CHARACTERIZATION OF EQUIMOLAR HIGH-ENTROPY ALLOY FROM Al-Ti-Co-Ni-Fe SYSTEM

GÓRECKI Kamil[1,*], BAŁA Piotr[1,2], CIOS Grzegorz[2], TOKARSKI Tomasz[2], KOZIEŁ Tomasz[1]

[1]AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Physical & Powder Metallurgy, Cracow, Poland, EU,* kgorecki@agh.edu.pl
[2]AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Cracow, Poland, EU

Abstract

In this paper a new high-entropy alloy from Al-Ti-Co-Ni-Fe system was examined. The alloy was synthesized by arc melting process. On the basis of theoretical assumptions, the alloy should obtain BCC structure. To verify theoretical assumptions, the structure was characterized by X-ray diffraction. Additionally, microstructural observations using scanning electron microscopy, equipped with energy dispersive spectroscopy X-ray spectrometer for elements distribution, were carried out. It was observed that examined alloy crystallized in FCC structure with additional unidentified phase. It was stated, that the obtained equimolar high-entropy alloy from Al-Ti-Co-Ni-Fe system has high hardness but is very brittle. During hardness measurements from the tips of the indentation cracks spread. A significant segregation of the elements was also observed.

Keywords: High-entropy alloy, SEM, EDS, hardness, microstructure

1. INTRODUCTION

High entropy alloys (HEAs) are a group of multi component alloys composed from at least five elements of 5-35 at.% each [1-4]. The solid solutions obtained on the basis of that kind of alloys are defined by specific thermodynamic parameters such as mixing enthalpy (ΔH_{mix} from -15 to 5 kJ/mol [5]), mixing entropy (ΔS_{mix} = 1.6 R, where R - gas constant [4]), differences of atomic sizes between the used alloying elements and the average value of the whole alloy δ (less than 6.6 %. [5]) and parameter $\Omega = (T_m \cdot \Delta S_{mix})/|\Delta H_{mix}|$ greater than 1.1, where T_m is melting temperature [5]). The structure of obtained alloys is quite simple - FCC, BCC or both, and it could be predicted on the basis of the Valence Electron Concentration (VEC) [6]. Despite of simple structure HEAs reveal some unconventional properties what makes them important in the modern Science. It has been reported that these kind of materials are resistant to high temperature and oxidation, reveals high hardness and wear resistance [3. 7-12].

In this paper an equimolar alloy form Al-Ti-Co-Ni-Fe system is examined. The calculated values of VEC (6.8) suggested that the obtained structure should be BCC, while the thermodynamic parameters are not fulfilled. The presented results allow to improve the knowledge about alloys located at the centre of the phase diagram of multicomponent systems that are mainly known close to the corners and edges [13].

2. EXPERIMENTAL

Equimolar High-Entropy Alloy from Al-Ti-Co-Ni-Fe system was synthesized using high purity elements (99.9 % and more) in arc furnace (AM Edmund Bühler) with water-cooled copper mould in Ar atmosphere. Ingot was at least five-time re-melted to obtain chemical homogeneity. For microscopic investigation a centre part of ingot was chosen. Microscopic observation was provided by the use of electron scanning microscope (FEI Versa 3D with EDAX EDS) on unetched specimen. Experiment was performed in used of backscattered electrons (BSE) mode. Crystallographic structure was investigated by the use of X-ray diffractometer (Panalytical

Empyrean) using Co Kα1 radiation (λ = 0.1789 nm). For XRD studies alloy was powdered. Hardness measurement was provided using Vickers indenter (Wilson Hardness Tukon 2500 tester) using 9.81 N force.

3. RESULTS AND DISCUSSION

The microstructure of examined alloy is shown in the **Figure 1**. The darker areas represent dendrites and the lighter areas represent interdendritic spaces. As it could be noted the both structures do not form in classical way - the dendrites are rather small and has an elongated shape.

