



# Article Mechanical Alloying Behavior and Thermal Stability of CoCrCuFeMnNi<sub>x</sub> High-Entropy Alloy Powders Prepared via MA

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Abstract: CoCrCuFeMnNi<sub>x</sub> (x = 0, 0.5, 1.0, 1.5, 2.0 mol, named as Ni<sub>0</sub>, Ni<sub>0.5</sub>, Ni<sub>1.0</sub>, Ni<sub>1.5</sub>, and Ni<sub>2.0</sub>, respectively) high-entropy alloy powders (HEAPs) were prepared via mechanical alloying (MA), and XRD, SEM, EDS, and vacuum annealing were used to study the alloying behavior, phase transition, and thermal stability. The results indicated that the Ni<sub>0</sub>, Ni<sub>0.5</sub>, and Ni<sub>1.0</sub> HEAPs were alloyed at the initial stage (5–15 h), the metastable BCC + FCC two-phase solid solution structure was formed, and the BCC phase disappeared gradually with the prolonging of ball milling time. Finally, a single FCC structure was formed. Both Ni<sub>1.5</sub> and Ni<sub>2.0</sub> alloys with high nickel content formed a single FCC structure during the whole mechanical alloying process. The five kinds of HEAPs showed equiaxed particles in dry milling, and the particle size increased with an increase in milling time. After wet milling, they changed into lamellar morphology with thickness less than 1 µm and maximum size less than 20 µm. The composition of each component was close to its nominal composition, and the alloying sequence during ball milling was Cu $\rightarrow$ Mn $\rightarrow$ Co $\rightarrow$ Ni $\rightarrow$ Fe $\rightarrow$ Cr. After vacuum annealing at 700~900 °C, the FCC phase in the HEAPs with low Ni content transformed into FCC2 secondary phase, FCC1 primary phase, and a minor  $\sigma$  phase. The thermal stability of HEAPs can be improved by increasing Ni content.

**Keywords:** high-entropy alloy powder; mechanical alloying; phase transition; vacuum annealing; thermal stability

## 1. Introduction

A high-entropy alloy (HEA) is a new alloy system designed by using the strategy of equal or near-equal atomic ratio and high mixing entropy, and it is also one of the three breakthroughs in modern metal materials [1-3]. The four core effects of an HEA produced via the combination of a variety of main elements, namely, high mixing entropy, lattice distortion, slow diffusion and cocktail effect, have resulted in many microstructures and properties different from traditional alloys, such as simple solid solution structure, high strength, good low-temperature plasticity, good corrosion resistance and oxidation resistance, and good physical properties [4–8]. HEA systems containing Co, Cr, Cu, Fe, Mn, and Ni have been widely studied. Their preparation and processing technologies mainly include arc melting [1,2], induction melting [9], thermal mechanical processing [10,11], mechanical alloying [12–14], hot pressing sintering [15,16], plasma sintering [17], laser surface cladding [18], water atomization [12], etc. In the alloy systems studied, the CoCrFeMnNi alloy has a single FCC solid solution phase, good thermodynamic stability, and excellent ductility, which was reported by Cantor [1], Otto [19], and Gali [20]. In addition, the CoCrFeMnNi alloy shows an excellent combination of high strength and large elongation, as well as excellent fracture toughness at room temperature and low temperature [21–26]. The CoCrCuFeNi alloy prepared by high-pressure torsion (HPT) and annealing shows two FCC phases (Cu-rich phase and Cu-lean phase) and high



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). aging hardness of 540 HV at 600 °C [27]. Hsu et al. [28] studied the corrosion behavior of the CoCrFeNiCu<sub>x</sub> alloy in 3.5% NaCl solution and found that the CoCrCuFeNi alloy showed poor corrosion resistance due to interdendritic Cu segregation. The CoCrCuFeNi alloy exhibits excellent deformability due to phase separation into ductile FCC phases [29].

Casting is the main method used to produce the above HEAs. However, component segregation (such as Cu-rich phase) and volatilization of Mn are often observed during casting [30,31]. MA is considered as a solid-state processing method that can alloy elemental powders at room temperature. It has been widely used in the preparation of advanced materials. Uniform microstructure and ultra-fine/nanocrystalline structure can be easily obtained by controlling appropriate ball milling process parameters, which will certainly expand the application field of HEAs [32,33].

In our previous work, we prepared  $Co_xCrCuFeMnNi$  and  $CoCr_xCuFeMnNi$  HEAPs using the MA process, studied their alloying behavior and magnetic properties, and found that some HEAPs have excellent soft magnetic properties and thermal stability [14,34,35]. Ni is also one of the main factors affecting the alloying behavior and properties of HEAs. The increase in Ni content can inhibit the formation of the intermetallic compound phase in the HEAs and promote the formation of an FCC phase, which is conducive to improving the plasticity and corrosion resistance of the HEAs [36,37]. The effect of Ni on the phase structure of stable HEAPs has not been reported, especially at high temperatures. The high-temperature stability of HEAPs is very important for the microstructure and properties of sintered alloys. Therefore, in this study, a mechanical alloying method was used to prepare CoCrCuFeMnNi<sub>x</sub> HEAPs, and their alloying behavior and thermal stability were emphatically studied in order to understand the effect of Ni on the microstructure of stable HEAPs, which will lay a preliminary foundation for the impact of powder superalloys on the microstructure and properties.

