1-1-2020

Study on the continuous phase evolution and physical properties of gas-atomized high-entropy alloy powders

Jui Ting Liang
National Taiwan University of Science and Technology

Kuei Chung Cheng
National Taiwan University of Science and Technology

Shih Hsun Chen
National Taiwan University of Science and Technology

Jing Han Chen
Louisiana State University

Shane Stadler
Louisiana State University

See next page for additional authors

Recommended Citation

Liang, J., Cheng, K., Chen, S., Chen, J., Stadler, S., Li, C., & Hsueh, C. (2020). Study on the continuous phase evolution and physical properties of gas-atomized high-entropy alloy powders. *Materials Research Express, 7* (2) https://doi.org/10.1088/2053-1591/ab5ee2

Study on the continuous phase evolution and physical properties of gas-atomized high-entropy alloy powders

Materials Research Express

OPEN ACCESS

RECEIVED
1 October 2019

REVISED
15 November 2019

ACCEPTED FOR PUBLICATION
4 December 2019

PUBLISHED
17 February 2020

PAPER

Study on the continuous phase evolution and physical properties of gas-atomized high-entropy alloy powders

Jui-Ting Liang[1], Kuei-Chung Cheng[1], Shih-Hsun Chen[1], Jing-Han Chen[2], Shane Stadler[2], Chia-Lin Li[3] and Chun-Hway Hsueh[3]

[1] Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei, 10607, Taiwan
[2] Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, United States of America
[3] Department of Materials Science and Engineering, National Taiwan University, Taipei, 10607, Taiwan

E-mail: shchen@mail.ntust.edu.tw

Keywords: high entropy alloys, gas atomization, annealing, AlCoCrFeNi, precipitation hardening

Abstract

In this study, AlCoCrFeNi high entropy alloy (HEA) powders were fabricated by gas atomization process, and the effects of annealing heat treatment on phase evolution and mechanical properties were investigated. The as-atomized powders have pure BCC phase with a spherical shape and equal composition distribution, and then the FCC and sigma phase sequentially generated after annealing. The mechanical property such as hardness was evidently enhanced, which was caused by precipitation hardening effect. After the raw powders were annealed at 600 °C, the FCC (Al–Ni) phase began to precipitate, the its phase intensity raised with the annealing temperature. Then, the sigma phase (Fe–Cr) formed as the annealing temperature reached 800 °C. Both mechanical properties and lattice constant were influenced by heating effect. According to the results, the lattice became loose with the increasing temperature. In summary, the mechanical properties and phase constitutions of gas-atomized AlCoCrFeNi HEA powders can be adjusted via annealing process, resulting in precipitation hardening effect.

1. Introduction

Recently, more and more efforts were devoted to discover the possibility brought by high entropy alloys (HEAs) since it was expounded by Yeh in 1995 [1–3]. Compared to traditional alloys, HEAs could simultaneously possess advantages of various aspects such as high ductility, good anti-corrosion resistance, and high temperature stability. HEA systems briefly were defined as the alloys composed of more than five elements, ranging from 5–35 at% for each [2, 4]. Different from traditional alloys, the characteristics of HEAs could not only be defined by one single base element, but brought in by the competition among multiple elements.

HEAs have developed over twenty years, but the promotion of applications was still limited by some drawbacks. For example, researchers usually commenced HEA with bulk materials seeking a substitute for structural purposes, and yet the product quality often suffered from some manufacturing defects, such as segregation and cracks, resulting from sluggish diffusion in cooling process [5]. In order to resolve these issues, HEA powders were developed by cooling rapidly at the rate up to 10^4 K sec^{-1} [6]. Relative to bulk materials, the rapid solidifying rate in a smaller dimension can be beneficial for preserving the near-liquid state in as-obtained powders without phase segregation.

