

Improved Performance of Sintered Alloys by Spark Plasma Sintering of Gas-atomized CoCrFeNi-Si High-entropy Alloy Powders with Ball Milling

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In this study, to improve the hardness of CoCrFeNi-Si alloys, CoCrFeNi-Si alloy powders prepared by gas atomization (Co_{28.5}Cr_{15.5}Fe_{28.5}Ni_{15.5}Si₁₂, Co₂₈Cr₁₅Fe₂₈Ni₁₅Si₁₄, and Co₂₂Cr₂₂Fe₂₂Ni₂₂Si₁₂) were processed by ball milling ($t = 0$ h, 25 h and 50 h) followed by the SPS method (1073 K, 50 MPa, holding for 10 min). MA 0h of Co_{28.5}Cr_{15.5}Fe_{28.5}Ni_{15.5}Si₁₂, Co₂₈Cr₁₅Fe₂₈Ni₁₅Si₁₄, and Co₂₂Cr₂₂Fe₂₂Ni₂₂Si₁₂ powders identified the main phase, the fcc phase, and the silicide Co₂Si by X-ray diffraction (XRD). According to the XRD results of the MA 25 h and 50 h powders of Co_{28.5}Cr_{15.5}Fe_{28.5}Ni_{15.5}Si₁₂, Co₂₈Cr₁₅Fe₂₈Ni₁₅Si₁₄, and Co₂₂Cr₂₂Fe₂₂Ni₂₂Si₁₂, a single fcc phase was formed. As for the cause, the MA also caused the Co₂Si compound to dissolve, and all elements were completely solid-soluted in the fcc matrix. According to the XRD results of the sintered samples after the SPS process, the sintered samples of Co_{28.5}Cr_{15.5}Fe_{28.5}Ni_{15.5}Si₁₂, Co₂₈Cr₁₅Fe₂₈Ni₁₅Si₁₄, and Co₂₂Cr₂₂Fe₂₂Ni₂₂Si₁₂ exhibited an fcc phase, FeSi compounds, and Co₂Si compounds. The hardness results showed that the Co₂₈Cr₁₅Fe₂₈Ni₁₅Si₁₄ sample was the hardest of the three sintered samples, which we believe is due to the fact that the higher the mixing entropy ΔS_{mix} (closer to the isoatomic composition), the higher the Si content, the higher the increase in hardness. Furthermore, the hardness of the three alloys increased with MA time; in this case, the increase in hardness can be attributed to the introduction of more transitions rather than to the MA plastic working.

Keywords: high-entropy alloy, spark plasma sintering, mechanical alloying, ball milling, silicon addition

1. Introductions

High-entropy alloys (HEAs) do not have a main component. They are multicomponent alloys obtained by blending five or more metallic elements at equiatomic fractions (5–35%)¹. Many elements in HEAs form single-phase solid solutions; they do not form intermetallic compounds. In conventional alloys, the base metal atoms are often surrounded by the same atoms, whereas, in HEAs, all atoms are surrounded by different atoms². This causes lattice distortion due to the different atomic sizes of the surrounding atoms. Therefore, HEAs exhibit unique properties such as excellent high-temperature strengths, high tensile strengths, and extremely low diffusion speeds^{3,4}.

Various systems with different structures, such as face-centered cubic (fcc)^{5,6}, body-centered cubic (bcc)^{7,8}, and fcc+bcc systems^{9,10}, have been reported for HEAs. In recent years, hexagonal close-packed (hcp) HEAs have also been developed and the definition of HEAs has been broadened. These HEAs are mainly produced by the arc melting or casting method. Microstructural separation and ingot metallurgy (IM) have been observed in the cast microstructures^{11–13}.