#### 2. Materials and Methods

 $CoCrCuFeMnNi_x$  (x = 0, 0.5, 1.0, 1.5, 2.0 mol, named as Ni<sub>0</sub>, Ni<sub>0.5</sub>, Ni<sub>1.0</sub>, Ni<sub>1.5</sub>, and Ni<sub>2.0</sub>, respectively) HEAPs were prepared via MA. The purity of Co, Cr, Cu, Fe, Mn, and Ni metal powder higher than 99.9 wt.% was provided by Beijing Guanjinli New Materials Co., Ltd. (Beijing, China), with an average particle size of about 75  $\mu$ m. The metal powders prepared according to the stoichiometric ratio (M<sub>Ni</sub>:M<sub>Co</sub>:M<sub>Cr</sub>:M<sub>Cu</sub>:M<sub>Fe</sub>:M<sub>Mn</sub> = x:1:1:1:1:1, x = 0, 0.5, 1.0, 1.5, 2.0, mol, M stands for moles.) were put into 304L stainless-steel vacuum ball mill vials with a ball-to-material ratio of 10:1. The material of stainless-steel mill balls is also 304 L, and the mass ratio of large balls to small balls is 1:1, with diameters of 10 mm and 5 mm, respectively. After being purged with high-purity argon for 5 min, they were installed on a QM-WX4 planetary ball mill (Nanjing Nanda Instrument Co., Ltd., Nanjing, China) for mechanical alloying. The rotational speed of the ball mill was 300 rpm. The working time of the ball mill was 30 min, with an interval of 20 min. The HEAPs were first dry-milled for 45 h, and a small amount of powder was taken at 0 h, 5 h, 10 h, 15 h, 30 h, and 45 h to study the phase evolution of the powders. After the dry grinding, an appropriate amount (about 20 mL) of anhydrous ethanol was added and wet ground for 5 h; then, we took the powders and placed them in a vacuum-drying oven for drying treatment. The treatment temperature was 50 °C and the time was 48 h. The dried HEAPs were annealed under vacuum conditions of  $6 \times 10^{-3}$  Pa and different temperatures (700 °C, 800 °C, and 900 °C) for 2 h to analyze the thermal stability.

An X-ray diffractometer (XRD, Bruker D8 ADVANCE, Bruker, Germany) with Cu-K $\alpha$  radiation was used to analyze the phase evolution of HEAPs. The wavelength was 1.54056 Å, the operating tube voltage and tube current were 40 kV and 40 mA, respectively, and the scanning angle was 20~90° (2 $\theta$ ). The scanning speed was 10°/min and the scanning step was 0.02°. The morphology and composition of HEAPs were observed and analyzed under a scanning electron microscope (SEM, Quanta 250, FEI, Czech) equipped with EDAX energy dispersion spectrometer (EDS). Particle sizes of the HEAPs were statistically investigated using Malvern laser particle size analyzer (Mastersizer 3000, Malvern, UK). Differential scanning calorimetry (DSC, STA 449 F3, Netzsch, Germany) was used for thermal analysis in high-purity argon atmosphere. The HEAPs were scanned in an alumina crucible with a temperature range of 25–1200  $^{\circ}$ C and a heating rate of 10  $^{\circ}$ C/min.

### 3. Results and Discussion

## 3.1. XRD Analysis of HEAPs

Figure 1 shows the XRD analysis results of CoCrCuFeMnNi<sub>x</sub> HEAPs after different ball milling times. From the XRD results of Ni<sub>0</sub> HEAP (Figure 1a), it can be seen that the original metal powder presented two groups of strong diffraction peaks, respectively, corresponding to the diffraction peaks of Cr and Mn at  $2\theta = 44.60^{\circ}$  and Cu, Fe and Co at  $2\theta = 43.34^{\circ}$ . After 5 h ball milling, the diffraction peaks of Cu, Mn, and Co basically disappeared, indicating that these three metal elements and some Cr and Fe are a mutually solid solution, forming a solid solution with FCC structure as the main structure. Cu, Mn, and Co are the first elements to dissolve, which may be related to their relatively low melting points. After milling for 10 h, the diffraction peak intensity of each element further decreased. After 15 h ball milling, the diffraction peaks of Fe and Cr elements can still be detected in the XRD spectrum, but the diffraction peaks of two FCC phases can be clearly observed, which were located at  $43.34^{\circ}$  and  $50.48^{\circ}$ , respectively. After 30 h ball milling, all the diffraction peaks of pure elemental elements disappeared, and there were only three FCC phase diffraction peaks at different angles on the XRD spectrum. There were no significant differences between the diffraction peaks after 45 h ball milling and after 30 h. After 50 h ball milling (45 h dry milling + 5 h wet milling), the diffraction peaks in the FCC phase were obviously widened, indicating that when the alloying is completed, the grain of HEAPs will be refined by further increasing the ball milling time [38].

