Vacuum 144 (2017) 80–85

Contents lists available at ScienceDirect

Vacuum

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

Microstructures and electrothermal properties of $Al_xCrFeNi$ multi-component alloys

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ARTICLE INFO

Article history:
Received 18 June 2017
Received in revised form
24 July 2017
Accepted 24 July 2017
Available online 26 July 2017

Keywords:
High-entropy alloy
Nanoparticle
Electrical resistivity
Thermal conductivity

ABSTRACT

$Al_xCrFeNi$ multi-component alloys were fabricated by vacuum arc-melting to study the effect of homogenization on microstructures of as-cast and homogenized alloys using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Besides, electrical resistivity and thermal conductivity of as-cast and homogenized alloys were also investigated. The results showed that no obvious differences of crystal structures and phase compositions between these as-cast and homogenizing alloys were presented. However, transmission electron microscope indicated that the ordered B2 NiAl intermetallic nanoparticles, which were distributed on the disordered BCC [Fe, Cr] solid solution of as-cast $Al_{1.2}CrFeNi$ alloy, disappeared after homogenization. For $Al_xCrFeNi$ alloys, the electrical resistivity increased with Al addition and dramatic increase of thermal conductivity was presented with increasing the homogenization temperatures. However, homogenization could decrease both electrical resistivity and thermal conductivity of as-cast alloys. The main factors influencing the changes of electrothermal properties of $Al_xCrFeNi$ alloys were the electron scattering affected by crystal defects, phase boundaries and temperatures.

1. Introduction

High-entropy alloy (HEA) has become a research hotspot since Yeh [1] et al. and Cantor [2] et al. first proposed this novel concept in metallic fields in 2004. According to the initial definition, HEAs are super solid solution alloys with much more principal elements than conventional alloys. This is used to make sure the mixture entropy of multi-component alloys is enough to keep the existence of solid solutions. Unique characteristics of HEAs, such as microstructures and properties, have attracted many researchers' attentions. There are many factors affecting microstructures and properties of HEAs. Among these, four core effects including high-entropy (thermodynamics), severe lattice distortion (structure), sluggish diffusion (kinetics) and cocktail effects (properties) are most basic [3]. During several years' investigation, more and more excellent work about HEAs including novel microstructures [4,5] and excellent properties [6–8] has been reported.

As one of the first known HEA system, AlCrFeNi-M (Co, Mo, Ti, et al.) has been investigated in many aspects. It has been identified that AlCoCrFeNi [9], $AlCrFeNiMo_x$ [10] and $AlCrFeNi_2Ti_{0.25}$ [11] all own two element-rich phases. For AlCoCrFeNi alloy, the matrix was mainly composed of Cr-Fe-Co type solid solution, and the nano precipitates were ordered NiAl. As Co element was replaced by Mo, NiAl phase still kept unchanged. However, with the increase of Mo, the other phase changed from Fe-Cr type solid solution dissolved with Mo to FeCrMo type σ phase. Similar changes occurred when the fifth element M became Ti. The dendrites of $AlCrFeNi_2Ti_{0.25}$ were enriched with Al-Ni-Ti and the interdendrites were composed of Cr-Fe. From all those HEAs mentioned above, it can be concluded that Al-Ni and Cr-Fe phase may be the basic constituent phases of AlCrFeNi-M type HEAs, which play an important role in microstructures and properties. And the diffusion of M and formation of M-rich region might only influence AlCrFeNi-M HEAs to a small degree. Therefore, in this paper, the microstructures and properties of quaternary $Al_xCrFeNi$ alloys excluding M element could be investigated, new insights would be provided for analyzing the

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http://dx.doi.org/10.1016/j.vacuum.2017.07.026
0042-207X/

microstructures and properties of AlCrFeNi-M type HEAs.

Due to the weak liquidity and castability of most HEAs, it is quite difficult to prepare for HEAs at large scales in casting methods. This retards the engineering applications of HEAs. Therefore, eutectic high entropy alloys, aiming at good castability, were proposed to address the problems facing the real applications [4]. Besides, the in-situ composite formed by eutectic organization could overcome the defects of most HEAs, such as excessive brittleness or insufficient strength. This strategy is quite useful to solve the problems for technological applications of HEAs and researchers have obtained bulk eutectic and near-eutectic HEAs with balanced strength and ductility in cast method directly [12]. However, there is still another factor inhibiting the industrial applications of HEAs. The cost of HEAs is much higher than that of conventional alloys. One effective solution is to explore the functional fields which own the characteristics of miniaturization and high value-added. So it is quite meaningful for developing HEAs towards the functional applications. And some researchers have paid attention to the physical properties of HEAs such as electromagnetic properties [13,14]. In their studies, the relationship between electrical resistivity and magnetic performance was investigated.

In the previous studies [15,16], the microstructure of as-cast $Al_xCrFeNi$ alloys has been investigated at the micrometer scale, specially $Al_{1.3}CrFeNi$ alloy which has the typical eutectic structure. But the distribution of alloy phases at the nanometer scale still kept mysterious. In addition, supersaturation and crystal defects were usually existed in the as-cast alloy ingots prepared by vacuum arc-melting method. As one of the heat treatments eliminating crystal defects, homogenization should have a significant effect on microstructures and properties of as-cast alloys.