The definition of HEA is broad, including fcc, bcc, fcc+bcc, and the more recently developed hcp system. These HEAs are mainly produced by IM methods such as arc melting and casting, but microstructure separation and inhomogeneous microstructure during casting have been observed. The powder metallurgy (PM) method has the advantage over the conventional IM method that it is more material efficient, requires little or no post-forming processing, and can be sintered in a form close to that of the final product. Therefore, it can be used for applications where precision and accuracy are of paramount importance. It has also been reported that the mechanical and chemical properties of HEA fabricated by the PM method are

different from those fabricated by the IM method.

It has also been reported that HEA made by the PM process has different mechanical properties compared to those made by the casting method. The PM process for HEA reportedly includes the mechanical alloying (MA) method using a planetary ball mill to obtain alloy powder and the gas atomizing (GA) method to obtain alloy powder from molten alloy. The GA method produces spherical metal powder particles by injecting inert high-pressure gas such as nitrogen or argon into the molten metal and then rapidly cooling and solidifying it into a powder. Because the particles are smooth and spherical in shape, the atomized powder has excellent flowability and is used in thermal spraying as a Co-based or Ni-based heat-resistant and wear-resistant alloy powder, or in powder high speed steel by hot isostatic pressing because of its low surface oxidation and high packing density. In this study, to improve the hardness of CoCrFeNi-Si alloys, CoCrFeNi-Si alloy powders prepared by gas atomization (HEA1-Co_{28.5}Cr_{15.5}Fe_{28.5}Ni_{15.5}Si₁₂, HEA2-Co₂₈Cr₁₅Fe₂₈Ni₁₅Si₁₄, and HEA3-Co₂₂Cr₂₂Fe₂₂Ni₂₂Si₁₂) were processed by ball milling ($t = 0$ h, 25 h, 50 h) followed by the spark plasma sintering (SPS) method (1073 K, 50 MPa, holding for 10 min).

2. Experimental methods

2.1 Alloy design

We performed parameter calculations to evaluate whether HEAs can be formed in the CoCrFeNi-Si system used in this study. The calculated parameters are the mixed entropy $-\Delta S_{\text{mix}}$, mixed enthalpy $-\Delta H_{\text{mix}}$, atomic radius ratio δ , omega parameter Ω , and VEC , defined by equations (1)–(5)¹⁴. Where x_i is the composition of element i , ΔH_{ij} is the enthalpy of the mixture of elements i and j , r_i is the atomic radius of element i , $T_{m,i}$ is the melting point of

element i , and VEC_i is the VEC of element i . The expressions of ΔH_{ij} , r_i , and VEC are presented in references¹⁵⁻¹⁷, respectively.

$$\Delta S_{mix} = -R \sum_{i=1}^n x_i \ln x_i \dots (1)$$

$$\Delta H_{mix} = 4 \sum_{j \neq i} \sum_{i=1}^n \Delta H_{ij} \dots (2)$$

$$\delta = \sqrt{\sum_{i=1}^n x_i \left[1 - \frac{r_i}{\bar{r}}\right]^2} \times 100 \dots (3) \quad \bar{r} = \sum_{i=1}^n x_i r_i$$

$$\delta = \sqrt{\sum_{i=1}^n x_i \left[1 - \frac{r_i}{\bar{r}}\right]^2} \times 100 \dots (4) \quad T_m = \sum_{i=1}^n x_i \times T_{m,i}$$

$$VEC = \sum_{i=1}^n x_i \times VEC_i \dots (5)$$

2.2 Sample and analysis

As starting materials, gas atomized powders (particle size: 32 μm) (HEA1, HEA2, and HEA3) were used and MA was performed for 0 h, 25 h, and 50 h in an Ar atmosphere. The treated powders were characterized by X-ray diffraction (XRD) tests and elemental analysis by SEM-EDX.

The SPS treatment was then carried out at 1073 K in a vacuum of $\sim 10^{-3}$ Pa. The SPS treated samples were characterized by XRD, density, and Vickers hardness.

