Kovove Mater. 62 2024 267–273
DOI: 10.31577/km.2024.5.267

Effect of heat treatment temperature on the microstructure and hardness of AlCoCrNiFe high-entropy alloy sintered by hot oscillating pressing

Ka Gao[1,2,3]*, Yanghu Hu[4], Zixiang Zhang[2], Chunyang Ren[2], Yan Xiong[5], Dejian Sun[6], Yang Gao[6]

[1] *Key Laboratory of Advanced Manufacture Technology for Automobile Parts (Chongqing University of Technology), Ministry of Education, Chongqing 401135, P. R. China*
[2] *Science Fund of Shandong Laboratory of Advanced Materials and Green Manufacturing at Yantai, Yantai 264000, P. R. China*
[3] *Material Corrosion and Protection Key Laboratory of Sichuan province, Zigong 643000, P. R. China*
[4] *State Key Laboratory of Metal Extrusion and Forging Equipment Technology (China National Heavy Machinery Research Institute Co., Ltd.), Xi'an 710000, P. R. China*
[5] *Hubei Provincial Key Laboratory of Green Materials for Light Industry, Hubei University of Technology, Wuhan 430068, P. R. China*
[6] *School of Materials Science and Engineering, Zhengzhou University of Aeronautics, Zhengzhou 450015, P. R. China*

Received 2 December 2023, received in revised form 12 April 2024, accepted 15 October 2024

Abstract

The effect of heat treatment (HT) temperature on the microstructure and properties of hot oscillating pressing (HOP) sintered AlCoCrNiFe high-entropy alloy (HEA) was studied. Before and after HT, it is basically composed of the BCC and FCC phases. As the HT temperature increases, the original powder interface of HEA gradually disappears and melts, the degree of powder particle bonding is strengthened, and the density is gradually increased. Its microstructure has been improved. However, the content of the BCC phase gradually precipitates to increase, and the thickness of the lamellar phase gradually increases. Therefore, as the HT temperature increases, its Vickers hardness gradually increases, reaching a maximum of approximately 423.6 HV_1. However, due to the increase in phase layer thickness, the increase in Vickers hardness gradually slows down at higher HT temperatures. It can be seen that an appropriate HT temperature is beneficial for obtaining high-density and high-performance AlCoCrNiFe HEA.

Key words: heat treatment temperature, AlCoCrNiFe high-entropy alloy, hot oscillating pressing, microstructure, property

1. Introduction

Since 2004, Ye et al. [1] proposed the multi-principal component alloy system, which is a multi-principal component high-entropy alloy (HEA), and defined this alloy as an alloy obtained from at least five or more components in a ratio of 5–35 % or equimolar ratio. The proposal of this theory breaks the traditional design concept of alloys, and at the same time, due to the high strength, high hardness, high thermal stability, high wear resistance, and corrosion resistance of this alloy, it opens the door to research on multi-component alloys [2–8]. Since the advent of high-entropy alloys, after more than a decade of exploration by researchers, the understanding of their properties has continued to increase, and the preparation methods of high-entropy alloys have also become more diverse. Currently, HEAs are mainly prepared using powder metallurgy [9], casting, and additive manufacturing [10]. The powder metallurgy method has received widespread attention as it can avoid segregation between different components during the melting process. However, conventional sintering techniques often have defects and technical deficiencies, resulting

