Sintering and heat treatment of $\text{Al}_{15}\text{Ti}_{5}\text{Co}_{35}\text{Ni}_{25}\text{Fe}_{20}$ high-entropy alloy

K Górecki$^{1,*}$, J Zýka$^2$, J Malek$^{2,3}$, J Horvát$^3$, J Čapek$^4$, P Bała$^{1,5}$

$^1$AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, Department of Physical & Powder Metallurgy, Krakow, Poland, EU,*
$^2$UJP PRAHA a.s., 15610 Prague 5, Zbraslav, Czech Republic, EU
$^3$Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Materials Engineering, 12000 Prague 2, Czech Republic, EU
$^4$Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Prague 2 12000, Czech Republic, EU
$^5$AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, Krakow, Poland, EU

E-mail: kgorecki@agh.edu.pl

Abstract. The new $\text{Al}_{15}\text{Ti}_{5}\text{Co}_{35}\text{Ni}_{25}\text{Fe}_{20}$ high entropy alloy was obtained by the powder metallurgy from the elemental powders (-325 mesh). The obtained alloy should be characterized by the dual BCC + FCC phase microstructure according to the valence electron concentration calculations (VEC=7.9). The main aim of the research was to determine the optimal conditions for sintering and heat treatment of $\text{Al}_{15}\text{Ti}_{5}\text{Co}_{35}\text{Ni}_{25}\text{Fe}_{20}$ high entropy alloy. The alloy was sintered for 40 minutes at 600 °C for the preliminary consolidation of the powders and initial diffusion of the material. Then samples were annealed at various temperatures: 700, 800, 900, 1000 °C for 1 hour. Samples after annealing were characterized by the XRD and SEM. For the chosen temperature the annealing time was elongated to 2, 3, 5, 10 and 20 hours. The chemical homogeneity was determined.

1 Introduction

The rapid development of modern technology includes high-entropy alloys (HEAs) which could be used instead of conventional metallic materials, which are mostly composed from one or two principal elements. HEAs are composed of at least five principal elements with concentrations of each between 5-35 at.%. Number of elements in alloys could be explained by the dependence between mixing entropy and enthalpy. It is considered that formation of solid solution phases in HEAs is possible when the mixing entropy is high enough to counterbalance the mixing enthalpy, what is observed when HEAs consist at least five principal elements [1–5]. HEAs usually form simple solid solution phases with FCC and/or BCC structures. The number of obtained phases is much lower than calculated by Gibbs phase rule, which directly results from effects of high entropy [6, 7]. As atoms of each principal element can be located in all lattice positions with equal probability, the multielement lattices are highly disordered. Furthermore as metallic diameters of the elements are different, this intensifies the disorder effect. At least HEAs could be considered like an atomic-scale composite, where interactions between principal
elements indicate indirect synergistic effect of all elements. It has been reported that HEAs have very good thermal stability and high-temperature strength [8–10].

As an alternative for mostly used methods of synthesis HEAs such like are melting [11–13] and mechanical alloying or spark plasma sintering [14–17] investigated in this paper Al$_{15}$Ti$_{5}$Co$_{3}$Ni$_{25}$Fe$_{20}$ alloy was synthesized by the use powder metallurgy.

2 Experimental

Al$_{15}$Ti$_{5}$Co$_{3}$Ni$_{25}$Fe$_{20}$ alloy (indexes represents atomic percent of elements) have been prepared from the metal base fine powders (~325 mesh; purity 99.9 at. pct.). Metal base powders have been mixed by 10 hours in the Turbula Shaker-Mixer under argon atmosphere. In order to intensify the mixing of powders the metal balls were used (ball to powder ratio 1:12). Mixed powders were pressed hydrostatically under pressure 400 MPa and sintered in vacuum furnace CLASSIC 5015T under pressure $10^{-3} – 10^{-5} \text{ Pa}$ (temperature 600 °C for 40 minutes). Sintering parameters have been chosen to avoid liquid phase (aluminum melting point 660 °C) and formation of intermetallic phases. However, these parameters were enough for the preliminary diffusion of elements.

