EFFECT OF CHROMIUM ADDITION ON STRUCTURE AND MICROSTRUCTURE OF HIGH-ENTROPY ALLOYS FROM Al-Ti-Co-Ni-Fe-(Cr) SYSTEM

Kamil GÓRECKI [1,*], Piotr BAŁA [1,2], Tomasz KOZIEŁ [1], Krzysztof PAJOR [1], Grzegorz CIOS [2], Jakub KAWAŁKO [2]

[1]AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Physical and Powder Metallurgy, Al. Mickiewicza 30, 30-059 Krakow, Poland, EU
kgorecki@agh.edu.pl

[2]AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Al. Mickiewicza 30, 30-059 Krakow, Poland, EU

Abstract

Multi-component alloys containing at least five elements in equimolar or near equimolar ratio are commonly known as High-Entropy Alloys. Despite the complex chemical composition, with the fulfilment of specific thermodynamic parameters, they are characterized by the existence of simple phases. During designing process of such materials VEC (Valance Electron Concentration) parameter is commonly used to predict the crystallographic structure of the alloy. Calculations are based on the percentage of individual elements and the number of each valence electron. Research presents the effect of chromium addition on the structure and microstructure of alloys from Al-Ti-Co-Ni-Fe-(Cr) system. The assumption is, that the addition of chromium will lower the value of the VEC parameter, and will results in the transition from FCC structure to FCC + BCC structure. Such crystallographic change should additionally lead to significant changes in the properties of these alloys, e.g. by hardness increasing.

Keywords: High-Entropy Alloys, VEC parameter, structure, microstructure

1. INTRODUCTION

High-entropy alloys belongs to the group of multiprincipal element alloys that are composed of at least five elements of 5 to 35 atomic pct. [1-3]. That kind of materials are characterised by several so called high entropy effects that are responsible for unique properties like: high hardness, thermal resistance, abrasion resistance and other [4-6]. One of the most interesting features results straightly from chemical composition of high-entropy alloys - despite of multicomponent composition HEA forms simple phases like face centered cubic (FCC) and body centered cubic (BCC) or both (FCC+FCC) [2,7-10]. Determining of crystallographic structure of high-entropy alloys is possible due to theoretical calculation of valance electron concentration parameter (VEC) and another thermodynamic factors like: mixing enthalpy or mixing entropy [11,12]. Phase composition could be calculated by given formula: VEC=Σci (VEC)i, where ci - mole fraction of each element and (VEC)i - number of valance electrons of each element. One-phase structures could be obtained for systems that fulfil all thermodynamic parameters and calculated value of VEC is lower than 6.88 (BCC) or higher than 8.00 (FCC). For values in the range of 6.89 to 7.99 both FCC and BCC phases coexists together [13]. Apart of configuration entropy the VEC parameter is most commonly used in designing of high-entropy alloys. Forming of solid state solutions depends on thermodynamic factors like: (1) mixing enthalpy (ΔH_{mix}), (2) parameter δ that refer to differences between average atomic size of particular elements, (3) parameter Ω that compare configuration entropy ΔS_{mix}, mixing enthalpy ΔH_{mix} and melting temperature T_m of whole alloy $\Omega = T_m \cdot \Delta S_{mix})/\Delta H_{mix}$. Optimal values of presented factors are following: ΔH_{mix} in the range of -15 to 5 kJ/mol, δ below 6,6% and Ω above 1,1 [14,15]. More complex analysis of influence of thermodynamic parameters on microstructure and structure of high-entropy alloys could be find in our other works (see [16]).

The main aim of presented work was the analysis of influence of increasing content of chromium in Al-Ti-Co-Ni-Fe-(Cr) system on their hardness and structure and microstructure. Obtained results were compared with theoretical assumptions.

2. EXPERIMENTAL

Investigated alloys were obtained using Arc Melting method (Arc Melter AM - Edmund Bühler GmbH) on water cold copper mould under argon atmosphere. Ingots were re-melted at least five times to ensure homogeneous distribution of elements in whole value of ingots. For synthesis only pure elements were used (at least 99.999 weight pct. purity). Subsequently samples were annealed for 20 h in 1100 °C in order to obtain chemical homogeneity. For microscopic (SEM - FEI Versa 3D with EDAX EDS) investigations samples were prepared using standard metallographic preparation. Alloys were also investigated by the use of X-ray powder diffraction (Panalytical Empyrean). Hardness measurements (Wilson Tukon 2500 Knoop/Vickers Automated Hardness Tester) were made using Vickers intender and 9.806 N force (HV1).