*Corresponding author: e-mail address: gaoka@usst.edu.cn

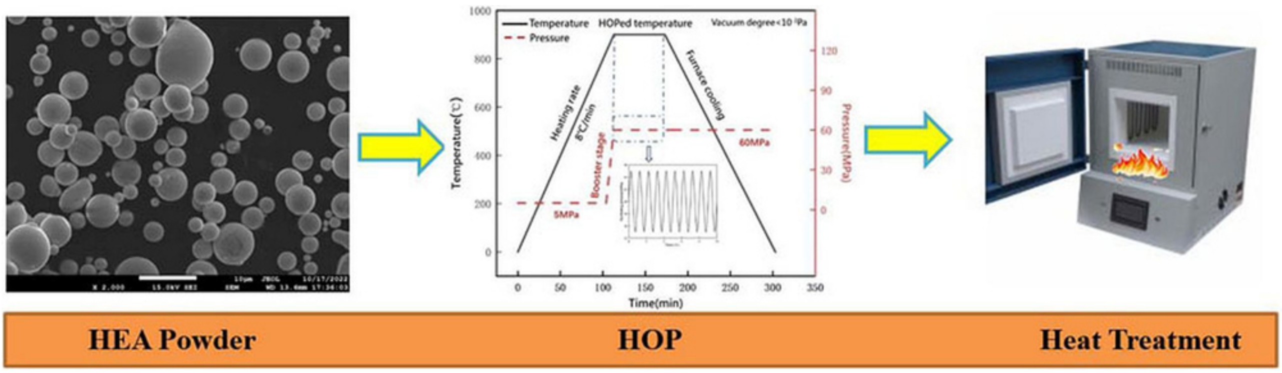

Fig. 1. Schematic diagram of experiment process.

in a lower relative density of sintered materials and abnormal grain growth. Recently, Xie and An et al. [11] reported a novel hot oscillating pressing (HOP) technology that is similar to traditional hot pressing (HP) processes by replacing static pressure with dynamic cyclic pressure. It can significantly suppress grain growth and obtain high-density materials and uniform microstructures, greatly improving its performance, and has been widely used in various materials, such as ZrO2 ceramics, WC-6Co hard alloy, W refractory alloy and AlCoCrNiFe high-entropy alloy [12–16], etc.

On the other hand, heat treatment (HT), as an important link in improving the performance of metals and alloys, is a heat treatment process that heats, insulates, and cools metal materials in the solid state, changing the surface or internal microstructure and phase composition of the material, thereby obtaining a metal hot working process that meets people's requirements and performance [17]. Due to the limitations of powder metallurgy sintering, it is difficult to achieve perfect usage requirements during the forming process, especially for workpieces with special requirements. It is necessary to eliminate the defects generated during preparation, further reduce component segregation and internal stress, and improve the properties of the alloy. Suitable heat treatment processes are crucial for obtaining higher entropy alloys with better microstructure and properties [18].

Based on this, this work conducted heat treatment on the hot oscillating pressing sintered AlCoCrNiFe high-entropy alloy. The influence of heat treatment temperature on the density, microstructure, and hardness properties of the alloy was explored. Moreover, the densification and phase coarsening evolution during its heat treatment process were analyzed.

2. Experiments and methods

This work uses AlCoCrNiFe (atomic ratio 20 %) (Beijing Zhongke Yannuo New Material Technology Co., Ltd., P. R. China) pre-alloy powder as the raw material. The powder has an average particle size of 12.5 μm shown in Fig. 1. The sintering of the powder was carried out in a hot oscillating pressing furnace (HOP-2020, E-field Materials Technology Co., Chengdu, China) with the vacuum ($< 10^{-3}$ Pa) using the process schematically illustrated in Fig. 1. First, the obtained powder was filled into a graphite die with an inner diameter of 30 mm and then heated to target temperatures of 900 ℃ with an oscillating pressure of 60 ± 5 MPa and a frequency of 1 Hz. After sintering for 1 hour, the sintered body was obtained. Then, the treated sintered body is subjected to heat treatment in a vacuum tube furnace (XD-1200NT, Zhengzhou Tianzong Electrical Equipment Co., Zhengzhou, P. R. China) at different temperatures (500, 600, and 700 ℃ for 1 hour, with a heating rate of 17.5 ℃ min^{-1}. The detailed experimental process is shown in Fig. 1. The resulting samples were named HT-500 ℃, HT--600 ℃, and HT-700 ℃, respectively.