Due to finding proper heat treatment temperature samples obtained after sintering have been annealed at varied temperatures: 700, 800, 900 and 1000 °C for 1 hour. After treatment samples have been investigated by Scanning Electron Microscope JEOL JSM 7600F (back-scattered electrons imaging; 15 kV) and by the XRD measurements (X’Pert PRO MPD in Bragg-Brentano geometry using cobalt X-ray tube 45kV, 30 mA with pinhole 4x1 mm2). Analysis of obtained data allows to choose one temperature of annealing (1000 °C) for further investigation where annealing time was elongated to 2, 3, 5, 10 and 20 hours.

3 Results and discussion

Parameter VEC and thermodynamic parameters calculated for obtained samples are presented in Table 1. Parameter VEC (Valence Electron Concentration) corresponds to the phase composition of alloy. For investigated sample calculated VEC is 7.9 what represents dual phase structure of obtained sample – BCC+FCC. $\Delta H_{\text{mix}}$ allows to predict the formation of solid solutions, calculated value fulfils criteria of the High-Entropy Alloys (-14.58 kJ/mol), even if the value of mixing entropy is high while the $\Delta H_{\text{mix}}$ is to low or to high the solid solution would not be formed. Rest of parameters $\delta$ (ratio between atomic radius of single alloy element to average atomic radius of alloy) and $\Omega = T_m \Delta S_{\text{mix}} / |\Delta H_{\text{mix}}|$ where $T_m = \sum c_i (T_m)_i$ , $(T_m)_i$ – melting point of each element) combined with $\Delta H_{\text{mix}}$ indicates formation of solid state. Calculated values fulfil the criteria – $\delta$ is 6.01 and $\Omega$ is 1.21.

| Table 1. Thermodynamic parameters calculated on the basis of chemical composition for the obtained sample and comparison with the values for model High-Entropy Alloys (HEA). |
|---|---|---|---|
| VEC | $\Delta H_{\text{mix}}$ [kJ/mol] | $\delta$ [%] | $\Omega$ |
| values for model HEAs | BCC $\leq$ 6.88; 8$\leq$FCC [18] | $-15 \div 5$ | <6.6 | $\geq$1.1 |
| values calculated for obtained sample | BCC+FCC 7.9 | -14.58 | 6.01 | 1.21 |

3.1 XRD analysis

Obtained XRD patterns were presented in Figure 1. Part A of the Figure presents the influence of varied temperatures of annealing on the phase composition while part B presents the influence of the time of heat treatment on the phase composition. In both cases the BCC and FCC phases were investigated. BCC phases were recognized as iron base solid solution (BCC1 – space group number 229) and as CoFe
phase (BCC2 – space group number 221). FCC phase were recognized as nickel base solid solution (space group number 225).

### 3.1.1 Varied temperatures of annealing

For the sample that was only sintered and have not been annealing, the BCC and FCC phases were observed. However, the patterns assigned as BCC1 and BCC2 phases were combined together. During the heat treatment with the increase of the temperature of annealing the aforementioned patterns became separated. Perhaps the additional patterns (CoFe phase) could be formed by the diffusion of cobalt in to Fe base solid solutions. In the case of FCC phase it should be noted that the intensity of patterns near 50, 60 and 70 °2θ increase with the temperature of annealing. Moreover, for the XRD patterns obtained for 1000 °C the intensity of patterns assigned to FCC phase is much higher than for the BCC phase patterns. It could be assumed that with the increase of temperature the samples are more homogenized. This fact determined choosing temperature 1000 °C for further investigations.

### 3.1.2 Varied time of thermal treatment

Extend of the time of heat treatment also affects the homogenization of material. For the 20 h of annealing the intensity of FCC patterns is almost two times higher than for the samples annealed by 1 h. Obtained patterns are sharp and well separated. It could be assumed that increase of the time of heat treatment causes more advanced homogenization. As it was aforementioned before in the case of the varied temperatures of annealing also in this case patterns combined of BCC phases separates.