3. RESULTS AND DISCUSSION

Nominal chemical compositions of investigated alloys are presented in **Table 1** and calculation of thermodynamic parameters of each alloy is presented in **Table 2**. According to presented values it should be pointed that all investigated alloys fulfil all conditions for forming of simple solid solutions. Calculated values of parameter VEC suggests that Alloys 1 and 2 should be characterized by forming of FCC phase while Alloys 3, 4 and 5 should be characterized by coexisted FCC and BCC phases. It should be noted, that increasing quantity of chromium results in decreasing of VEC value and forming BCC and FCC phases instead of single phase solid solution.

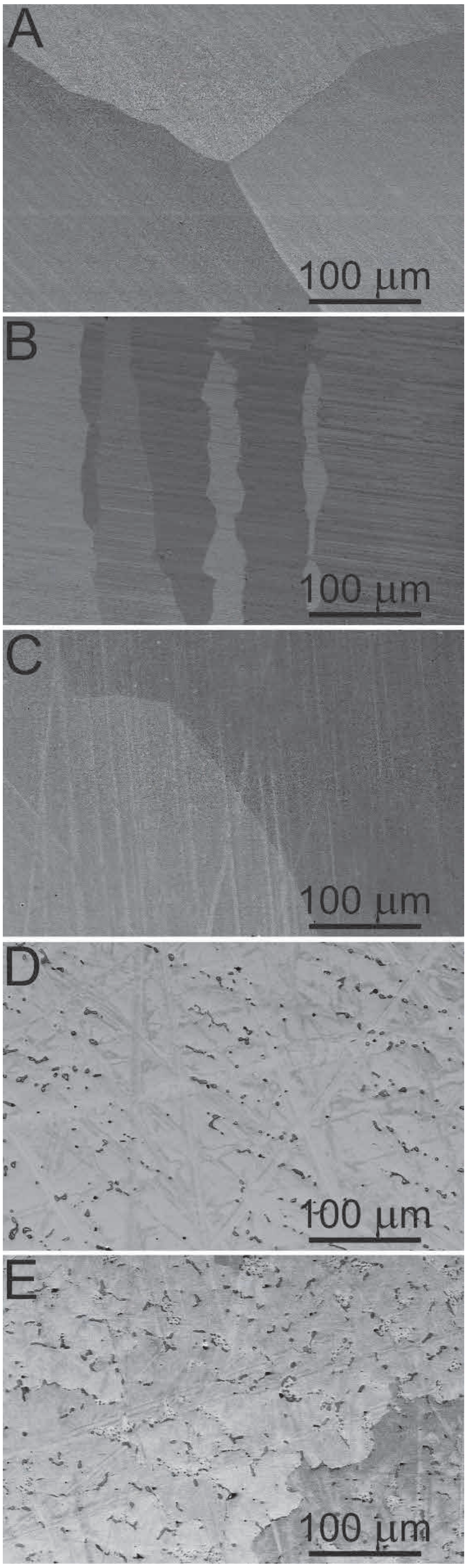
Table 1 Nominal chemical composition of investigated alloys (at.%)

	Al	**Ti**	**Co**	**Ni**	**Fe**	**Cr**
Alloy 1	5	5	35	35	20	—
Alloy 2	5	5	30	30	20	10
Alloy 3	5	5	20	30	20	20
Alloy 4	5	5	30	20	20	20
Alloy 5	5	5	20	20	20	30

Table 2 Thermodynamics factors of investigated alloys

	VEC (-)	ΔH_{mix} (kJ/mol)	ΔS_{mix} (J/mol·K)	δ (%)	Ω (-)
Alloy 1	8.60	-9.54	11.27	4.76	2.04
Alloy 2	8.25	-10.12	13.08	4.77	2.28
Alloy 3	7.95	-10.52	13.52	4.78	2.31
Alloy 4	7.85	-10.00	13.52	4.77	2.44
Alloy 5	7.55	-9.96	13.52	4.78	2.50

SEM Analysis micrographs of investigated alloys allow to notice, that Alloys 1, 2 and 3 (**Figures 1 A-C**) are characterized by big, homogeneous grains. Those conclusions are proved also by EDS investigations (**Figures 3-5**). Despite the complex chemical composition (at least 5 principal elements) it is possible to obtained simple solid solutions.



◄**Figure 1** SEM micrographs of investigated alloys: A - Alloy 1, B - Alloy 2, C - Alloy 3, D - Alloy 4, E - Alloy 5.

Coexistence of additional phases is clearly noticeable at images presented for Alloys 4 and 5 (**Figures 1D** and **1E**). Darker areas visible in **Figure 2A** (Alloy 4) could be assigned as BCC phase and lighter areas inside darker one could be assigned as FCC' phases. That phase (FCC') probably precipitate during heat treatment of investigated alloy. Forming of additional phases causes the separation of elements between phases. Lighter areas - matrix (FCC and FCC') are enriched in chromium and iron, while darker areas (BCC) are enriched in aluminium, titanium and slightly in nickel. Cobalt is evenly distributed. Analysis of element distribution and possibilities of their mutual substitution allow determining of possible crystallographic structures of each investigated phase. Coexistence of two simple phases proves the theoretical calculations of VEC value and other thermodynamic parameters.