The Archimedes method was used to measure the bulk density of the AlCoCrNiFe high-entropy alloy before and after heat treatment (five measurements were made for each sample). The phase composition of the alloy was analyzed using an X-ray diffractometer (XRD, SmartLab, Rigaku, Tokyo, Japan). Scanning electron microscopy (SEM, JSM-7001F, JEOL Ltd., Tokyo, Japan) was used to observe and analyze the microstructure and microstructure evolution process of AlCoCrNiFe high-entropy alloy. At the same time, the average grain size was measured from SEM images taken at the polishing surface using the marking method. The Vickers hardness was tested by a Vickers hardness tester (HVS-1000, Ji'nan Fangyuan Test Instrument Co., Ji'nan, P. R. China).

3. Results and discussion

3.1. Phase composition

Firstly, to characterize the microstructure evolu-

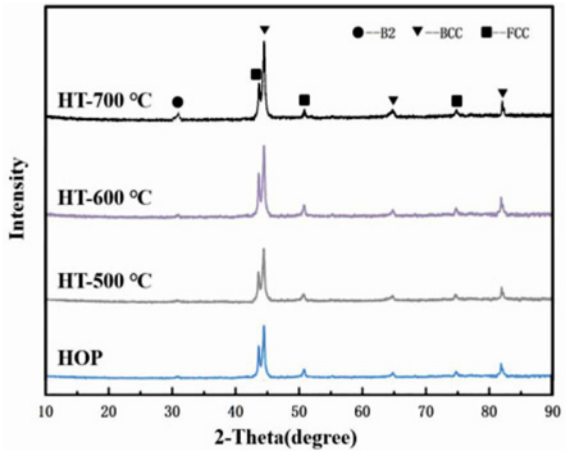

Fig. 2. XRD spectra of AlCoCrNiFe high-entropy alloy sintered by hot oscillating pressing under different HT temperatures: (a) HOP, (b) HT-500 ℃, (c) HT-600 ℃, and (d) HT-700 ℃.

tion of the AlCoCrNiFe high-entropy alloy sintered by hot oscillating pressing at different heat treatment temperatures, Fig. 2 shows the XRD results of the samples at different HT temperatures. It can be seen that the AlCoCrNiFe HEA before and after heat treatment all consisted of FCC, BCC, and a small amount of B2 phase, which was consistent with the results reported in the study [15]. The difference was that after heat treatment, the diffraction peak intensity of BCC and B2 phases in HEA was increased, and with the increase in heat treatment temperature, the intensity of the above two phases gradually increased. This was mainly due to the increased heat treatment temperature, which promoted the diffusion and solid solution degree between low-temperature elements in the sintered body. That resulted in a significant increase in the content of diffusion BCC and B2 phases (with stronger diffraction peak intensity).

3.2. Microstructure

As shown in Fig. 3, the microstructure morphology of the HOP-sintered AlCoCrNiFe high-entropy alloy before and after different heat treatment temperatures (500, 600, and 700 ℃) is presented. According to the above XRD results and research reports [15, 16], it can be seen that the microstructure of the