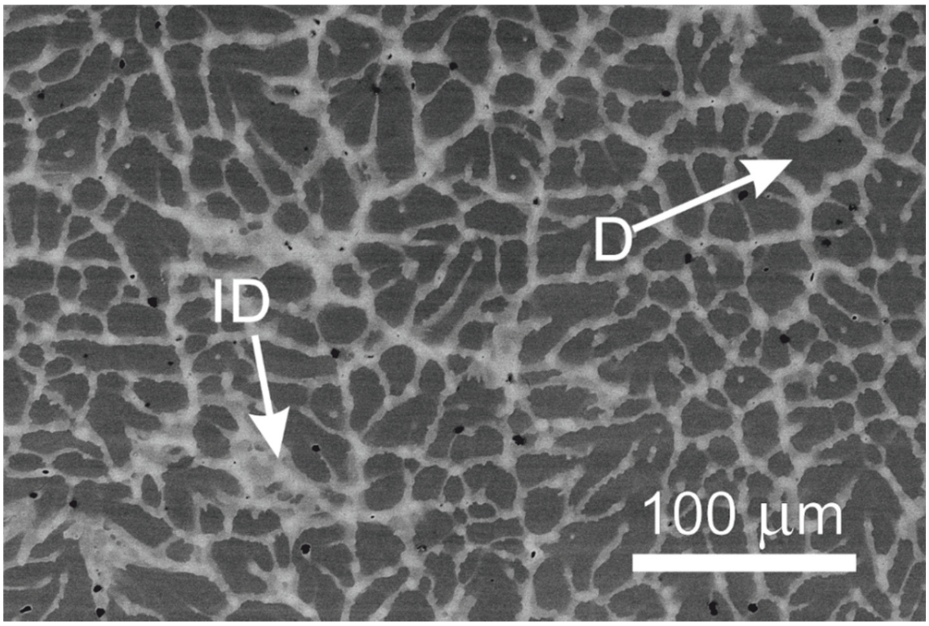

Figure 1 Microstructure of investigated alloy SEM: BSE. Dendrites (D), interdendritic spaces (ID)

The analysis of the element distribution (EDS Map - **Figure 2**) allows to observe a significant segregation. According to the substitution theory is could be assumed that the nickel, cobalt and iron should exist in microstructure next to each other because of the mutual solubility. Furthermore, these elements are characterized by the similar metallic size (near to 0.25 nm) [14], what should amplify the phase homogeneity instead of strong element segregation. On the basis of EDS Maps, it is easily to notice that interdendritic spaces are strongly enriched in iron and less in cobalt, while the dendrites are enriched in aluminum, titanium and nickel. It should be also noted that cobalt is the only one that is quite uniformly distributed.

XRD measurements (**Figure 3**) allow identify the FCC Heusler Phase type AlFeNiTi even though according to the VEC calculations the equimolar alloy from this system should be characterized only by BCC phase. Probably the reason why the BCC structure is not observed is because thermodynamic parameters (**Table 1**) ΔH_{mix}, δ, Ω are not fulfilled. For investigated alloy ΔH_{mix} = -26.40 kJ/mol, δ = 7.46% and Ω = 0.83 while according to [5] ΔH_{mix} should be between -15 to 5 kJ/mol, δ < 6.6% and $\Omega \geq$ 1.1 and this is why alloy is not solid solution. It could be assumed that the VEC parameter could be used to predict the structure only in the case of solid state alloys. There is also some unidentified phase.

Table 1 Thermodynamic parameters calculated for equimolar alloy

	ΔH_{mix} (kJ/mol)	δ (%)	ΔS_{mix} (J/mol·K)	Ω
Calculated values	-26.40	7.46	13.38	0.83

