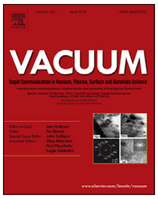
Vacuum 150 (2018) 84–95

Contents lists available at ScienceDirect

Vacuum

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



Microstructure evolution and strengthening mechanism of $Al_{0.4}CoCu_{0.6}NiSi_x$ (x=0–0.2) high entropy alloys prepared by vacuum arc melting and copper injection fast solidification

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ARTICLE INFO

Article history:
Received 26 October 2017
Received in revised form
21 December 2017
Accepted 16 January 2018
Available online 6 February 2018

Keywords:
High entropy alloys
Phase transformation
Solid solution strengthening
Fine grain strengthening
High strength
Excellent plasticity

ABSTRACT

The work prepared $Al_{0.4}CoCu_{0.6}NiSi_x$ (x = 0, 0.05, 0.1, 0.2) high entropy alloys by vacuum arc melting (M_x) and copper injection fast solidification (I_x), discussed the influence of trace Si and rapid cooling on the alloys' microstructures and mechanical properties, analyzed the alloys' strengthening mechanism and evaluated the proportion of different strengthening effects on the improved mechanical properties. The results showed that M_x had a fcc + $L1_2$ structure, but it transformed to fcc + $L1_2$ + minor bcc when x = 0.1 and 0.2. I_x had a fcc + $L1_2$ structure except $I_{0.2}$ (fcc + $L1_2$ + minor bcc). With the increase of silicon, M_x's hardness increased from 193 HV to 334 HV and I_x's hardness increased from 216 HV to 395 HV. $M_{0.2}$'s yield strength increased to 588 MPa, which was 2 times than that of M_0, the fracture strength and plastic deformation were 3074 MPa, 40.5%. I_x's yield strength increased to 690 MPa, which was 2.3 times than that of M_0, the fracture strength and plastic deformation reached 3407 MPa, 33.1%. The alloys' strengthening mechanism was the formation of bcc phase, solid solution strengthening and fine grain strengthening. And the strengthening effect of bcc phase was greater than fine grain strengthening and the fine grain strengthening effect was greater than solid solution strengthening.

1. Introduction

High entropy alloys (HEAs) [1–3], also known as multicomponent alloys [4], which break through the traditional single or dual principal component alloy design concept, have attracted much research attention in the past time [2,3]. According to the definition of Yeh [1], HEA is composed of at least five elements in equimolar or near equimolar ratio (each with the concentration between 5 and 35 at.%) and has a high mixing entropy with a simple solid solution structure. Although the high mixing entropy in HEAs can help to stabilize solid solutions (fcc, bcc or hcp structure [5–7]), most HEAs reported in the literature were multiple phases rather than a single solid solution phase [8–11]. Recently, researchers also called the multicomponent alloys composed of four principal elements or the multicomponent alloys whose atomic percentages are greater than 35% as HEAs [12–15]. Due to the high entropy effect in thermodynamics, the lattice distortion effect in microstructure, the sluggish diffusion effect in dynamics and the cocktail effect in performance, HEAs have many outstanding properties, such as high strength [16,17], good ductility [17] and other interesting properties [18–24].

For the research system of HEAs, the most typical HEAs were AlCoCrCuFeNi and its derived alloys (AlCoCrFeNi, AlCrCuFeNi, AlCrFeNi, CoCrFeMnNi, etc) [9,25–29]. But the quaternary alloy AlCoNiCu or its derived alloys were rarely researched, only Yeh [30] has researched AlCoNiCu HEA's phase structure of fcc + bcc, but not studied its performance. For the preparation of HEAs, there were many preparation methods of HEAs and their patterns were very diverse [31–48], in which, most HEAs were always made in bulk by vacuum arc melting or vacuum induction melting [31,32]. For HEAs' mechanical properties (including compressive and tensile properties), it was already known that in general single-phased bcc-structured HEAs have limited ductility [49], while single-phased fcc-structured HEAs could have excellent ductility but their strength is low [50], so how to reach the both high strength and excellent ductility is a challenge [51]. To solve the problem, there has been some methods: (i) changing the design idea of HEAs, such