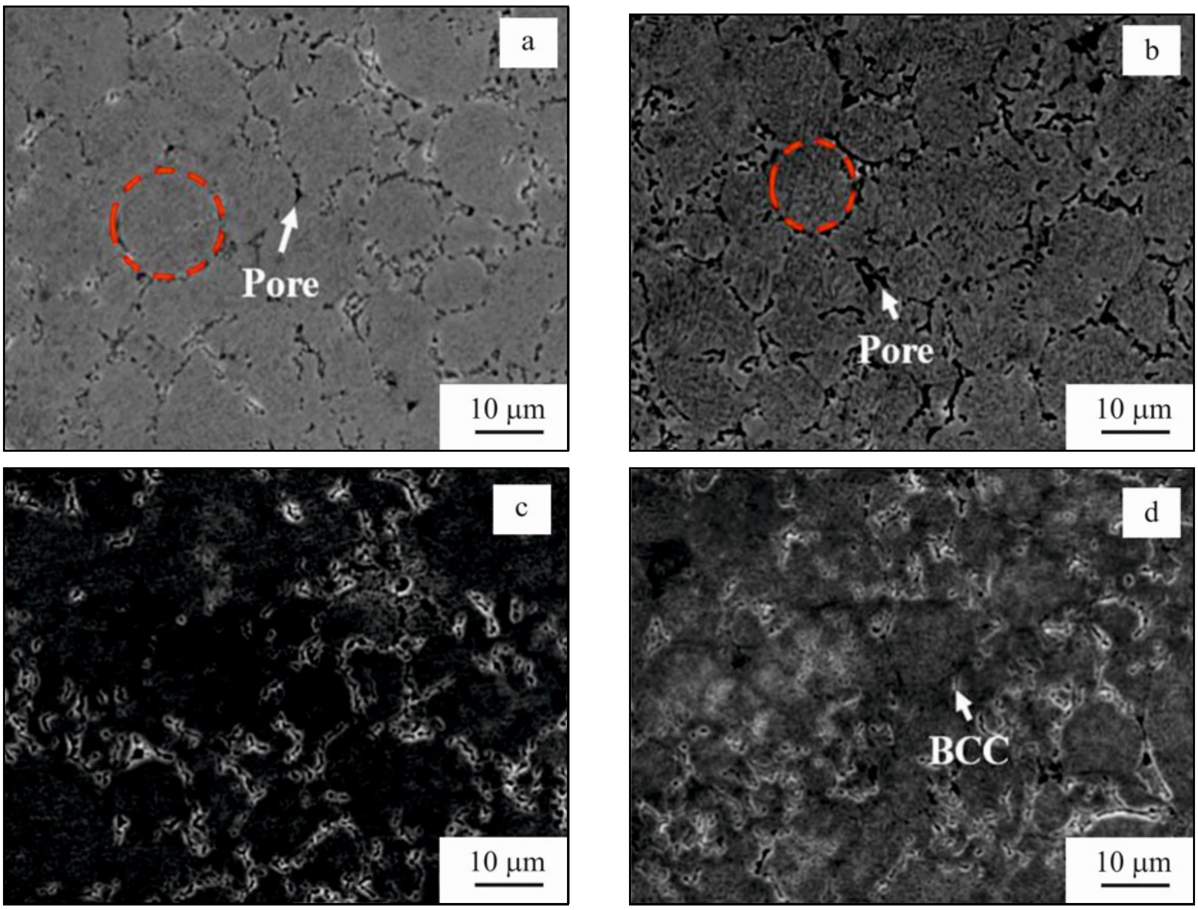

Fig. 3. Microstructure of AlCoCrNiFe high-entropy alloy at different HT temperatures.

AlCoCrNiFe HEA was mainly composed of the FCC + BCC phase, as shown in Fig. 3a. The gray color represented the FCC phase, the gray-white color represented the BCC phase, and the black color represented the pores at the original powder interface, which was in good agreement with the results in Fig. 2. The HOP-sintered AlCoCrNiFe high-entropy alloy was a coupled eutectic-equiaxed crystal structure composed of FCC and BCC. The interface contour of the original powder was more obvious, and the bonding degree between particles was not tight. Then, the density might not be high. The microstructure of HEA alloy after heat treatment at different temperatures was still composed of the above two phases, basically maintaining the morphology of equiaxed grains before heat treatment. However, as the heat treatment temperature increased, the precipitates at the grain boundaries of the powder continued to increase, the BCC phase in the gray-white part also gradually increased, and the original powder interface gradually disappeared. This ultimately led to the merger and growth between the powders, which promoted the coarsening of the structure and the change of phase volume fraction, as shown in Figs. 3b–d. At the same time, as the heat treatment temperature increased, the powder bonding degree of high-entropy alloys improved, the porosity reduced, and their density was more dense compared to the sintered sample. After heat treatment, its pores were eliminated to some extent. This work suggested that this might be due to the increased diffusion rate of lower melting point elements in HEA alloys caused by heat treatment, which promoted the precipitation of the BCC phase and microstructure coarsening. At the same time, as the heat treatment temperature increased, the diffusion of elements at the grain boundaries of the powder promoted the mutual bonding of the interfaces, which to some extent improved the tightness and density of the interfaces, optimized the microstructure, and may have a promoting effect on its performance.