3. Results and discussion

3.1 Alloy design

Table 1 shows the calculation results for each parameter. If $\delta \leq 6.6$, the difference in the atomic radius ratio of the constituent elements is small, while, if $\Omega \geq 1.1$, ΔS_{mix} is as large as possible and the absolute value of ΔH_{mix} is close to zero. If these conditions are met, the possibility of forming a solid solution is high¹⁴. If $VEC > 8.0$, an fcc single phase is formed, if $VEC \leq 6.78$, a bcc single phase is formed, and, if $6.87 \leq VEC < 8.0$, an fcc + bcc two-phase structure is formed. Considering the results of the present calculations and these conditions, the following conclusions can be summarized.

- (1) HEA1: The possibility of solid solution formation is higher because of $\delta \leq 6.6$ and $\Omega \geq 1.1$. As $6.87 \leq VEC < 8.0$, a two-phases fcc + bcc structure is formed.
- (2) HEA2: The possibility of solid solution formation is higher because of $\delta \leq 6.6$ and $\Omega \geq 1.1$. As $6.87 \leq VEC < 8.0$, a two-phases fcc + bcc structure is formed.
- (3) HEA3: The possibility of solid solution formation is higher because of $\delta \leq 6.6$ and $\Omega \geq 1.1$. As $6.87 \leq VEC < 8.0$, a two-phases fcc + bcc structure is formed.

Table 1 ΔS_{mix} , ΔH_{mix} , δ , Ω , VEC and T_m for CoCrFeNi-Si.

	$\Delta S_{mix} / \text{JK}^{-1}$	$\Delta H_{mix} / \text{kJ}$	δ	Ω	VEC	T_m / K
HEA 1	1.55R	-18.0	2.10	1.27	7.81	1769.0
HEA 2	1.56R	-20.0	2.21	1.14	7.72	1767.2
HEA 3	1.59R	-18.7	2.11	1.29	7.74	1837.2

3.2 XRD test of MA powder

XRD tests were performed to identify the phases formed in the MA powder; the results are shown in **Figures 1-3**. These figures show that the results of fcc phase and Co_2Si compounds was identified in MA 0 h, while a single fcc phase was identified in MA 25 h and 50 h on three alloys

powders.

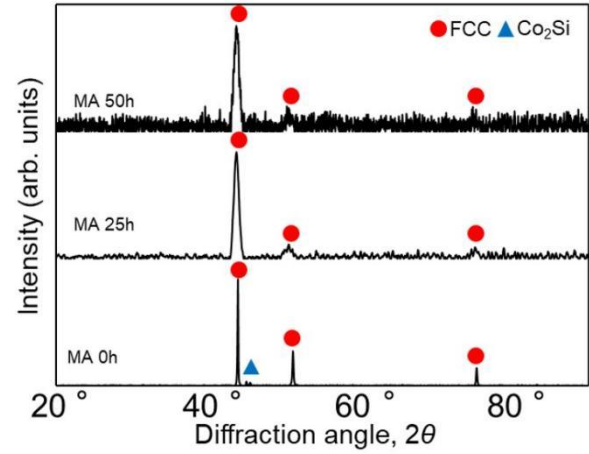


Figure 1 Result of X-ray diffraction patterns for powders of HEA1.

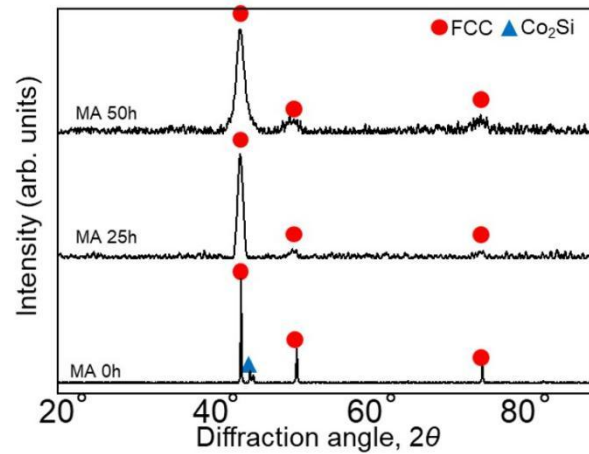


Figure 2 Result of X-ray diffraction patterns for powders of HEA2.