With an increase in milling time, the phase transition of  $Ni_{0.5}$  and  $Ni_{1.0}$  HEAPs was the same as that of Ni<sub>0</sub> HEAP. After 5 h ball milling, the diffraction peaks of Cu, Mn, and Co elements disappeared, and the diffraction peaks of Cr, Fe, and Ni elements could still be observed. After 30 h and 45 h ball milling, a single FCC solid solution structure was formed. After 50 h ball milling, the diffraction peak width of the FCC phase increased significantly, and the HEAP grains were refined. The phase evolution of Ni<sub>1.5</sub> and Ni<sub>2.0</sub> HEAPs during 50 h ball milling was similar to that of  $Ni_{0.5}$  alloy powders, but the solid solution structure of Ni<sub>1.5</sub> and Ni<sub>2.0</sub> HEAPs after 5–30 h ball milling was a single FCC phase. The above results show that there are two main factors affecting the phase evolution of CoCrCuFeMnNi<sub>x</sub> HEAPs during ball milling. One is the influence of alloying element content on its phase evolution, and the second is the influence of different milling time on the phase evolution. Alloying elements mainly affect the final phase structure of the HEAPs. For example, when  $Ni_0$  and  $Ni_{0.5}$  HEAPs were milled for 5–30 h, a solid solution structure was formed with the BCC phase as the main phase and FCC phase as the secondary phase, while  $Ni_{1.5}$  and  $Ni_{2,0}$  HEAPs were in a single FCC solid solution phase structure. Different ball milling time mainly affects the intensity and width of the diffraction peaks of CoCrCuFeMnNix HEAPs. At the beginning of ball milling, each metal element absorbed energy during the ball milling process and formed a solid solution structure with each other, leading to a weakening in the intensity of the diffraction peak. The extension of ball milling time and the addition of process control agent (wet milling for 5 h) led to a reduction in and broadening of the intensity of diffraction peaks.



**Figure 1.** XRD patterns of CoCrCuFeMnNi<sub>x</sub> HEAPs after different ball milling time: (**a**) Ni<sub>0</sub>, (**b**) Ni<sub>0.5</sub>, (**c**) Ni<sub>1.0</sub>, (**d**) Ni<sub>1.5</sub>, (**e**) Ni<sub>2.0</sub>.

According to the XRD results in Figure 1, the lattice parameters, grain size, lattice strain, and dislocation density of the FCC phase of Ni<sub>0</sub> HEAP after different ball milling times can be calculated using Formulae (1)~(4). The lattice constant (*a*) is calculated via Equation (1):

$$a = \frac{\lambda}{2\mathrm{sin}\theta}\sqrt{h^2 + k^2 + l^2} \tag{1}$$

where  $\lambda$  is the X-ray wavelength (1.54056 Å),  $\theta$  is the diffraction angle, and *h*, *k*, and *l* are Miller exponents. The grain size (*d*) and lattice strain ( $\varepsilon$ ) of Ni<sub>0</sub> HEAP are calculated via Equations (2) and (3).

$$d = \frac{K\lambda}{\beta\cos\theta} \tag{2}$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{3}$$

where  $\beta$  and  $\theta$  are the measured half width of the spectral line and the diffraction angle of the corresponding peak position, respectively. *K* is taken as 0.89. The dislocation density ( $\rho$ ) of the FCC phase in HEAPs can be calculated using Formula (4):

$$\rho = \frac{2\sqrt{3}\varepsilon}{db} \tag{4}$$

$$b = \frac{\sqrt{2}a}{2} \tag{5}$$

where *b* is the Burgers vector.

Figure 2 shows the relationship curve between milling time and lattice parameters, grain size, lattice strain, and dislocation density. It can be seen from Figure 2a that the lattice parameters and grain size of the FCC phase of Ni<sub>0</sub> HEAP decreased with an increase in ball milling time. Figure 2b shows that the lattice strain and dislocation density increased with the increase in ball milling time. The grain size of the HEAP was between 9 and 20 nm, which indicates that the alloying elements form the FCC structure of nanocrystalline supersaturated solid solution under the action of mechanical alloying. Wang et al. [39] studied the alloying behavior of (CoCrFeNiMn)  $_{90}M_{10}$  (M = Al, Hf) high-entropy alloy powder using the MA method and found that prolonged ball milling time resulted in a significant decrease in grain size and an increase in lattice strain, a phenomenon similar to the results of this study.



**Figure 2.** Relevant parameters of FCC phase in  $Ni_0$  HEAP after different ball milling time: (**a**) grain size and lattice constant; (**b**) lattice strain and dislocation density.

Figure 3 shows the XRD pattern of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling. It can be seen that each HEAP has a single FCC solid solution phase structure. It can be observed from Figure 3b that with the increase in Ni content, the diffraction peak of the FCC phase gradually shifts to a large angle. The shift in the diffraction peak is generally affected by the grain size and lattice distortion. The addition of smaller Ni atoms will occupy the lattice points with larger atomic radius, making the lattice constant slightly smaller. According to the characteristics of HEAs, more constituent elements will increase the entropy value of HEAs, thus increasing the lattice distortion. As the atomic radius difference between each component atom in CoCrCuFeMnNi<sub>x</sub> HEAs is small, its contribution to the shift in the diffraction peak is smaller than that of lattice distortion, so the diffraction peak shifts to a large angle with the increase in Ni content.



**Figure 3.** (a) XRD pattern of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling; (b) enlarged view of  $35-55^{\circ}$ .