3.3. Densification

This work conducted density analysis to investigate further the effect of heat treatment on the HOP-sintered AlCoCrNiFe high-entropy alloy. Figure 4 shows the relative density of the AlCoCrNiFe high-entropy alloy before and after heat treatment. It can be seen that, due to the low sintering temperature, the density of the AlCoCrNiFe high-entropy alloy was only 95.4 % under HOP sintering at 900 ℃. However, after heat treatment, especially after 500 ℃ heat treatment, its density increased significantly, reaching about 98.5 %. As the heat treatment temperature increased, the relative density of the AlCoCrNiFe HEA was gradually increased, and ultimately, the highest density could be reached at 99.2 % in the HT-700 ℃ sample. This was in good agreement with the microstructure results in Fig. 3. It is worth noting that as the HT temperature increased, although the density of HEA gradually increased, its growth rate was significantly slowed. This work argued that some defects, such as pores and shrinkage porosity, were inevitable during the HOP-sintered AlCoCrNiFe HEA [16], which, to some extent, affected the relative density of the alloy. The alloy underwent long-term insulation during heat treatment, increasing its atomic diffusion ability. The atoms in the alloy were migrated to other positions, filling vacancies in the alloy. On the other hand, some grain boundaries were melted in Fig. 3. The reduction of grain boundaries increased the density of the alloy. When the heat treatment temperature increased and the density of the alloy became higher, the alloy became denser, and the resistance to atomic migration increased, causing its density growth to slow down gradually. However, heat treatment has somewhat improved the density of HOP-sintered AlCoCrNiFe HEA, which improves performance.

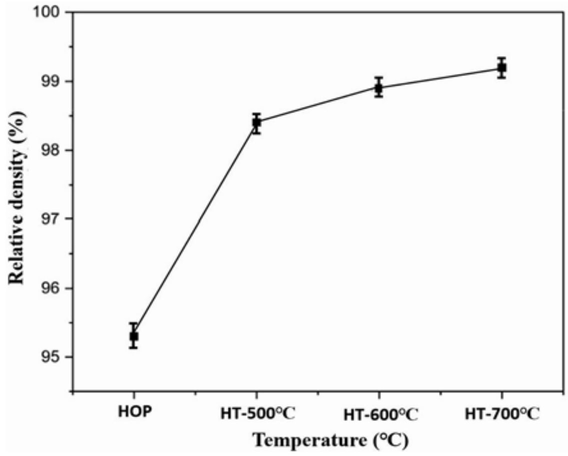

Fig. 4. Relative density of AlCoCrNiFe high-entropy alloy at different HT temperatures.

3.4. Phase volume fraction and lamellar thickness

From the microstructure evolution mentioned above (Fig. 3), it can be seen that with the increase in heat treatment temperature, the microstructure, porosity, and other defects of the HOP-sintered AlCoCrNiFe high-entropy alloy had been improved before and after heat treatment, but there had been phenomena of microstructure coarsening and changes in phase volume fraction. Especially, when the heat treatment temperature was 700 ℃, there was a significant coarsening of the dual-phase eutectic lamellar structure (increasing the thickness of the phase