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https://doi.org/10.1016/j.vacuum.2018.01.031

as using the eutectic alloy concept to design multi-phased eutectic high entropy alloy (EHEA) instead of single-phased high entropy alloy (SPHEA) [51,52], (ii) elements addition, such as adding B, Nb, Si, etc to the matrix HEA [53–55], (iii) controlling solidification process, such as using the rapid cooling method to prepare HEA [56,57] and (iv) reprocessing, such as thermo-mechanical and heat treatment [58]. The purpose of the above methods was mainly to change HEAs' phase from single phase to “fcc + bcc” or “fcc + hcp” dual-phase structures. Since element addition method is simple and convenient, it is a good choice to use this method to promote the phase transformation and optimize the mechanical properties. As we know, silicon has negative mixing enthalpy and large atomic radius difference with other elements and it is a well-known bcc former and stabilizer, so it was used to improve HEAs' strength. But massive addition of silicon would result in an increase of the brittle phase and a decrease of plasticity seriously. For example, the research conclusion of Liu [59] showed that the addition of large amount of silicon ($Al_{0.5}CoCrCuFeNiSi_{0.8}$) would result in an obvious decrease in strength and plasticity. Therefore, Si can not be added too much, only a small amount of silicon can be used to improve HEAs' mechanical properties and ensure the alloys' excellent plasticity. But the upper limit of Si content has not been specifically reported in the literature at the present time. From the published articles [33,59–61], we can summarize that when the general atomic percentage of Si is below 7.4%, HEAs containing Si have high strength and excellent ductility. On the other hand, HEAs' strengthening mechanism caused by trace silicon has not been studied in detail so far.

For the above mentioned problems, based on the AlCoCuNi HEA which is less studied currently, the work prepared its derived fcc structured $Al_{0.4}CoCu_{0.6}Ni$ HEA bulk with excellent plasticity but low strength by the most commonly used vacuum arc melting method, which has not been researched. Since Si is cheaper, lighter, convenient for adding and a good bcc stabilizer, it improved the alloy's strength and remained its excellent plasticity by trace Si addition (Note: the upper limit atomic percentage of Si was selected to be 6.25%, that is, the maximum value of x is 0.2). Besides, since the copper injection fast solidification technology has higher cooling rate (which can produce finer grains), it used the technology preparing $Al_{0.4}CoCu_{0.6}NiSi_x$ (x = 0–0.2) HEAs with higher strength and good plasticity. And it discussed the influence of trace Si addition and rapid cooling on the microstructures and mechanical properties of arc melted and copper injected HEAs, analyzed the alloys' strengthening mechanism in detail, built a solid solution strengthening model of $Al_{0.4}CoCu_{0.6}NiSi_x$ (x = 0–0.2) HEAs and evaluated the proportion of different strengthening patterns on the improved mechanical properties of HEAs using the model and Hall-Petch relation. The HEAs with high strength and excellent plasticity were designed and prepared due to the formation of new bcc phase, solid solution strengthening and fine grain strengthening. It realized the combination of HEAs' high strength and excellent plasticity.

2. Materials and methods

The $Al_{0.4}CoCu_{0.6}NiSi_x$ (x = 0, 0.05, 0.1, 0.2) master alloys were prepared by vacuum arc melting under a Ti-getted high-purity argon atmosphere in a water-cooled copper crucible. Elemental Al, Co, Ni, Cu, Si of above 99.9 wt% purity were used as raw materials. After the raw materials were filled into the water-cooled copper crucible, non-consumable Edmund Bühler vacuum arc-melting furnace (Compact Arc Melter MAM-1) was sucked below a pressure of 3×10^{-3}Pa with the mechanical pump and turbo molecular pump and protective argon gas (the purity was 99.999%) through the vacuum arc melting furnace was kept under a constant pressure of 0.05 MPa. Before the melting of master alloys, Ti balls were firstly melted to absorb the oxygen and other impurities in the atmosphere for further purification of the protective argon gas. To ensure the alloys' chemical homogeneity, melting was repeated for at least three times and was accompanied by electromagnetic stirring in the last two times. The arc melted master alloy ingots were 40 g and 30 mm in diameter (defined as M_x).

