compound phases [5]. At the earlystage of HEAs development, researchers mainly paid attention to obtain a single-phase massive solid solution. As known, strength and ductility are always simultaneously expected in the practical application of materials. However, previous single-phase HEAs studies have indicated that it is difficult to simultaneously achieve high strength and good ductility, which will impede their applications as the structural materials. The HEAs with FCC crystal structures exhibited high ductility but the strength was not high enough [6], while the single-phase BCC structured alloys showed high strength while sacrificing of ductility [7]. Given this, recently, much research effort has been spend on exploring dual-phase or multi-phase HEAs with a mixture of FCC phase, BCC phase, and HCP phase or intermetallic phase via the design of microalloying treatment for HEAs. By tuning the content of the trace alloying elements, a proper combination of the soft phase and the hard phase as well as a desired combination of strength and ductility could be achieved. This is then the familiar composite idea [8]. The CoCrFeNi-based eutectic HEAs (EHEAs) alloying with various Nb and Zr contents were prepared by He et al. [9] and Huo et al. [10], respectively. Both of the two types of CoCrFeNiNb$_{0.5}$ and CoCrFeNiZr$_{0.5}$ alloys consisted of a ductile FCC phase and a hard laves phase, and exhibited excellent comprehensive mechanical properties. The alloying effect of the rare-earth element Gd on CoCrCuFeNi alloy has been studied by our previous work [11]. It was found that the microstructure changed from FCC phase plus Cu-rich FCC phase to FCC phase plus hexagonal structure phase with adding of minor Gd element and the mechanical properties of CoCrCuFeNi HEA increased correspondingly. As pointed by Liu et al. [12], the hard intermetallic particles could be used to tailor the mechanical performance of the HEAs. They found that the CoCrFeNiMo$_{0.3}$ alloy can be significantly strengthened with only small loss

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of ductile through the σ and μ precipitated particles. Furthermore, as mentioned in previous literature [13], that the minor addition of Ti into the CoCrFeNi matrix could induce the formation of coherent nano-precipitates, which could strengthen the matrix alloy. Most recently, carbon, as an alloying element of HEAs, has attracted a large number of research interests due to its substantial effect on the microstructure and properties of HEAs [14–18]. The carbon doped HEAs studies [14–16] have shown that the integrated mechanical properties of HEAs can be optimized through alloying with the interstitial element carbon, followed by a set of mechanical working as well as annealing processing treatments.

Inspired by these previous investigations, in the present study, the alloying addition of carbon was added into the AlFeCoNi matrix. Note that all the principle elements in this studied HEA are not the carbide forming elements except that Fe is the weak carbide-former. Unlike previous studies, in this study, the matrix alloy is the BCC structured HEA and no strong carbide forming elements in the studied alloys. What is more, carbon has larger negative mixing enthalpy with other principle elements in the alloy [19] and the atomic size of carbon element is much smaller than that of the other constituent elements [20], corresponding values are listed in Table 1. Subsequently, the influence of carbon on the microstructure, phase compositions and mechanical behavior of this HEA were systematically investigated and ascertained. Therefore, it is necessary and interesting to get better understanding of the effect of added carbon on the microstructure and properties of the BCC-type HEA.

2. Experimental detail

The alloys with composition of AlFeCoNiC$_x$ (x = 0, 0.02, 0.04, 0.08, 0.17, the corresponding atomic percent (at%) of C in alloys is 0, 0.5, 1.0, 2.0, and 4.1 respectively. Hereafter, the alloys with different carbon content were denoted as C0, C0.5, C1.0, C2.0, and C4.1 respectively.) were produced by melting of the constituent elements in a vacuum arc melting furnace with a water-cooled Cu crucible under a Ti-gettered high-purity argon atmosphere. Each ingot was re-melted at least six times to improve homogeneity. For compression test, cylindrical samples with a dimension of 3 mm in diameter and 6 mm in length were prepared using the wire electrical discharge machining, and both ends as well as surface of samples were polished. An Instron 3382 electronic testing machine was employed for test at room temperature with a strain rate of 5×10^{-4} s^{-1}. To compensate the errors caused by the stiffness of the compression machine, the strain-stress curves were determined after correcting the machine stiffness. Hardness measurements were conducted, using a Vickers hardness tester (HVS-1000) under a load of 500 g for 10 s, and for each specimen, at least 10 measurements were carried out to obtain an average value.