Therefore, besides the conventional characterizing methods of X-ray diffraction and scanning electron microscopy, transmission electron microscopy was used to analyze the microstructures and phases of as-cast and homogenized $Al_xCrFeNi$ multi-component alloys in the nanometer scale. Meanwhile, it is known that there is a quantitative relationship called Wiedeman-Franz law between electrical resistivity and thermal conductivity of alloys. On the basis of this law, the relationship between microstructures and electrical resistivity of as-cast and homogenized $Al_xCrFeNi$ alloys was investigated. Besides, thermal conductivity changes of as-cast and homogenized $Al_xCrFeNi$ alloys with Al addition at different temperatures were analyzed, aiming to look for the factors influencing these physical properties of $Al_xCrFeNi$ alloys. This might promote the development of HEAs in functional alloy fields.

2. Experimental

All $Al_xCrFeNi$ (Al molar ratio, x = 0.9–1.3) ingots were prepared by vacuum arc-melting under a Ti-gettered argon atmosphere and the purity of metal particles were above 99.9 wt %. Before processed, non-consumable vacuum arc-melting furnace (HVYH-2) was kept below a pressure of 5×10^{-3}Pa, and protective argon through the vacuum arc-melting furnace was maintained under a constant pressure of 0.07 MPa. Also, flushing furnace by pumping vacuum was repeated for two times to remove the remaining air. These samples were flipped and remelted in a water-chilled copper mold at least five times to improve the chemical homogeneity. For further investigations, half ingots were homogenized at 1000 °C for 8 h and subsequently furnace-cooled to room temperature using a box furnace (KSL 1400X A3).

The crystal structure of samples were identified by the X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation operated in the condition of 40 kV, 30 mA. The scanning angle (2θ) ranged from 20° to 100° with a scanning rate of 5°/min. These specimens were etched in the aqua regia and microstructures were observed by the scanning electron microscopy (SEM, FEI Nova Nano 430) equipped with the energy dispersive spectroscopy (EDS). For further investigation, thin foils of as-cast and homogenized samples, which were processed by the ion beam thinner (Gatan 600B), were observed using the transmission electron microscopy (TEM, FEI Tecnai G2 F20) with energy dispersive X-ray spectroscopy (EDX).

According to ASTM B193-02(2014), measurements and calculations of electrical resistivity at room temperature were obtained by a precise resistance tester (Jinko JK2516). And the thermal conductivity of as-cast and homogenized alloys at different temperatures (25 °C, 160 °C, 320 °C, 480 °C, 640 °C and 800 °C) were directly measured by the laser thermal conductance meter (Netzsch LFA457).

3. Results and discussion

3.1. Microstructures and phases of as-cast and homogenized alloys

The XRD patterns of as-cast $Al_xCrFeNi$ alloys could be seen in our previous word [15], which illustrates the XRD patterns of homogenized $Al_xCrFeNi$ alloys. From the comparison of XRD patterns between as-cast and homogenized alloys in Fig. 1, it can be identified that all $Al_xCrFeNi$ alloys contained duplex BCC structures including ordered B2 NiAl intermetallic and disordered BCC [Fe, Cr] solid solution. Compared to the as-cast alloys, no obvious differences of $Al_xCrFeNi$ alloys exist after homogenization. The crystal structures and phase types of these homogenized alloys are maintained. So it can be inferred that the homogenized $Al_xCrFeNi$ alloys also have ordered B2 NiAl intermetallic and disordered BCC [Fe, Cr] solid solution.

Though crystal structures and phase types of $Al_xCrFeNi$ alloys show similar in the as-cast and homogenized states, phase morphologies of homogenized alloys become quite different with those of as-cast alloys. It has been identified that as-cast $Al_xCrFeNi$ alloys owned regular phases including NiAl intermetallic and [Fe, Cr] solid solution, which were presented in the spinodal decomposed structures of the alloy matrices [15,16]. For homogenized $Al_xCrFeNi$ matrices, the high-magnification images in Fig. 2a ~ e show much coarser and more irregular than as-cast ones. But it does not mean that all these alloys have fully spinodal decomposed microstructures. Take $Al_{1.3}CrFeNi$ alloy for example, obvious deformation

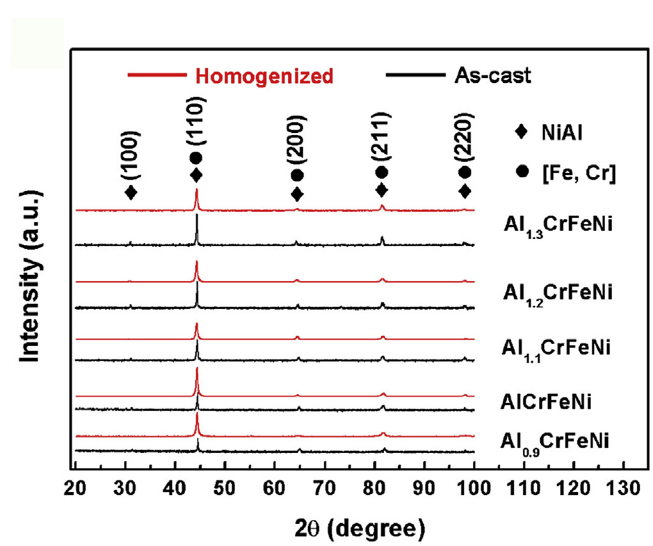

Fig. 1. XRD patterns of as-cast and homogenized $Al_xCrFeNi$ alloys.