In this study, AlCoCrFeNi HEAs alloy system was selected as target material which has an equatomic composition and dual-phase (BCC + FCC) [7]. AlCoCrFeNi is a kind of HEA which was well investigated, so the database including phase constitution, hardness and melting point was established. It has good strength, resistance to corrosion and high temperature stability. Gas-atomization process can deliver the desired powder quality and was adopted in our experiments. With a rapid cooling rate, the state of AlCoCrFeNi alloy powders would be preserved at the high-temperature state [8–10], including composition distribution and microstructure. The powders for HEAs were seldom investigated but gas atomization process which was

conducted in this research is a mature process for powder. It could reserve the initial phase of HEAs and obtain homogeneous composition and spherical shape. The as-obtained powders were only composed of pure BCC phase. When the annealing temperature was raised above 600 °C, BCC phase began to turn into FCC phase. According to our findings, a suitable annealing treatment can promote the growth of FCC phase in as-atomized powders. Although some studies in determining the characteristics of AlCoCrFeNi were published, the discussions on continuous phase evolution were rarely reported [11, 12]. The higher annealing temperature, the more FCC phases were promoted, and the phase intensity also increased with the annealing time. In addition to the phase constitution, the practical physical and chemical properties at high-temperature are important information, but not easy to be evaluated. *In-situ* observation was hence conducted in our experiments to monitor the change accompanying with the temperature.

After annealing treatment, the phase constitution and element distribution were different from initial states, resulting in the change of mechanical properties. Hence, the effects of annealing time and temperature on phase evolution and the mechanical properties of different phase constitution were investigated using scanning electron microscopy, energy dispersion, x-ray diffraction and nanoindentation.

2. Experimental procedures

The target material, AlCoCrFeNi HEA powders were fabricated from pure elements with purity above 99.9%. At first, raw element ingots were pre-melted together as a liquid mixture. In order to avoid oxidization and obtain high quality powders, the protection of argon atmosphere was introduced. The liquid mixture was poured through an insulated crucible into gas nozzle, and then the melt was made into droplets by using a gas stream of high pressure. The solidified powders were cooled down to ambient temperature after the whole melt was delivered. The as-atomized AlCoCrFeNi powders were sieved with two step process: the first one is to remove overlarge and irregular particles by a 200 mesh, and then the uniform and circular particles with diameters between 50 and 70 μm are collected for subsequent annealing experiments.

Commonly, AlCoCrFeNi is a dual-phase alloy by the conventional metallurgical synthesis; however, the as-atomized powder is of pure BCC phase, resulting from the rapid cooling process. The phase transition temperature of AlCoCrFeNi powder from BCC to FCC is about 600 °C. Subsequently, minor sigma phase precipitated beyond 800 °C, and the phase constitution would keep stable before re-melted [13]. In order to study the effect of high annealing temperatures on the phenomenon of phase transition, as-atomized powders were annealed at various temperatures from 500 to 1200 °C at an interval of 100 °C. Since the rapid-solidifying atomized powders might be reserved at its metastable state, the continuous phase evolution is a useful information to observe the formation of new phase and the degree of crystallinity with temperature. Thus, the *in situ* high-temperature XRD were conducted in this study. The heating rate of *in situ* XRD is 200 °C/min and the temperature was kept for 1 h at every section.

The microstructure and elements distribution of AlCoCrFe Ni powders were investigated by field-emission scanning electron microscopy (FE-SEM, JEOL7900F) equipped with an energy dispersive spectrometer (EDS). The crystallinity identification for *in situ* annealing treatments was conducted using x-ray diffractometer (XRD, Bruker D8 advance eco) combined with a vacuum heating stage. Nano-indenter (Bruker TI-980 TriboIndenter) was applied to measure the hardness of powders with different phase constitutions.

3. Results and discussion

Figure 1(a) shows the SEM image and element composition of as-atomized AlCoCrFeNi powders, and the EDS results collected from the selected area reveal an equatomic ratio of each element. According to the observation, the powders are of complete spherical appearance and its average particle size is 64.5 $\pm$ 3.2 μm. After confirming the basic features of AlCoCrFeNi powders, the element mapping was carried out and shown in figure 1(b), suggesting an identical distribution of all constitutions. Due to the rapid cooling process, the AlCoCrFeNi powders had no sufficient time to react and diffuse and the five constitutions were distributed evenly.