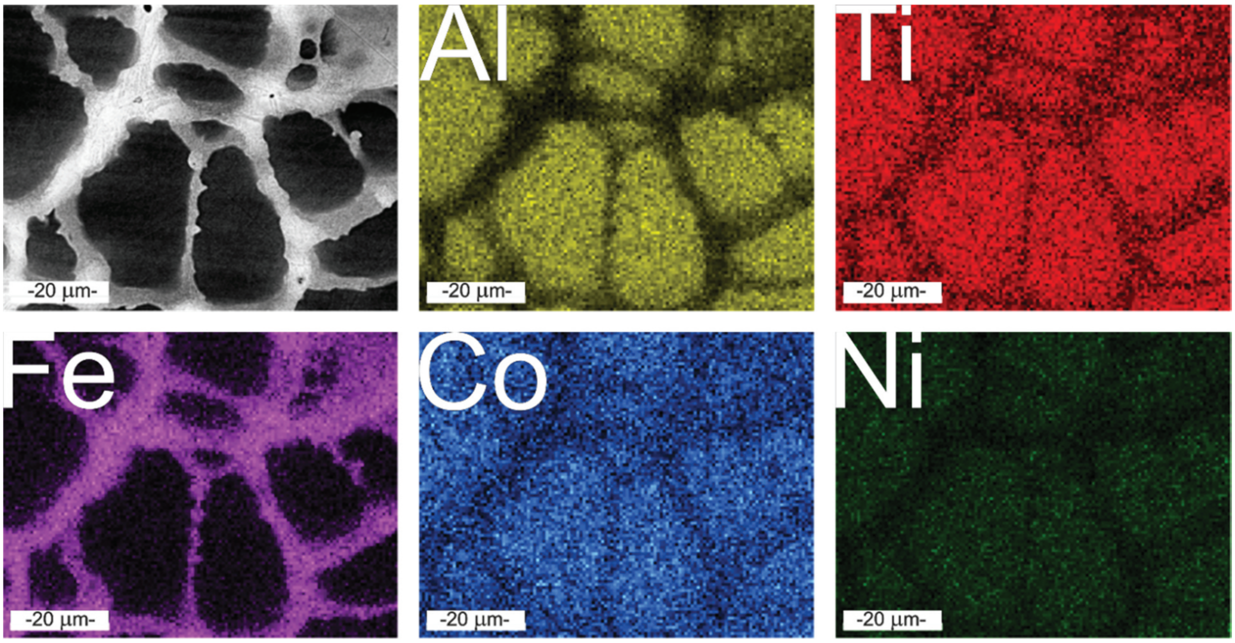

Figure 2 EDS maps of element distribution

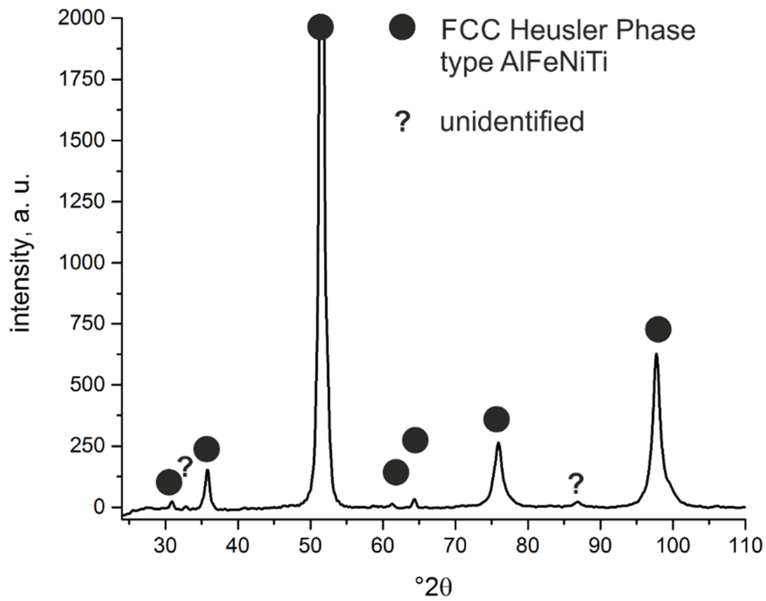

Figure 3 XRD pattern with identified FCC Heusler Phase and unidentified phase

In addition, hardness measurements were provided. Hardness of investigated alloy is approx. 660±3 HV1. There were observed cracks spreading from tips of indentation. It shows that alloy is very fragile.

4. CONCLUSIONS

Investigated equimolar alloy do not fulfil conditions to form a solid solution. Small and elongated dendrites, enriched in aluminium, nickel and titanium, were observed in the microstructure. Based on VEC parameter the alloy should obtain BCC structure, yet it has FCC Heusler Phase structure. It is concluded that VEC parameter can be used only for these High-Entropy Alloys, which fulfil ΔH_{mix}, δ and Ω conditions to form solid solution. Hardness of investigated alloy is high, but from tips of indentation cracks spread.

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