More complex microstructure could be observed in the micrographs obtained for Alloy 5 (**Figure 2B**). Darker areas visible in images could be assigned as BCC phases, lighter areas as FCC' precipitates inside FCC matrix. Analysis of microstructure of Alloy 5 in comparison with EDS measurements (**Figure 7**) allows to observe additional very light areas enriched only in chromium. That additional phase was not predicted by calculations of VEC parameter. Similarly to Alloy 4 darker phases (BCC) are enriched by aluminium, titanium and slightly in nickel. Lighter matrix is enriched in iron. Cobalt is homogenously distributed over area, excluding additional phase enriched by chromium. It should be noted that additional phase could be assigned as BCC phase, because of well-know ability to create BCC structure in high-entropy systems by chromium. This ability results from low value of VEC parameter (VEC_{Cr}=6). Change of synthesis parameters or synthesis methods could prevent forming of additional phases not predicted by theoretical calculations. Powder metallurgy combined with suitable heat treatment seems to be promising method of synthesis of high-entropy alloys that contain chromium [17]. Separation of chromium occurs during crystallization when excess of that element is pushed to the front of the crystallization, which probably results from exceeding the solubility limit of chromium that could be dissolved in proposed element system.

XRD patterns obtained for investigated alloys (**Figure 8**) shows that all alloys are characterised by occurrence of only one phase (FCC), what is a proper observation for Alloys 1, 2 and 3. In a case of Alloys 4 and 5 microstructure consists of FCC matrix and additional phases (BCC and Cr-rich), that were not observed at diffractograms. Additional phases could be observed by use of more sensitive methods like TEM (planned for the future investigation).