Figure 2 presents the XRD spectra of gas-atomized AlCoCrFeNi powders after annealing at 500 and 900 °C for 48 h. Not only did the composition of as-atomized powders distribute as a nearly liquid state, but also the crystalline structure was of pure BCC phase before its phase transformation temperature (600 °C) [7]. After annealing in the vacuum furnace at 900 °C for 48 h, the phase transition of FCC and sigma phase was induced because of sufficient heat energy and temperature. The element distribution of 900 °C-annealed powders was recorded in figure 3. Compared with the raw powders, the differences in phase and composition became evident, in which Cr segregated from Al and Ni, to form a Cr-rich phase. The element compositions of specific points are listed in table 1. Point 1 and 3 located in Cr-rich area; the Cr contents were up to 47.6% and 87.5, respectively. Al

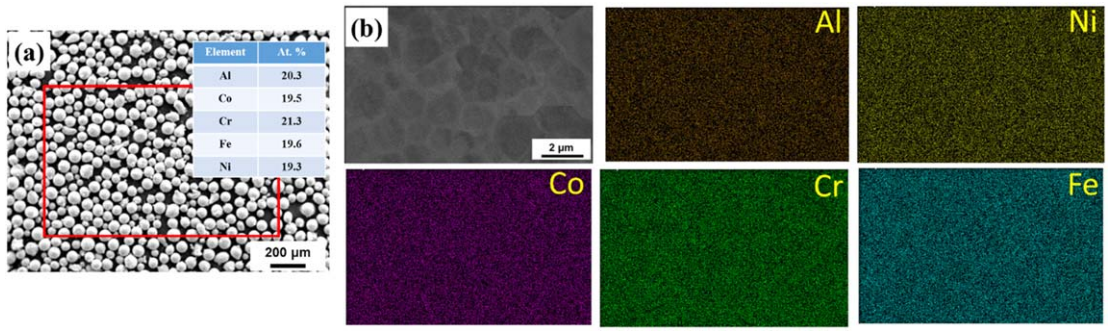

Figure 1. (a) SEM image and (b) element mapping of as-atomized AlCoCrFeNi powders.

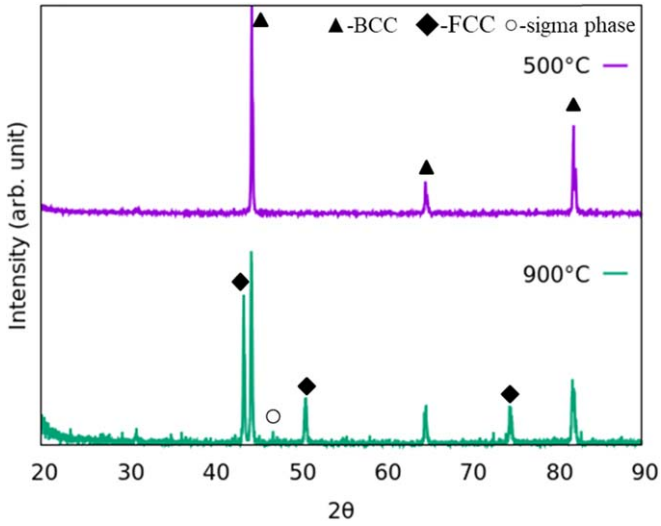

Figure 2. XRD spectra of gas-atomized AlCoCrFeNi powders after annealing at 500 and 900 °C for 48 h.