![Figure 1](image_url)

**Figure 1.** XRD patterns of investigated alloy: A – varied temperatures of annealing, B – varied time of annealing at 1000 °C.
3.2 Scanning Electron Microscopy

Microstructures of samples obtained after heat treatment are presented in Figure 2. At the presented figures the bright and dark areas could be noted, that represents phases described by the XRD measurements. Obtained materials are characterized by the huge porosity. The mechanical pore (MP) and diffusion pore (DP) could be observed. First type of pores is created during the hydrostatic pressing and second type during the diffusion of elements atoms. It should be noted that with the increase of the temperature the amount of darker areas and amount of diffusions pores increase. Both phenomena could be explained by the easier diffusion activated by increase of temperature. Not only temperature influences the diffusion activation, the time of annealing also indicate better chemical homogeneity of sintered materials.

![Figure 2. Microstructures of investigated alloy after different heat treatment (SEM:BSE). Top line of figures represents the various temperatures of annealing, time of treatment 1h. Bottom line of figures presents the various time of treatment in the same temperature (1000 °C); MP - mechanical pore, DP - diffusion pore.](image)

The EDS map of elements distribution for sintered material (Figure 3) shows that the obtained material is highly heterogeneous. It should be noted that the areas enriched by nickel are also enriched by aluminium and partially by titanium.

![Figure 3. EDS map of elements distribution for sample after sintering.](image)
The EDS map of element distribution obtained for the sample annealed at temperature 1000 °C for 1 hour is presented in Figure 4. Analysis of obtained data allows observing much better homogenization of chemical composition than for sample after only sintering. The brighter area is enriched by iron and cobalt while the darker area is enriched by aluminium, titanium and partially by nickel.

![Figure 4](image1.png)

**Figure 4.** EDS map distribution of elements for sample after sintering and annealing at 1000 °C for 1 hour.

Extend of the time of annealing from 1 hour to 20 hours allows observing the increase of homogeneity of elements distribution, especially titanium and cobalt (Figure 5). Aluminium enriched darker areas while iron enriched brighter areas.

![Figure 5](image2.png)

**Figure 5.** EDS map distribution of elements for sample after sintering and annealing at 1000°C for 20 hours.
On the basis of data obtained by the SEM and XRD it could be said that the darker areas of examined samples are enriched by aluminium and nickel that constitute the FCC phase (nickel-based solid state solution), while brighter areas represents the BCC phase (iron-based solid state solution).

4 Conclusions

According to obtained data and calculated values of thermodynamic parameters it is possible to obtain the High-Entropy Alloys from the elemental powders by the powder metallurgy techniques. Sintering of powders in the temperature 600 °C by 40 minutes it is not enough for fully homogenization of alloy, however in those conditions the diffusion of elements is activated. XRD measurements allow to determine dual phase structure composed from BCC and FCC phases. BCC phase corresponds to the iron-based solid solution and to the FeCo phase while the FCC corresponds to the nickel-based solid solution. XRD data confirms theoretical assumptions. It should be noted that increase of temperature and time of annealing leads to the homogenization of chemical and phase composition – separation of BCC phases with decreasing of BCC2 phase; increasing of FCC phase amount; nickel, titanium and aluminium tend to enrich the darker areas of microstructure while iron and cobalt enrich the brighter areas of microstructure. With the increase of both parameters the amount of diffusion pores increase, what also confirm the homogenization of the material.

Acknowledgements

Research supported by Ministry of Science and Higher Education Republic of Poland (project No. 15.11.110.428)