## 3.2. Microstructure of HEAPs

Figure 4 shows the SEM photos of the Ni<sub>0</sub> HEAP after different ball milling times. It can be seen that the original powder after 0 h ball milling (Figure 4a) is in an irregular shape, and its particle size is less than 75  $\mu$ m. Due to the intense impact and collision between the powder particles and the grinding balls, between the powder and the tank or between the powder and the powder under high-energy ball milling, the cold welding effect occurs, so the particle size of the HEAP increases significantly after 5 h (Figure 4b) and 10 h (Figure 4c) ball milling. With a further increase in ball milling time, the powder particles that are cold welded together will be broken into smaller particles, so the average particle size of the high-entropy alloy powder after 15 h ball milling (Figure 4d) is relatively small, and the shape of the powder tends to be equiaxed. In the process of ball milling, the powder particles repeatedly go through the cycle of extrusion deformation-welding-crushing, so that their grains are continuously refined, thus obtaining fresh crystal faces, increasing the contact area of the atomic reaction, shortening the diffusion distance between atoms, and promoting the formation of alloying. However, due to the agglomeration between the powders, the particle size of the powder milled for 30 h (Figure 4e) and 45 h (Figure 4f) is relatively large.



**Figure 4.** SEM photos of Ni<sub>0</sub> HEAP after different ball milling times: (**a**) 0 h, (**b**) 5 h, (**c**) 10 h, (**d**) 15 h, (**e**) 30 h, (**f**) 45 h.

Figure 5 shows the SEM photos of the Ni<sub>1.5</sub> HEAP after different ball milling times. Figure 6 shows the median diameter (Dv50) of the Ni<sub>1.5</sub> HEAP after different ball milling times. It can be seen from Figure 5a that the micromorphology of the Ni<sub>1.5</sub> HEAP after 0 h ball milling is similar to that of Ni<sub>0</sub> HEAP, which also presented an irregular shape. As can be seen from Figure 6, the particle size of  $Ni_{1.5}$  powder at 0 h was about 53 µm. After 5 h ball milling (Figure 5b), the micromorphology of the  $Ni_{1.5}$  HEAP was close to a nearly spherical particle shape, and the average particle size was reduced to 43 µm. After 10 h and 15 h ball milling (Figure 5c,d), the particle size increased to about 46 µm and 52 µm. After ball milling for 30 h (Figure 5e), the particle size of the powder particles further increased to 75 µm and showed agglomeration. After ball milling for 45 h (Figure 5f), the size of agglomerated particles further increased by about 78 µm. The micromorphology of  $Ni_{0.5}$ ,  $Ni_{1.0}$ , and  $Ni_{2.0}$  HEAPs during mechanical alloying was similar to that of  $Ni_0$  and  $Ni_{1.5}$  alloy powders.



**Figure 5.** SEM photos of Ni<sub>1.5</sub> HEAP after different ball milling times: (a) 0 h, (b) 5 h, (c) 10 h, (d) 15 h, (e) 30 h, (f) 45 h.



Figure 6. Dv50 of CoCrCuFeMnNi<sub>1.5</sub> HEAP under different milling times.

Figure 7 shows the SEM morphology and energy spectrum analysis results of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling. Figure 8 shows the Dv50 of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling. It can be seen that the micromorphology of the alloy powders after wet milling was irregular lamellar, and the thickness was less than 1  $\mu$ m. As can be seen from Figure 8, with the increase in Ni content, the particle size of HEAPs first increased from 19  $\mu$ m to 25  $\mu$ m and then decreased to 18  $\mu$ m, but the reason is still unclear. EDS analysis shows that the composition of each HEAP was close to its nominal composition. Therefore, CoCrCuFeMnNi<sub>x</sub> HEAPs with fine grains and uniform chemical composition can be successfully prepared via MA. Mechanical alloying can effectively enhance the solid solubility behavior of alloying elements, thereby improving the solid solubility of constituent elements and forming a more stable phase structure [39,40].



Figure 7. SEM photos of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling: (a) Ni<sub>0</sub>, (b) Ni<sub>0.5</sub>, (c) Ni<sub>1.0</sub>, (d) Ni<sub>1.5</sub>, (e) Ni<sub>2.0</sub>.



Figure 8. Dv50 of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling.

3.3. Mechanical Alloying Behavior of HEAPs

During the whole process of mechanical alloying of CoCrCuFeMnNi<sub>x</sub> HEAPs, except that Ni<sub>1.5</sub> and Ni<sub>2.0</sub> powders are always single FCC solid solution phase structure, the

other alloys are all transited from the FCC + BCC solid solution phase to the single FCC phase. In the binary phase diagram, most of the components in equilibrium are finite solid solutions, so these two solid solutions are supersaturated solid solutions. The increase in solid solubility is closely related to milling time. With the extension of milling time, the severe deformation of the powder leads to a large number of structural defects and higher lattice strain, which can effectively improve the diffusion rate between atoms and the solubility of the solid solution. Equation (6) is the thermodynamic expression:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \tag{6}$$