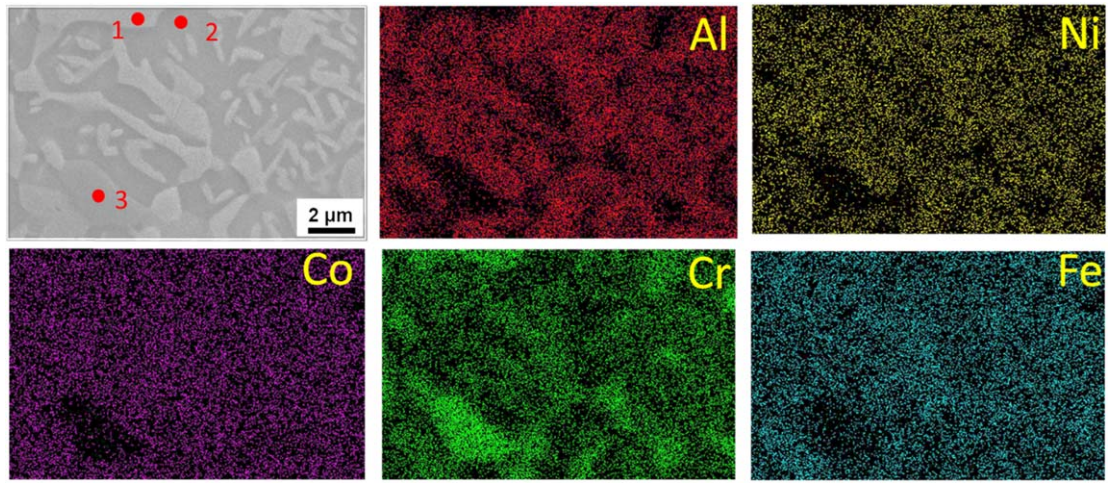

Figure 3. Element mapping of annealed AlCoCrFeNi powders after annealing at 900 °C for 48 h.

and Ni elements simultaneously gathered around Cr-rich areas (as point 2) and resulted in (Al, Ni)-rich FCC precipitates [13]. With sufficient time and energy, every element tends to reach their stable states, resulting in dual BCC + FCC phases.

Table 1. The results of EDS analysis of AlCoCrFeNi powders after annealing at 900 °C for 48 h. Points No. 1 to 3 are marked in figure 3.

Point No.	Element (at%)				
	Al	Ni	Cr	Fe	Co
1	1.8	5.4	47.6	26.3	18.8
2	31.5	30.0	6.4	12.9	19.2
3	0.9	2.1	87.5	6.1	3.4

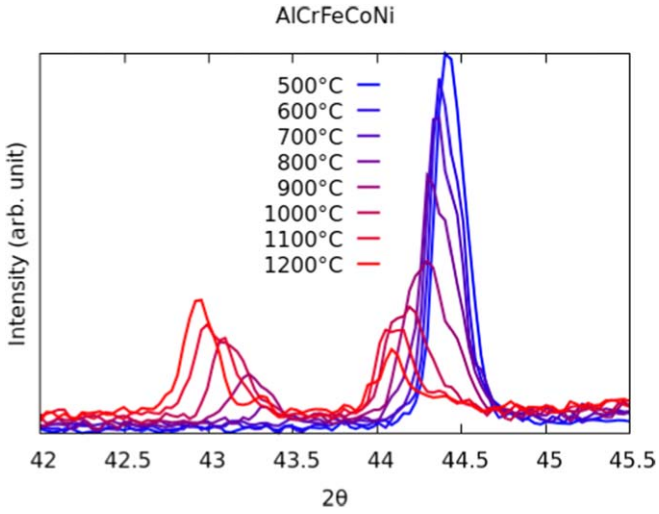

Figure 4. *In-situ* x-ray diffraction measurements for AlCoCrFeNi powders at different annealing temperatures.

To investigate the phase transition of AlCoCrFeNi powders, the as-atomized powders were annealed at various temperatures from 500 to 1200 °C with an interval of 100 °C. Figure 4 shows the results of *in situ* x-ray diffraction patterns. It can be found that the as-atomized powders kept pure BCC phase below 600 °C, agreeing with that the FCC phase transition temperature of AlCoCrFeNi is 600 °C [14]. When the temperature reached 600 °C, the BCC phase began to turn into FCC phase. Thus, the intensity of BCC peak was getting lower with temperature while that of FCC phase was increasing till 1200 °C. Because the higher the temperature the more the energy, the sigma phase (Fe–Cr) subsequently began to gather and precipitate while the temperature raised up to 900 °C. Above 1000 °C, the FCC to BCC ratio was higher than one, implying the FCC phase became the dominated crystalline structure. In addition to the change in FCC to BCC ratio, the locations of diffraction peaks also shifted toward low-angle direction. For a better understanding, the degree shifts were converted to the change in the lattice constant of structure, as shown in figure 5. With the increasing temperature, the width of diffraction peaks was becoming broader due to the stronger atomic vibration. The linear thermal expansions are about 8.2×10^{-6} and $18.2 \times 10^{-6}\,k^{-1}$, respectively, for BCC and FCC phases in AlCoCrFeNi HEAs between 500 to 1200 °C. The BCC phase has better stability than FCC phase. While the external force applied on the HEAs powder, e.g. annealing process gave the powder heat energy so that the crystal began to expand, and the BCC was more stable so that the expand value of FCC was two times of BCC.