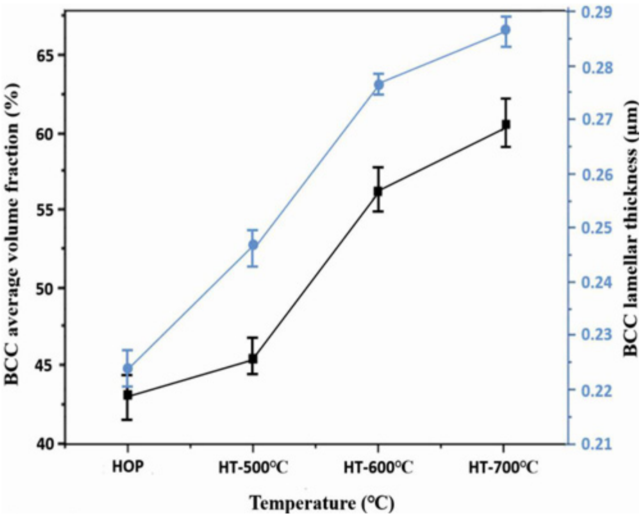

Fig. 5. BCC phase volume fraction (a) and lamellar thickness (b) of AlCoCrNiFe high-entropy alloy at different HT temperatures.

layer), and the integral number of the phase inside the particles also transformed. Therefore, this work statistically analyzed the BCC phase volume fraction and phase lamellar thickness of the AlCoCrNiFe high-entropy alloy sintered by HOP at different HT temperatures, as shown in Fig. 5. As the heat treatment temperature increased, the volume fraction of the BCC phase in HOP AlCoCrNiFe HEA was increased. Interestingly, at higher HT temperatures, the volume fraction of the BCC phase was rapidly increased. In addition to the change in phase volume fraction, the lamellar thickness of the BCC phase in the microstructure was also increased with the increase in heat treatment temperature, with the largest increase at 700 ℃, reaching a maximum of about 0.286 μm. The overall trend of change was consistent with the evolution of microstructure. Based on the above discussion, this work believed that the changes in the BCC phase volume fraction and phase lamellar thickness before and after heat treatment might have a certain impact on the properties of AlCoCrNiFe high-entropy alloys.

3.5. Hardness

Figure 6 shows the Vickers hardness of HOP-sintered AlCoCrNiFe HEA before and after heat treatment. It can be seen that before heat treatment, the hardness of the HOP-sintered AlCoCrNiFe high-entropy alloy was only 318.7 HV1. After heat treatment, the hardness of the AlCoCrNiFe high-entropy alloy was gradually increased with the increase of the heat treatment temperature, and the maximum hardness value in the HT-700 ℃ sample could be reached at 423.6 HV1. Among them, the hardness value in the HT-500 ℃ sample was about 381.8 HV1, and its

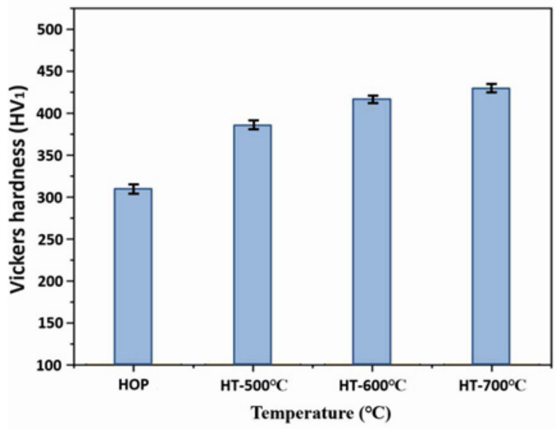

Fig. 6. Vickers hardness of AlCoCrNiFe high-entropy alloy at different HT temperatures.

hardness performance had been significantly improved compared to before heat treatment. After heat treatment at 600 and 700 ℃, the increase in hardness decreased, which was consistent with the density change pattern in Fig. 4.

This work considered that the properties of AlCoCrNiFe high-entropy alloys were mainly closely related to their density and microstructure. The higher the density and the smaller the thickness of the phase lamellar, the better their performance. In this work, the HOP-sintered AlCoCrNiFe HEA was subjected to heat treatment. At different temperatures, its density and microstructure were improved, the BCC phase content increased, the original powder interface disappeared, and the interface bonding strength was strengthened. Thereby, its hardness performance was improved. Then, as the heat treatment temperature increases, the thickness of the phase lamellar gradually increases, which is not conducive to improving performance to a certain extent. This was also why the performance increase decreased at higher temperatures.