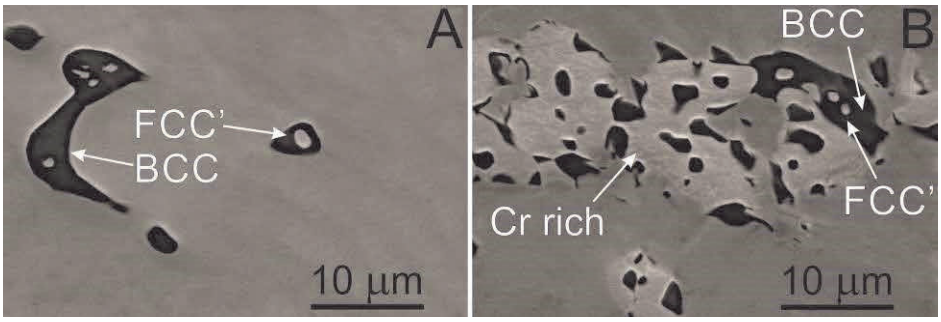


Figure 2 SEM - magnification of selected areas for A - Alloy 4 and B - Alloy 5

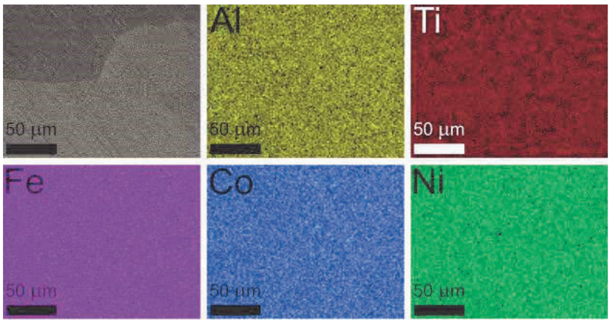


Figure 3 EDS map for Alloy 1

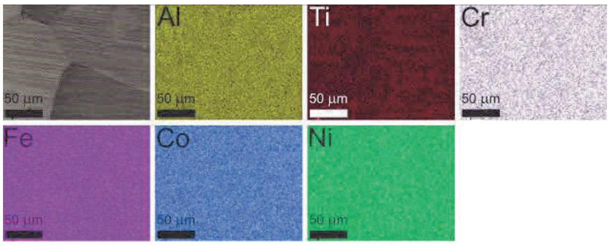


Figure 4 EDS map for Alloy 2

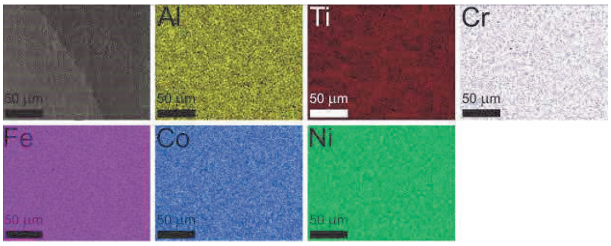


Figure 5 EDS map for Alloy 3

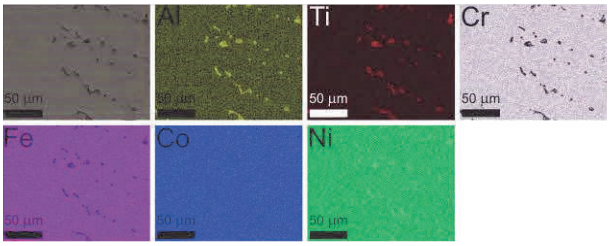


Figure 6 EDS map for Alloy 4

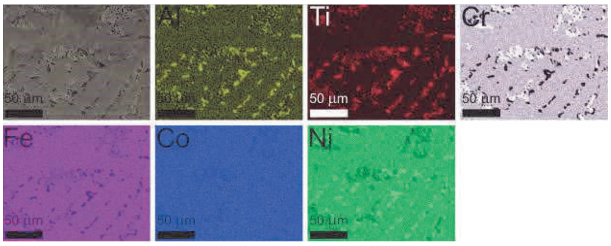


Figure 7 EDS map for Alloy 5

Results of hardness measurements are presented in **Table 3**. It could be noted, that Alloys 4 and 5, despite of occurrence of BCC phases, are not characterized by increase of hardness in comparison with other alloys. Furthermore, for Alloy 5 decrease of average hardness is clearly noticeable. Obtained results can be explained by inhomogeneous distribution of additional BCC phases in FCC matrix. Standard deviation of obtained values calculated for Alloys 2 and 3 results from huge diversity of grain size what results from Arc Melting method. Areas close to copper mould are characterised by smaller grains size what indicate faster crystallization. Smaller grains are characterized by higher hardness because of larger volume of grain boundaries, which are natural barrier for plastic deformation. That effect could be changed by plastic deformation with subsequent heat treatment that leads to homogenisation of grain size. Most interesting values of hardness measurements were obtained for Alloy 5 - occurrence of Cr-rich phase causes inhomogeneous dispersion of that element, what indicate reducing the effect of solution strengthening in the material.

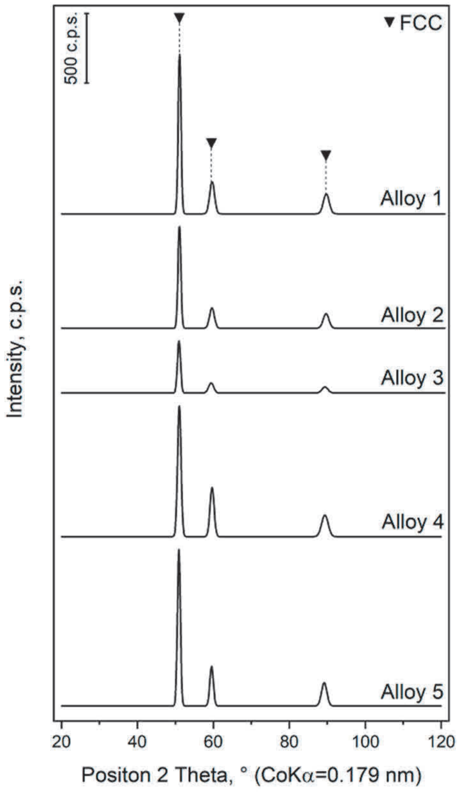


Figure 8 XRD patterns of investigated alloys

Table 3 Hardness of investigated alloys

Alloy 1	370 ± 10 HV1
Alloy 2	350 ± 20 HV1
Alloy 3	360 ± 30 HV1
Alloy 4	360 ± 15 HV1
Alloy 5	330 ± 10 HV1

4. CONCLUSIONS

Analysis of obtained results allowed conclude that:

1) Alloy 1, 2, 3 and 4 are characterized by occurrence of simple phases like FCC or FCC+BCC (FCC as matrix).
2) Heat treatment of Alloys 1, 2 and 3 allow obtaining fully homogenous dispersion of elements in whole material.
3) In the case of Alloy 4 and 5 during heat treatment additional phases are formed - BCC excretions in FCC matrix.
4) Theoretical calculations of parameter VEC for Alloy 3 suggest coexisting of mixture of BCC and FCC phases, but investigations indicate occurrence of only one phase - FCC.
5) Despite of occurrence of BCC and FCC in Alloys 4 and 5 the hardness of these materials not increase because of formation of areas enriched by chromium.
6) Alloy 5 is characterized by occurrence of Cr-rich phase that were not predicted by theoretical calculations.

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