Because the melting temperature of AlCoCrFeNi is about 1360 °C, a low-pressure environment would induce atoms to escape from solid state early. In other words, a vacuum annealing treatment could promote the breaking of atomic bonding before reaching its melting point [15]. While the annealing temperature was higher than 1200 °C, and AlCoCrFeNi powders transformed back to the high-temperature state of BCC only. The combination of vacuum environment and long-time heat treatment further caused the powders to partially melt at temperatures below its melting point. According to our previous finding [11]' a contiguous piece of the AlCoCrFeNi ingot with a grain size of hundreds of micrometers was obtained after annealing the powders at 1200 °C for 48 h [14].

Compared to the initial state of gas-atomized AlCoCrFeNi powder, some characteristics of annealed one have been considerably changed, including composition distribution, phase constitution, and lattice constant. In addition, the mechanical properties of alloys often depend on their microstructure and phase constitution. The performance in mechanical properties is one of the interesting applications, in which superior

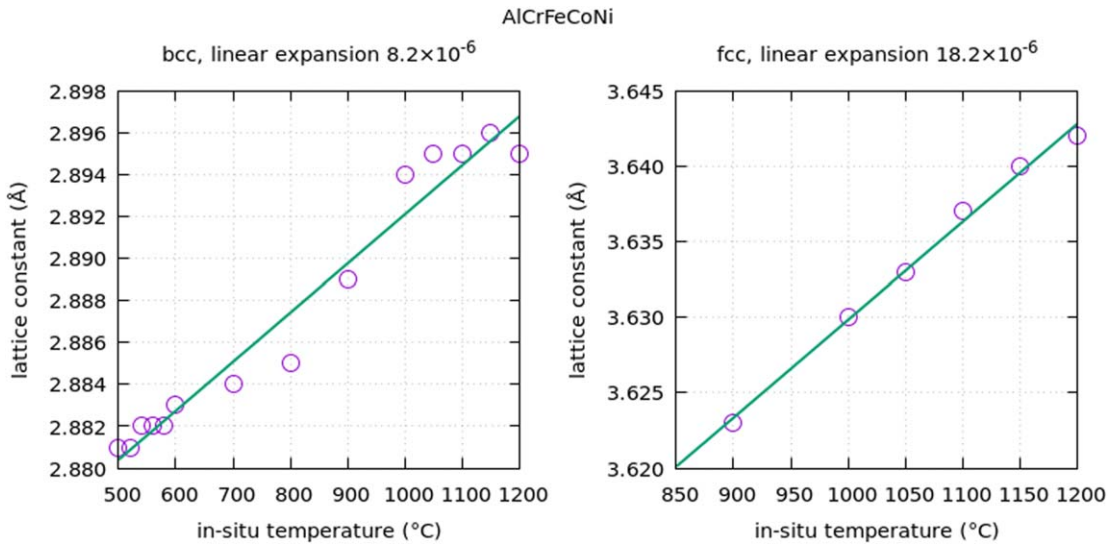

Figure 5. Relationship between the lattice constant and temperature of gas-atomized AlCoCrFeNi powders at temperatures ranging from 500 °C to 1200 °C.