where *T* is the absolute temperature,  $\Delta G_{mix}$  is the Gibbs free energy, and  $\Delta H_{mix}$  and  $\Delta S_{mix}$  are the mixing enthalpy and mixing entropy, respectively. Thermodynamic theory indicates that  $\Delta H_{mix}$  ( $|\Delta H_{mix}|$ ) represents the ordering and segregation trend of alloying elements, and  $\Delta S_{mix}$  represents the ability of random distribution of alloying elements in the lattice. Therefore, according to Formula (6),  $|\Delta H_{mix}|$  and  $\Delta S_{mix}$  can be used to evaluate the resistance and driving force of solid solution formation. In the process of mechanical alloying, nanocrystals gradually form, resulting in a large number of grain boundaries, which can store a large number of  $\Delta H_{mix}$ , so the contribution of  $\Delta H_{mix}$  to  $\Delta G_{mix}$  can be ignored. The high positive value of  $T\Delta S_{mix}$  can significantly reduce  $\Delta G_{mix}$ , so the solid solution phase will be preferentially formed in the mechanical alloying process.

Table 1 lists the mixing enthalpy ( $\Delta H_{mix}$ ), mixing entropy ( $\Delta S_{mix}$ ), atomic size difference ( $\delta$ ), thermodynamic parameters ( $\Omega$ ), and valence electron concentration (*VEC*) of the CoCrCuFeMnNi<sub>x</sub> HEA system calculated by Formula (7)~(11). Their calculation formulae are as follows:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^{n} 4\Delta \mathbf{H}_{ij}^{mix} c_i c_j \tag{7}$$

$$\Delta S_{mix} = -R \sum_{i=1}^{n} c_i \ln c_i \tag{8}$$

$$\delta = \sqrt{\sum_{i=1}^{n} c_i (1 - r_i / (\sum_{i=1}^{n} c_i r_i))^2}$$
(9)

$$\Omega = \frac{\sum_{i=1}^{n} c_i (T_m)_i \Delta S_{mix}}{|\Delta H_{mix}|}$$
(10)

$$VEC = \sum_{i=1}^{n} c_i (VEC)_i \tag{11}$$

where *n* is the elemental number of alloys,  $c_i$  and  $c_j$  are the atomic percentages of the *i*th and *j*th elements,  $\Delta H_{ij}^{mix}$  is the mixing enthalpy of binary liquid alloy, and their values can be obtained in reference [41]. R is the gas constant,  $r_i$  is the atomic radius of the *i*th element, which can be obtained from reference [42].  $(T_m)_i$  and  $(VEC)_i$  are the melting point and valence electron concentration (VEC) of the *i*th element, respectively.

Table 1. Thermodynamic parameters of CoCrCuFeMnNi<sub>x</sub> HEA system.

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Alloy	$\Delta H_{mix}$	$\Delta S_{mix}$	Ω	δ	VEC
Ni <sub>0</sub>	4.16	13.38	55.33	3.15	8.20
Ni <sub>0.5</sub>	2.58	14.70	98.05	3.07	8.36
Ni <sub>1.0</sub>	1.44	14.90	17.81	3.01	8.50
Ni <sub>1.5</sub>	0.615	14.78	41.38	2.92	8.61
Ni <sub>2.0</sub>	0	14.53	-	2.85	8.71

According to the solid solution formation criteria shown in Table 2, the mixing enthalpy  $\Delta H_{mix}$ , mixing entropy  $\Delta S_{mix}$ ,  $\delta$ , and  $\Omega$  of CoCrCuFeMnNi<sub>x</sub> HEA are all within the range of solid solution formation criteria, so the alloy system tends to form a solid solution phase. In addition, the *VEC* values in the alloy system are greater than 8, and its phase tends to form

a single FCC structure, which is consistent with the XRD results in Figure 3. It can be seen that the valence electron concentration criterion is suitable for predicting the formation of solid solution phase in the CoCrCuFeMnNi<sub>x</sub> HEA system.

Table 2. Formation criteria of solid solution of HEAs.

Proponent	Empirical Rules
Hume-Rothery [43]	$f \ge 5, -40 < \Delta H_{mix} < 10 \text{ KJmol}^{-1}, d < 12\%$
Zhang [44]	$-20 < \Delta H_{mix} < 5 \text{ KJmol}^{-1}, 12 < \Delta S_{mix} < 17.5 \text{ JK}^{-1} \text{mol}^{-1}, \delta < 6.4\%$
Yang [45]	$\Omega \geq 1.1, \delta \leq 6.6\%$
Wang [46]	$\gamma < 1.175$
Guo [47]	FCC (VEC < 6.87), FCC + BCC (6.87 $\leq$ VEC < 8), BCC (VEC $\geq$ 8)

The phase formation mechanism of HEAPs is mainly related to the alloying behavior of components during mechanical alloying. Due to the small difference in physical properties and electronegativity of elements in the CoCrCuFeMnNi<sub>x</sub> HEA system, the alloying process is mainly diffusion-controlled. The diffusion rates of alloying elements are different due to their physical properties. Chen et al. [48] showed that elements with a low melting point or brittle crystal structure may be preferentially dissolved during ball milling. Figure 9 shows the melting point and thermal conductivity of each element in the CoCrCuFeMnNi HEA system [14]. The melting points of Co and Ni are very similar, but Ni with an FCC phase has higher plasticity than Co with an HCP phase, so the alloying of Co occurs before Ni. Therefore, the alloying sequence of CoCrCuFeMnNi<sub>x</sub> HEAPs during ball milling is  $Cu \rightarrow Mn \rightarrow Co \rightarrow Ni \rightarrow Fe \rightarrow Cr$ .