The copper injected $Al_{0.4}CoCu_{0.6}NiSi_x$ (x = 0, 0.05, 0.1, 0.2) alloys (defined as I_x) were prepared in a Edmund Bühler vacuum arc melting furnace. The inside diameter of injected copper mold was 3 mm and the length was 50 mm. After the vacuum degree was sucked to 3×10^{-3}Pa, filling high-purity argon gas into the arc furnace cavity and gasholder and ensuring the pressure difference was between 0.02 MPa and 0.05 MPa. After the Ti balls were melted and oxygen was adsorbed, one part of the master ingots (about 7–8 g) were re-melted and then injected into the copper mold under the pressure difference to obtain the 3 mm rod-shaped sample.

The preliminary phase structure was examined by a Rigaku/max 2400 X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm) operated in the condition of 45 kV, 40 mA. The scanning angle (2θ) ranged from 30° to 100° with a scanning rate of 8°/min. The detailed microstructural analysis was studied by a FEI Tecnai G2 F30 transmission electron microscope (TEM) with energy dispersive X-ray spectroscopy (EDX). Thin-foil TEM specimens were prepared by mechanical thinning followed by ion milling (Struers TenuPol-5). The samples were etched in the aqua regia and the microstructures of them were analyzed using OLYMPUS-60 metallographic microscope (OM) and Quangta-200 scanning electron microscope(SEM) equipped with energy dispersive spectrometry (EDS) operated at secondary electron mode. Chemical compositions in the different locations of the HEA samples were analyzed by EDS. For estimating the difference of actual elements contents from the starting materials in the HEAs, the actual average atomic percentages of the composition elements are listed in Table 2 ‘O’ (Note: the starting designed atomic percentages of the composition elements are shown in Table 2 ‘N’).

Vickers micro-hardness was measured by HXD-1000 micro-hardness tester. The load was 100 g, loading time was 15s and the average value from 7 points was taken as the final test result. The room temperature quasi-static compression tests were conducted using CMT4105 testing machine with an initial strain rate of 1×10^{-3} s^{-1}. The dimensions of compressive specimens were Φ3 × 6 mm. Three tests were performed to ensure the accuracy of data. Shear modulus and Poisson's ratio of the polished specimen with a dimension of $5.0 \times 5.0 \times 2.5$ mm^3 were measured using resonant ultrasound spectroscopy, RUSpec, Teclab.

3. Results

3.1. Phase structures

The XRD patterns of M_x and I_x alloys are shown in Fig. 1(a), (b). It was shown that the phase structures of $Al_{0.4}CoCu_{0.6}NiSi_x$ (x = 0, 0.05) were all fcc, but that of $M_{0.1}$, $M_{0.2}$ and $I_{0.2}$ transformed to fcc + minor bcc dual phase structures. Besides, the extra micro diffraction peaks of M_x and I_x (see the red arrow marks of $(110)_{ordered\ fcc}$ position in Fig. 1(a), (b)) appeared proving the alloys have ordered fcc structure. And the percentage of $M_{0.2}$ alloy's bcc diffraction peak intensity was slightly more than that of $I_{0.2}$, which can also be verified by the chemical compositions in section 3.2 (see Table 2). Trace silicon increased the lattice distortion effect of M_x and I_x, so the diffraction peaks shifted to right and the lattice constants became smaller (see the $(111)_{fcc}$ and $(110)_{bcc}$ peaks of Fig. 1(a), (b)). The fast cooling rate from copper injection fast