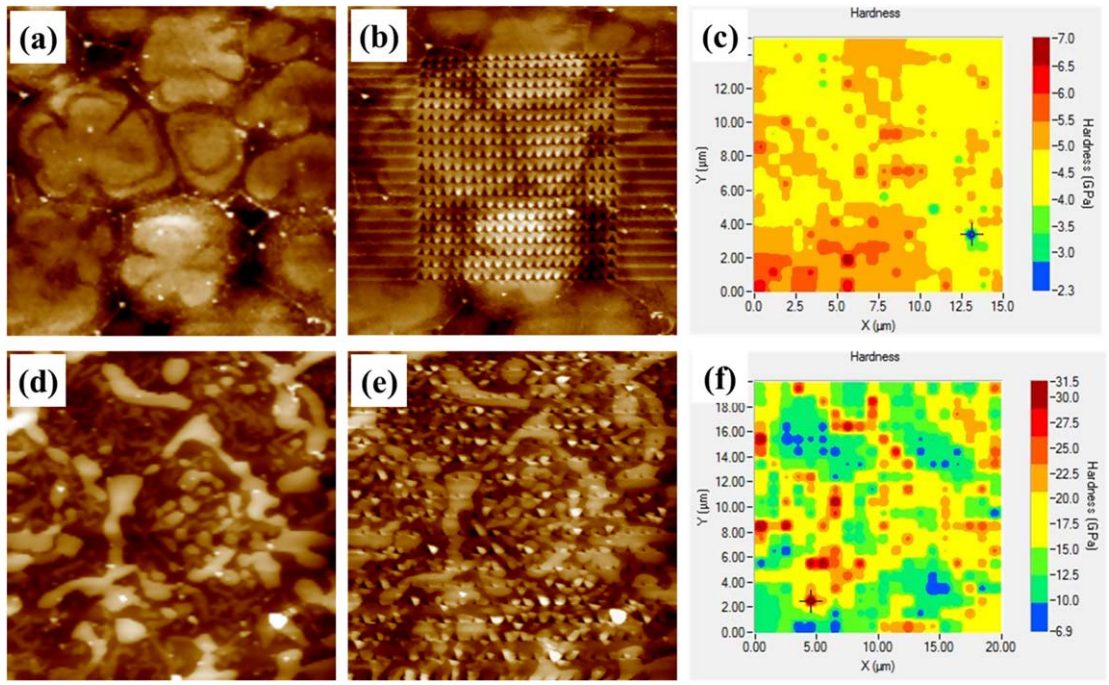

Figure 6. SPM images of (a) original and (b) 20 × 20 matrix-indented surface and (c) hardness distribution of as-atomized AlCoCrFeNi powder. SPM images of (d) original and (e) 20 × 20 matrix-indented surface and (f) hardness distribution of AlCoCrFeNi powder after annealing at 900 °C for 3 h.

characteristics could be delivered by HEAs. The hardness and elastic modulus of as-atomized and annealed AlCoCrFeNi powders were examined using a nanoindenter. Figure 6(a) shows the SPM image of the cross-sectional surface of as-atomized AlCoCrFeNi powder, which was scanned by the diamond tip with a normal force of 3 μN. Originally, the cross-sectional surface had a mirror finish; then, the height distribution was caused by the distinct resistances of grains to the normal loading on tip during scanning. Therefore, the darker the color, the lower the hardness. Figure 6(b) further show the SPM image of original and 20 × 20 matrix-indented surfaces of as-atomized powders. The matrix of indentation is of 20 × 20 points, the distance between indented sites is about 0.75 μm, and the results of hardness, mapping is shown in figure 6(c). The average hardness is 4.87 ± 0.49 GPa, ranging from 2.3 to 7.0 GPa; however, the majority was ranging from 5 to 6 GPa, suggesting a relatively flat surface.

Figures 6(d)–(f) present the SPM images and hardness distribution of AlCoCrFeNi powders after annealing at 900 °C for 3 h. Referring to the results of element mapping, the irregular or long strip precipitates are Cr-rich sigma phase or Al–Ni rich FCC phases. The average hardness was recorded as 15.96 ± 5.31 GPa, and its variation of hardness is much larger than as-atomized one because of the change of phase constitution and precipitation hardening effects, such that the maximum hardness also increased. The high hardness regions correspond to the light areas in figure 6(e), which verifies that precipitation hardening is an important mechanism for obtaining a high strength AlCoCrFeNi HEA alloy.