References

[1] Yeh J W, Chen S K, Lin S J, Gan J Y, Chin T S, Shun T T, Tsau C H and Chang S Y 2004 Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes, Adv. Eng. Mater. 6 (2004) 299–303
[2] Ranganathan S 2003 Allooyed pleasures: Multimetallic cocktails, Curr. Sci. 85 (2003) 1404–1406.
[3] Chen T K, Wong M S, Shun T T and Yeh J W 2005 Nanostructured nitride films of multi-element high-entropy alloys by reactive DC sputtering, Surf. Coatings Technol. 200 (2005) 1361–1365
[4] Yeh J W, Lin S, Chin T, Gan J, Chen S, Shun T T, Tsau C H and Chou S Y 2004 Formation of simple crystal structures in Cu-Co-Ni-Cr-Al-Fe-Ti-V alloys with multiprincipal metallic elements, Metall. Mater. Trans. A. 35 (2004) 2533–2536
[5] Hsu C, Yeh J W, Chen S and Shun T 2004 Wear Resistance and High-Temperature Compression Strength of Fcc CuCoNiCrAl0.5Fe Alloy with Boron Addition, Metall. Mater. Trans. A. 35A (2004) 1465–1469.
[6] Cantor B 2014 Multicomponent and High Entropy Alloys, Entropy 16 (2014) 4749–4768.
[7] Cantor B, Chang I T H, Knight P and Vincent A J B 2004 Microstructural development in equiatomic multicomponent alloys, Mater. Sci. Eng. A. 375–377 (2004) 213–218.
[8] Yao M J, Pradeep K G, Tasan C C and Raabe D 2014 A novel, single phase, non-equiatomic FeMnNiCoCr high-entropy alloy with exceptional phase stability and tensile ductility, Scr. Mater. 72–73 (2014) 5–8.
[9] Otto F, Dlouhý A, Somsen C, Bei H, Eggener G and George E P 2013 The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy, Acta Mater. 61 (2013) 5743–5755.
[10] Senkov O N, Scott J M, Senkova S V, Miracle D and Woodward C F 2011 Microstructure and room temperature properties of a high-entropy TaNbHfZrTi alloy, J. Alloys Compd. 509 (2011) 6043–6048
[11] Gwalani B, Soni V, Choudhuri D, Lee M, Hwang J Y, Nam S J, Ryu H, Hong S H and Banerjee R 2016 Stability of ordered L12 and B 2 precipitates in face centered cubic based high entropy alloys - Al 0.3 CoFeCrNi and Al 0.3 CuFeCrNi 2, Scr. Mater. 123 (2016) 130–134.
[12] Ng C, Guo S, Luan J, Wang Q, Lu J, Shi S and Liu C T 2014 Phase stability and tensile properties of Co-free Al0.5CrCuFeNi2 high-entropy alloys, J. Alloys Compd. 584 (2014) 530–537.
[13] Górecki K, Bała P, Cios G, Koziel T, Stepień M and Wieczerzak K 2016 The influence of cooling rate during crystallization on the effective Partitioning coefficient in High-Entropy Alloys from Al-Ti-Co-Ni-Fe system, Metall. Mater. Trans. A. 47 A (2016) 3257–3262
[14] Mohanty S, Gurao N P and Biswas K 2014 Sinter ageing of equiatomic Al20Co20Cu20Zn20Ni20 high entropy alloy via mechanical alloying, Mater. Sci. Eng. A. 617 (2014) 211–218.
[15] Bo R 2014 Age hardening of AlCrMoNiTi High Entropy Alloy prepared by powder metallurgy, Rare Met. Mater. Eng. 43 (2014) 1286–1290.
[16] Chen W, Fu Z, Fang S, Xiao H and Zhu D 2013 Alloying behavior, microstructure and mechanical properties, J. Mater. 51 (2013) 854–860.
[17] Fang S, Chen W and Fu Z 2014 Microstructure and mechanical properties of twinned mechanical alloying and spark plasma sintering, Mater. Des. 54 (2014) 973–979.
[18] Guo S, Ng C, Lu J and Liu C T 2011 Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys, J. Appl. Phys. 109 (2011) 103505-2–103505-5.
[19] Yang X and Zhang Y 2012 Prediction of high-entropy stabilized solid-solution in multi-component alloys, Mater. Chem. Phys. 132 (2012) 233–238.
[20] Miracle D, Miller J, Senkov O, Woodward C, Uchic M and Tiley J 2014 Exploration and development of High Entropy Alloys for structural applications, Entropy 16 (2014) 494–525.