Figure 9. Melting point and thermal conductivity of elements in CoCrCuFeMnNi HEA system [14].

Generally, the solid solubility of an alloy is mainly affected by the following three factors: (1) crystal structure, (2) the atomic size of the constituent elements (i.e., the atomic size difference), (3) chemical compatibility between constituent elements (i.e., electronegativity difference or  $\Delta H_{mix}$ ). In the process of mechanical alloying, the dissolution of components may be mainly affected by the crystal structure and atomic size difference, while the chemical compatibility between components has little influence on it, because a large number of mixing enthalpies are limited in the grain boundary of nanocrystals. Therefore, during mechanical alloying of CoCrCuFeMnNix HEAPs, Cu and Mn elements are the first to finish alloying. In addition, some studies have shown that in the process of mechanical alloying, elements with similar crystal structure and atomic size often dissolve each other to form solid solutions [49]. Therefore, when Ni is contained in the high-entropy alloy, the Cu and Mn elements that first completed alloying may dissolve into the Ni element, forming an FCC solid solution structure with the same crystal structure as the Ni element. In addition, Praveen et al. [50] also showed that Ni can be used as a solvent for the FCC solid solution phase, because the melting point of Ni is higher than that of Cu and Mn, and the diffusion rate is lower than that of Cu and Mn. Similarly, most Fe atoms can be dissolved into Cr as a solvent to form a BCC solid solution phase structure. Due to the HCP structure of Co

(closely packed hexagonal crystal structure), its alloying behavior may be affected by the atomic size difference and chemical compatibility, which are different from the other five constituent elements. If the influence of atomic size difference is taken into account, Co atoms tend to dissolve into Ni to form the FCC solid solution phase, because the atomic size difference between Co and Ni is smaller than that between Co and Cr. If chemical compatibility between component elements is considered, Co atom tends to dissolve into Cr, because Co-Cr has the most negative mixing enthalpy (Table 3), and the two have a strong binding force.

Element	Со	Cr	Cu	Fe	Mn	Ni
Со	0	-4	6	-1	-5	0
Cr	-	0	12	$^{-1}$	2	-7
Cu	-	-	0	13	4	4
Fe	-	-	-	0	0	-2
Mn	-	-	-	-	0	-8
Ni	-	-	-	-	-	0

Table 3. Mixing enthalpy of binary liquid alloy of the CoCrCuFeMnNi HEA system (KJ/mol) [42].

However, the research on Co<sub>x</sub>CrCuFeMnNi HEAPs shows that an increase in Co is beneficial to the formation of the FCC solid solution phase [14]. The research of Fu et al. [51] also shows that the elimination of Co will reduce the FCC solid solution phase in Al<sub>0.6</sub>NiFeCrCo HEA. It can be inferred that in the CoCrCuFeMnNi<sub>x</sub> HEA system, the number of Co atoms dissolved in Ni is greater than that in Cr. In addition, it can be seen from the XRD spectrum shown in Figure 1 that after 5 h of ball milling, except for the weakening of the corresponding diffraction peaks of Cr and Fe, the diffraction peaks of other alloying elements basically disappeared, forming a solid solution structure dominated by BCC. After prolonging the milling time (30 h), due to the high-entropy effect and the solid solubility expansion caused by mechanical alloying, this unstable BCC solid solution phase is decomposed, and then the FCC structure dominated by Cu is formed. At this time, the competition mechanism in the CoCrCuFeMnNi<sub>x</sub> HEA system will play a leading role; that is, the amount of FCC-stable elements and BCC-stable elements will determine the final stable phase of the alloy system: when the current content exceeds the latter and the difference is not large, the FCC + BCC mixed phase will be formed; when the current content exceeds the latter and the difference is large, a single FCC phase will be formed. Therefore, after 50 h ball milling, CoCrCuFeMnNi<sub>x</sub> HEAPs all have a single FCC solid solution structure. However,  $Ni_{1.5}$  and  $Ni_{2.0}$  HEAPs are always single FCC phase during ball milling, and there is no decomposition of BCC phase, which is mainly affected by the competition mechanism. During the ball milling process, Cu, Mn, Co, and Ni are the first to complete the alloying, generating a large number of FCC solid solution phases with structural defects and high lattice strain. When Fe and Cr elements are decomposed, the FCC solid solution phase with a large number of defects will preferentially dissolve Fe and Cr atoms, so Ni<sub>1.5</sub> and Ni<sub>2.0</sub> HEAPs are always single FCC solid solution structures. In conclusion, the main composition of the FCC solid solution phase in CoCrCuFeMnNi $_x$ HEAPs is Ni (Cu, Mn, Co), and the main composition of the BCC solid solution phase is Cr (Fe, Co).