4. Conclusions

In this study, the phase evolution of as-atomized AlCoCrFeNi powders was investigated by using *in situ* x-ray diffraction combined with vacuum annealing processes. As-prepared powders present a spherical shape with homogeneous composition distribution. Thus, the raw powders also show identical properties in hardness and phase constitution of pure BCC phase. To further inspect the influence of annealing process, the results of *in situ* XRD spectra at temperature ranging from 500 °C to 1200 °C indicated the formation of FCC phase with the increase of lattice constant. The linear thermal expansions are about 8.2×10^{-6} and $18.2 \times 10^{-6}\,k^{-1}$ for BCC and FCC phases, resulted from the differences of high temperature stability of two crystal structures in AlCoCrFeNi HEAs between 500 to 1200 °C, respectively. The phase constitution changed from pure BCC phase to (BCC + FCC + sigma) phase; thus, the higher variation of hardness distribution was caused by precipitation hardening effect. In summary, the annealing process could make AlCoCrFeNi powders become harder with the higher strength. The crystal of AlCoCrFeNi powders became loose when the annealing temperature reached 1200 °C and returned to the initial phase constitution.

Acknowledgments

Authors acknowledge support from the Ministry of Science and Technology of Taiwan under Project Nos. 107-2221-E-011-009-MY3, and 107-2218-E-011-017, and the support by the Research Center for Intelligent Medical Devices, Ming Chi University of Technology. Shane Stadler acknowledges support from the US Department of Energy, Office of Basic Energy Sciences under Award No. DE-FG02-13ER46946.

ORCID iDs

Shih-Hsun Chen https://orcid.org/0000-0002-5750-6470

References

[1] Huang K H and Yeh J W 1996 *A study on the multicomponent alloy systems containing equal-mole elements.* (Hsinchu: National Tsing Hua University)
[2] Yeh J W *et al* 2004 Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes *Adv. Eng. Mater.* **6** 299–303
[3] Yeh J W 2006 Recent progress in high entropy alloys *Ann. Chim. Sci. Mat.* **31** 633–48
[4] 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** 213–8
[5] Zhang Y, Zuo T T, Tang Z, Gao M C, Dahmen K A, Liaw P K and Lu Z P 2014 Microstructures and properties of high-entropy alloys *Prog. Mater Sci.* **61** 1–93
[6] Mullis A M, Farrell L, Cochrane R F and Adkins N J 2013 Estimation of cooling rates during close-coupled gas atomization using secondary dendrite arm spacing measurement *Metall. Mater. Trans.* B **44** 992–9
[7] Wang W R, Wang W L, Wang S C, Tsai Y C, Lai C H and Yeh J W 2012 Effects of Al addition on the microstructure and mechanical property of AlxCoCrFeNi high-entropy alloys *Intermetallics* **26** 44–51
[8] Yang X and Zhang Y 2010 Cryogenic resistivities of NbTiAlVTaLax, CoCrFeNiCu and CoCrFeNiAl high entropy alloys ed Y F Zhang, C W Su, H Xia and P F Xiao *Advanced materials and processing 2010, proceedings of the 6th international conference on ICAMP, Yunnan, 19–3 July*
[9] Zhang D L 2004 Processing of advanced materials using high-energy mechanical milling *Prog. Mater Sci.* **49** 537–60
[10] Basak C B, Krishnan M, Kumar R, Abdullah K K and Anantharaman S 2014 Characterization and process evaluation of Ni–Ti–Fe shape memory alloy macro-spheres directly fabricated via rotating electrode process *J. Alloys Compd.* **597** 15–20
[11] Butler T M and Weaver M L 2016 Oxidation behavior of arc melted AlCoCrFeNi multicomponent high-entropy alloys *J. Alloys Compd.* **674** 229–44
[12] Wang Y P, Li B S, Ren M X, Yang C and Fu H Z 2008 Microstructure and compressive properties of AlCrFeCoNi high entropy alloy *Mater. Sci. Eng.* A **491** 154–8
[13] Wang W R, Wang W L and Yeh J W 2014 Phases, microstructure and mechanical properties of AlxCoCrFeNi high-entropy alloys at elevated temperatures *J. Alloys Compd.* **589** 143–52
[14] Cheng K C, Chen J H, Stadler S and Chen S H 2019 Properties of atomized AlCoCrFeNi high-entropy alloy powders and their phase-adjustable coatings prepared via plasma spray process *Appl. Surf. Sci.* **478** 478–86

[15] Gaskell D R 2008 *Introduction to the thermodynamics of materials* 5th ed. (LLC: Taylor & Francis Group)