4. Conclusions

The effect of different heat treatment temperatures on the microstructure and properties of AlCoCrNiFe high-entropy alloy sintered by hot oscillating pressing (HOP) was investigated. The HOP-sintered AlCoCrNiFe high-entropy alloy mainly comprises the BCC and FCC phases before and after heat treatment. As the heat treatment temperature increases, the original powder interface of the high-entropy alloy gradually disappears and melts, the degree of powder particle bonding is strengthened, the porosity is gradually reduced, and the density is gradually increased. Its microstructure has been improved. However, the content of the BCC phase gradually precipitates and increases, and the thickness of the lamellar phase gradually increases. Therefore, as the heat treatment temperature increases, its Vickers hardness gradually increases, reaching a maximum of approximately 423.6 HV1. However, due to the increase in phase layer thickness, the increase in density and Vickers hardness gradually slows down at higher heat treatment temperatures. It can be seen that an appropriate heat treatment temperature can be beneficial for obtaining high-density and high-performance AlCoCrNiFe high-entropy alloys.

Acknowledgements

This research work is supported by the National Natural Science Foundation of China (51904277, 52374370), the Opening Foundation of Key Laboratory of Advanced Manufacture Technology for Automobile Parts, Ministry of Education (2022 KLMT05), the Project of Zhongyuan Critical Metals Laboratory (GJJSKFYB202405), the Opening Project of Material Corrosion and Protection Key Laboratory of Sichuan province (2024CL12), the Science Fund of Shandong Laboratory of Advanced Materials and Green Manufacturing at Yantai (AMGM2024F19), the Open Fund of Hubei Provincial Key Laboratory of Green Materials for Light Industry, Hubei University of Technology (202307A04), the State Key Laboratory of Metal Extrusion and Forging Equipment Technology, China National Heavy Machinery Research Institute Co. Ltd. (S2308100.W13).

References

[1] J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau, S. Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes, Adv. Eng. Mater. 5 (2004) 299–303. https://doi.org/10.1002/adem.200300567

[2] B. Gludovatz, A. Hohenwarter, D. Catoor, E. H. Chang, E. P. George, R. O. Ritchie, A fracture-resistant high-entropy alloy for cryogenic applications, Phys. Inorganic Chemistry 6201 (2014) 1153–1158. https://doi.org/10.1002/chin.201447007

[3] M. L. Wang, H. Z. Cui, Y. Q. Zhao, C. M. Wang, Q. Song, A simple strategy for fabrication of an FCC-based complex concentrated alloy coating with hierarchical nanoprecipitates and enhanced mechanical properties, Mater. Des. 180 (2019) 107893. https://doi.org/10.1016/j.matdes.2019.107893

[4] W. P. Chen, Z. Q. Fu, S. C. Fang, Y. P. Wang, H. Q. Xiao, D. Z. Zhu, Processing, microstructure and properties of Al0.6CoNiFeTi0.4 high entropy alloy with nanoscale twins, Mater. Sci. Eng. A 565 (2013) 439–444. https://doi.org/10.1016/j.msea.2012.12.072

[5] Y. Y. Chen, T. Duval, U. D. Hung, J. W. Yeh, H. C. Shih, Microstructure and electrochemical properties of high entropy alloys – A comparison with type-304 stainless steel, Corros. Sci. 47 (2005) 2257–2279. https://doi.org/10.1016/j.corsci.2004.11.008

[6] Y. J. Hsu, W. C. Chiang, J. K. Wu, Corrosion behavior of $FeCoNiCrCu_x$ high-entropy alloys in 3.5% sodium chloride solution, Mater. Chem. Phys. 2 (2005) 112–117. https://doi.org/10.1016/j.matchemphys.2005.01.001

[7] R. Sriharitha, B. S. Murty, R. S. Kottada, Alloying, thermal stability and strengthening in spark plasma sintered $Al_xCoCrCuFeNi$ high entropy alloys, J. Alloys Compd. 583 (2014) 419–426. https://doi.org/10.1016/j.jallcom.2013.08.176