## 3.4. Thermal Stability of HEAPs

Figure 10 shows the DSC curve of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling. It can be seen that the trend of DSC curves of the five HEAPs is basically consistent, and there are long exothermic curves in a range from room temperature to 400 °C, which is related to the increase in the lattice strain of alloy powders and the release of internal stress such as crystal structure transformation. The smaller exothermic peaks of Ni<sub>0</sub>, Ni<sub>0.5</sub>, Ni<sub>1.0</sub>, and Ni<sub>1.5</sub> HEAPs can be observed at 624 °C, 617 °C, 629 °C, and 892 °C, respectively. However, no obvious exothermic peak was found in the Ni<sub>2.0</sub> HEAP. The appearance of a small

Nio 4. Ni<sub>0</sub> 417 800 624°C Ni<sub>1.0</sub> Heat flow (mW/mg) 3. Ni<sub>1</sub> Ni<sub>2.0</sub> 617°C 0.0 892°C 629°C -3.0 200 600 800 1000 1200 400 Temperature (<sup>0</sup>C)

exothermic peak in DSC curves of HEAPs may be related to the release of internal stress at high temperature and the phase transformation of the supersaturated solid solution.

Figure 10. DSC Curves of CoCrCuFeMnNi<sub>x</sub> HEAPs after 50 h ball milling.

According to the DSC curve results, the XRD results of the CoCrCuFeMnNi<sub>x</sub> HEAPs milled for 50 h after 2 h vacuum annealing at 700 °C, 800 °C, and 900 °C are shown in Figure 11. It can be seen from Figure 11a that the  $Ni_0$  HEAP had a single FCC solid solution phase structure in the ball milling state. After annealing at 700 °C, the FCC phase decomposed into a Cu-rich FCC2 phase, a heavy Cr-rich  $\sigma$  phase, and slightly Cr-rich FCC1 phase. After annealing at 800 °C, the relative contents of the three changed, and after annealing at 900 °C, there was no significant change compared with that of 800 °C. The phase transformation of the Ni<sub>0.5</sub> HEAP after annealing at 700~900  $^{\circ}$ C is roughly the same as that of the  $Ni_0$  HEAP (Figure 11b). After annealing at three temperatures, the FCC phase of the Ni<sub>1.0</sub> HEAP was decomposed into FCC1 and FCC2 phases and no obvious  $\sigma$  phase (Figure 11c). Ni<sub>15</sub> HEAP had no obvious phase transformation after vacuum annealing at 700 °C, but the FCC phase was also decomposed into FCC1 and FCC2 phases after annealing at 800 °C and 900 °C (Figure 11d). Ni<sub>2.0</sub> HEAP had no obvious phase transformation after annealing at 700~900 °C (Figure 11e). This shows that the FCC phase in CoCrCuFeMnNi<sub>x</sub> HEAPs will be transformed into FCC1 primary phase, FCC2 secondary phase, and a minor  $\sigma$  phase after annealing at a certain temperature. It can be seen that the FCC phase formed by mechanical alloying is a metastable supersaturated solid solution phase, which will undergo phase transformation during high-temperature annealing. In the Co<sub>x</sub>CrCuFeMnNi HEAP system, an increase in Co content led to an increase in the metastable FCC solid solution content of the alloy. After high-temperature vacuum annealing, the FCC phase decomposed into two solid solution phases, FCC1 and FCC2, with a more stable structure [34]. However, Ni seems to have higher FCC stability because Ni<sub>2.0</sub> HEAP still retains its original phase structure without phase separation after vacuum annealing at 700–900 °C, thereby exhibiting excellent thermal stability. Therefore, the increase in Ni content can effectively improve the stability of the FCC phase in HEAPs and avoid phase transformation.



**Figure 11.** XRD results of CoCrCuFeMnNi<sub>x</sub> HEAPs after vacuum annealing at different temperatures: (a) Ni<sub>0.5</sub>, (b) Ni<sub>0.5</sub>, (c) Ni<sub>1.0</sub>, (d) Ni<sub>1.5</sub>, (e) Ni<sub>2.0</sub>.

## 4. Conclusions

CoCrCuFeMnNi<sub>x</sub> HEAPs were prepared via MA to generate materials with nanocrystals with metastable structures. The effects of milling time and vacuum annealing temperature on the mechanical alloying behavior, phase transformation, and thermal stability were studied. When the milling time was less than 15 h, the three HEAPs Ni<sub>0</sub>, Ni<sub>0.5</sub>, and Ni<sub>1.0</sub> consisted of metastable BCC + FCC phases. After ball milling for more than 30 h, the three HEAPs all formed FCC phases with a more stable structure. Ni<sub>1.5</sub> and Ni<sub>2.0</sub> HEAPs were composed of a single FCC phase with a more stable structure during the entire ball milling process. Five kinds of HEAPs formed nearly spherical particles after dry grinding and formed a lamellar morphology after wet grinding. The particle size was finer, and the element content was close to the nominal composition. HEAPs with low Ni content transformed from the FCC phase to FCC1 + FCC2 +  $\delta$  (Ni<sub>0</sub> and Ni<sub>0.5</sub>) phases or FCC1 + FCC2 phases (Ni<sub>1.0</sub>) after vacuum annealing at 700–900 °C, while Ni<sub>2.0</sub> powder remained a single FCC phase after high-temperature annealing, exhibiting excellent thermal stability, indicating that Ni content has an important stabilizing effect on the structure of the FCC phase in HEAs. **Author Contributions:** Methodology, B.Z. and Y.Z.; Investigation, B.R., R.Z. and A.J.; Resources, C.C.; Data curation, J.L.; Writing—original draft preparation, B.R.; Writing—review and editing, R.Z.; Project administration, J.L.; Funding acquisition, R.Z. and J.L. All authors have read and agreed to the published version of the manuscript.