The crystal structures were characterized by X-ray diffraction (XRD) with the Cu-Ka radiation scanning from 20° to 100° at a scanning speed of 4°/min. For characterization of microstructure and fracture surface morphology, a Hitachi S-4800 scanning electron microscope (SEM) was used. The compositions of the as-cast alloys were investigated by the SEM energy-dispersive spectrometry (EDS). A JEM-2010 transmission electron microscopy (TEM) was employed to further characterize the crystal structures and microstructures of the alloys before compression. The SEM specimens were initially polished to 3000-grit SiC paper and, then, mechanical polished and, finally, the microstructures of alloys were revealed by etching in a weak solution of nitric acid and alcohol. To prepare sample for TEM observation, the prepared samples were first mechanically ground to 30 μm thick, and then were thinned using a Gatan Precision Ion Polishing System (PIPS).

Table 1
The mixing enthalpy, ΔH_{mix} (kJ/mol), of atomic pairs among elements in the AlFeCoNiC$_x$ (x = 0, 0.02, 0.04, 0.08, 0.17) alloys calculated by Miedema's approach [19].

Elements	Atomic radius (Å)	Co	Ni	Al	C
Fe	1.24	− 1	− 2	− 11	− 50
Co	1.25	–	0	− 19	− 42
Ni	1.24	–	–	− 22	− 39
Al	1.43	–	–	–	− 36
C	0.77	–	–	–	–

3. Results and discussion

3.1. Crystal structure identification

The XRD patterns of the as-cast AlFeCoNiC$_x$ alloys were shown in Fig. 1. As shown in Fig. 1, the AlFeCoNi alloy (marked as C0) only exhibits the reflection of ordered BCC (B2) crystal structure, which corresponded to the result reported previously by Zuo et al. [21]. When the x value reaches 0.02 (marked as C0.5), a peak with very faint intensity around 49.06° occurs, indicating the existence of a small quantity of FCC phase. For the AlFeCoNiC$_{0.04}$ alloy (marked as C1.0), another two minor reflection peaks corresponding to two FCC phase appear beside the (110) peak of the B2 phase. From Fig. 1b and c, one can obviously observe these new weak peaks of the FCC phase. Nevertheless, with increase of the carbon content, the intensity of the FCC diffraction peaks gradually increase, implying that the addition of carbon promotes the FCC phase formation. It is noticed that, with addition of 2.0 at% C (i.e., alloy C2.0), a weak peak around 23.9° is found which corresponds to the (110) peak of the ordered FCC phase. In order to make it clearly, the diffraction patterns around the 2θ range of 18–42° are enlarged in Fig. 1b. Based on the XRD analysis, the ordered FCC and FCC phases appeared in the diffraction patterns can be identified as AlCo$_3$C$_{0.5}$ (κ-carbide) type and CFe$_{15.1}$ (γ-austenite) type forms with the space group *Pm-3m* and *Fm-3m*, respectively. It should be pointed out that, here, the ordered FCC phase (AlCo$_3$C$_{0.5}$) is the E2$_1$ type κ-carbide phase, and the E2$_1$ crystal structure is similar to the L1$_2$ (Ni$_3$Al phase in Ni-based supperalloys) except that a carbon atom occupying the octahedral interstice at the body center of the L1$_2$ [22]. Similar with C2.0 alloy, the C4.1 alloy contains B2 and E2$_1$ as well as FCC phases.

3.2. Microstructure characterization

The microstructures of the as-cast alloys with carbon addition prior to room-temperature compression test were presented in Fig. 2. As shown in Fig. 2a, the AlFeCoNi HEA (i.e., alloy C0) exhibits a single-phase feature, which is confirmed to be the B2 phase according to the XRD pattern shown in Fig. 1. It can be clearly seen that, a small amount of secondary phase precipitation were observed in the C0.5 alloy (Fig. 2b), coinciding with the minor peak mentioned in the XRD analysis. For the C1.0 alloy (see Fig. 2c), it is surprising to found that the columnar structure evidently transformed into the dendrites (DR), and the precipitates preferred to form the interdendrites (ID). With the carbon concentration further increasing, the morphology of the C2.0 and C4.1 alloys resemble the dendritic microstructure of C1.0 alloy, while the volume fraction of the ID region increases accordingly. It is apparent that the grain size of the C1.0, C2.0 and C4.1 alloys is smaller compared to the C0 alloy, indicating that the C addition could lead to the refinement of grains. The volume fraction of the DR and IR regions for the C0.5, C1.0 and C2.0 alloys are shown in Fig. 2f, which is measured by image analysis from the SEM images. It clearly showed that the fraction of the ID region increases, while the DR region decreases consistently with increasing the carbon content from 0.5 to 2.0 at%. However, even though the carbon content reaches 2.0, the DR region still as the major (volume fraction ~64.8%) and the ID region was still the minor phase (volume fraction ~35.2%). As seen in Fig. 2c, d and e, the microstructures of C1.0 and C2.0 as well as C4.1 alloys mainly consisted of DR and ID regions. A cautionary note is in order, some