[8] M. H. Chuang, M. H. Tsai, W. R. Wang, S. J. Lin, J. W. Yeh, Microstructure and wear behavior of $Al_xCo_{1.5}CrFeNi_{1.5}Ti_y$ high-entropy alloys, Acta Mater. 59 (2011) 6308–6317. https://doi.org/10.1016/j.actamat.2011.06.041

[9] S. Mohanty, T. N. Maity, S. Mukhopadhyay, S. Sarkar, N. P. Gurao, S. Bhowmick, K. Biswas, Powder metallurgical processing of equiatomic AlCoCrFeNi high entropy alloy: Microstructure and mechanical properties, Mater. Sci. Eng. A 679 2017 299–313. https://doi.org/10.1016/j.msea.2016.09.062

[10] Y. F. Kao, T. J. Chen, S. K. Chen, J. W. Yeh, Microstructure and mechanical property of as-cast, -homogenized, and -deformed $Al_xCoCrFeNi$ ($0 \leq x \leq 2$) high-entropy alloys, J. Alloys Compd. 488 (2009) 57–64. https://doi.org/10.1016/j.jallcom.2009.08.090

[11] Z. P. Xie, L. Shuang, L. N. An, A novel oscillatory pressure-assisted hot pressing for preparation of high-performance ceramics, J. Am. Ceram. Soc. 97 (2014) 1012–1015. https://doi.org/10.1111/jace.12869

[12] J. S. Li, J. Y. Fan, Y. Yuan, J. L. Liu, K. Zhao, D. G. Liu, Z. P. Xie, L. N. An, Effect of oscillatory pressure on the sintering behavior of ZrO_2 ceramic, Ceram. Int. 46 (2020) 13240–13243. https://doi.org/10.1016/j.ceramint.2020.02.100

[13] K. W. Wang, K. Zhao, J. L. Liu, D. G. Liu, T. Li, W. Li, Z. Z. Sun, L. An, Interplay of microstructure and mechanical properties of WC-6Co cemented carbides by hot oscillating pressing method, Ceram. Int. 47 (2021) 20731–20735. https://doi.org/10.1016/j.ceramint.2021.04.063

[14] K. Gao, D. Y. Liu, T. Y. Ma, J. L. Zhao, D. J. Sun, Y. Gao, K. M. Pan, Oscillating pressure sintered W-Cu refractory alloy with high density and hardness under lower temperature, Int. J. Refract. Met. Hard Mater. 102 (2022) 105702. https://doi.org/10.1016/j.ijrmhm.2021.105702

[15] K. Gao, C. J. Zhao, W. Zhao, D. J. Sun, Y. Gao, Z. H. Wang, L. N. An, W-Ti refractory alloy with high hardness forged using dynamic pressure-assisted hot pressing, Int. J. Refract. Met. Hard Mater. 114 (2023) 106241. https://doi.org/10.1016/j.ijrmhm.2023.106241

[16] K. Gao, D. Y. Liu, D. J. Sun, Y. Gao, Z. H. Wang, L. N. An, Microstructure and properties of AlCoCrNiFe high-entropy alloy sintered by hot oscillating pressing, Intermetallics 154 (2023) 107802. https://doi.org/10.1016/j.intermet.2022.107802

[17] V. V. Palacheva, A. G. Mochugovskiy, D. G. Chubov, A. N. Koshmin, V. V. Cheverikin, J. Cifre, Influence of mechanical and heat treatment on structure evolution and functional properties of Fe-Al-Tb alloys, Mater. Lett. 310 (2022) 131521. https://doi.org/10.1016/j.matlet.2021.131521

[18] K. Lan, W, Ding, Y. T. Yang, Effect of heat treatment on microstructure and mechanical properties of Ti-containing low alloy martensitic wear-resistant steel, China Foundry 20 (2023) 329–338. https://doi.org/10.1007/s41230-023-3023-4