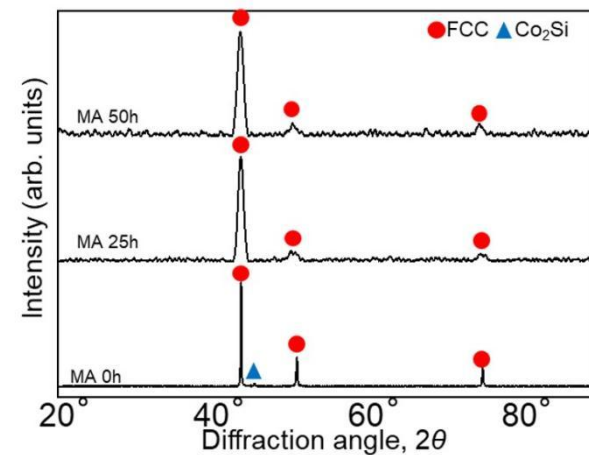


Figure 3 Result of X-ray diffraction patterns for powders of HEA3.

3.2 Hardness of sintered sample

The results of the micro-Vickers hardness test performed to investigate the surface hardness of the sintered alloys are shown in **Figure 4**. **Figure 4** shows that the hardness increased with MA time. HEA1 is the softest among the

three alloys. HEA2 is the hardest of the three alloys. There are two main reasons for this phenomenon: one is the difference in powder shape and the other is the difference in grain size of silicides in the powder. These results suggest that the smaller effect of precipitation strengthening led to the decrease in hardness. The hardness tends to increase as the mixing entropy ΔS_{mix} increases (closer to isoatomic composition) and as the Si content increases.

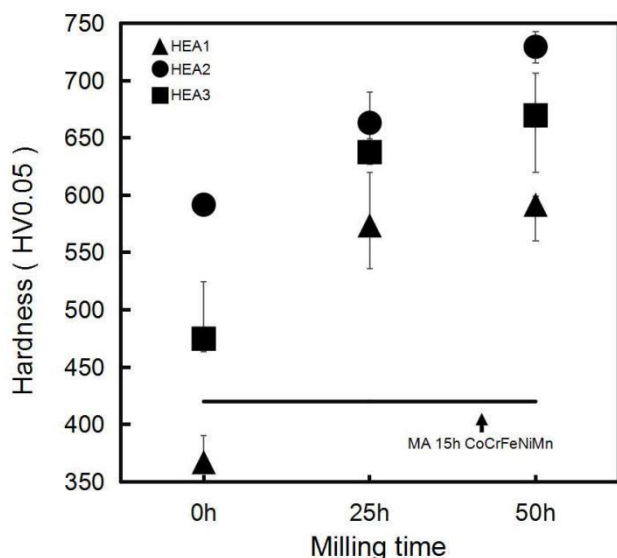


Figure 4 Hardness test for CoCrFeNi-Si sintered samples.

4. Conclusions

(1) According to the XRD test on the MA powder, the results of fcc phase and Co_2Si compounds was identified in MA 0 h, while a single fcc phase was identified in MA 25 h and 50 h on three alloys powders.

(2) According to the micro-Vickers hardness test, it shows that the hardness increased with MA time. $\text{Co}_{28.5}\text{Cr}_{15.5}\text{Fe}_{28.5}\text{Ni}_{15.5}\text{Si}_{12}$ is the softest among the three alloys. $\text{Co}_{28}\text{Cr}_{15}\text{Fe}_{28}\text{Ni}_{15}\text{Si}_{14}$ is the hardest of the three alloys.

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