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### References

- 1. Cantor, B.; Chang, I.T.H.; Knight, P.; Vincent, A.J.B. Microstructure development in equiatomic multicomponent alloys. *Mater. Sci. Eng. A* 2004, 375–377, 213–218. [CrossRef]
- Yeh, J.W.; Chen, S.K.; Lin, S.J.; Can, J.Y.; Chin, T.S.; Shun, T.T. Nanostructured high entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater.* 2004, *6*, 299–303. [CrossRef]
- 3. Ranganathan, S. Alloyed pleasures: Multimetallic cocktails. Curr. Sci. 2003, 85, 1404–1406.
- Xing, Y.; Li, C.J.; Mu, Y.K.; Jia, Y.D.; Song, K.K.; Tan, J.; Wang, G.; Zhang, Z.Q.; Yi, J.H.; Eckert, J. Strengthening and deformation mechanism of high-strength CrMnFeCoNi high entropy alloy prepared by powder metallurgy. *J. Mater. Sci. Technol.* 2023, 132, 119–131. [CrossRef]
- Dewangan, S.K.; Mangish, A.; Kumar, S.; Sharma, A.; Ahn, B.; Kumar, V. A review on high-temperature applicability: A milestone for high entropy alloys. *Eng. Sci. Technol.* 2022, 35, 101211. [CrossRef]
- 6. Zhao, Q.C.; Pan, Z.M.; Wang, X.F.; Luo, H.; Liu, Y.; Li, X.G. Corrosion and passive behavior of Al<sub>x</sub>CrFeNi<sub>3-x</sub> (x = 0.6, 0.8, 1.0) eutectic high entropy alloys in chloride environment. *Corros. Sci.* **2022**, *208*, 110666. [CrossRef]
- Yang, D.N.; Liu, Y.; Han, T.Y.; Zhou, F.; Qu, N.; Liao, M.Q.; Lai, Z.H.; Zhu, J.C. High thermal stability and oxidation behavior of FeCrNiAl-based medium-entropy alloys prepared by powder metallurgy. J. Alloys Compd. 2022, 918, 165562. [CrossRef]
- Kumari, P.; Gupta, A.K.; Mishra, R.K.; Ahmad, M.S.; Shahi, R.R. A comprehensive review: Recent progress on magnetic high entropy alloys and oxides. *J. Magn. Magn. Mater.* 2022, 554, 169142. [CrossRef]
- Duan, S.C.; Kang, J.; Cho, J.; Lee, M.; Mu, W.Z.; Park, J.H. Manufacturing an ultra-low-sulfur CoCrFeMnNi high-entropy alloy by slagging through induction melting with ferroalloys feedstock. *J. Alloys Compd.* 2022, 928, 167080. [CrossRef]
- Sathiaraj, G.D.; Ahmed, M.Z.; Bhattacharjee, P.P. Microstructure and texture of heavily cold-rolled and annealed fcc equiatomic medium to high entropy alloys. *J. Alloys Compd.* 2016, 664, 109–119. [CrossRef]
- Gludovatz, B.; George, E.P.; Ritchie, R.O. Processing, microstructure and mechanical properties of the CrMnFeCoNi high-entropy alloy. JOM 2015, 67, 2262–2270. [CrossRef]
- 12. Yim, D.; Jang, M.J.; Bae, J.W.; Moon, J.; Lee, C.-H.; Hong, S.-J.; Hong, S.I.; Kim, H.S. Compaction behavior of water-atomized CoCrFeMnNi high-entropy alloy powders. *Mater. Chem. Phys.* **2018**, *210*, 95–102. [CrossRef]
- Gao, F.; Sun, Y.; Hu, L.; Shen, J.; Liu, W.C.; Ba, M.Y.; Deng, C. Microstructural evolution and thermal stability in a nanocrystalline lightweight TiAlV<sub>0.5</sub>CrMo refractory high-entropy alloy synthesized by mechanical alloying. *Mater. Letter.* 2022, 329, 133179. [CrossRef]
- 14. Zhang, J.J.; Ren, B.; Zhao, R.F.; Liu, Z.X.; Cai, B.; Zhang, G.P. Effect of Co on the microstructure and oxidation behavior of Co<sub>x</sub>CrCuFeMnNi high entropy alloy powders. *Micron* **2021**, *142*, 102995. [CrossRef]
- 15. Ren, B.; Zhao, R.F.; Jiang, A.Y.; Yu, Y. Microstructure and oxidation behavior of CoCr<sub>x</sub>CuFeMnNi high-entropy alloys fabricated by vacuum hot-pressing sintering. *Micron* **2022**, *158*, 103291. [CrossRef]
- 16. Alvaredo, P.; Torralba, J.M.; García-Junceda, A. Sintering of high entropy alloys: Processing and properties. *Encycl. Mater. Met. Alloys* **2022**, *3*, 362–371. [CrossRef]
- 17. Toroghinejad, M.R.; Pirmoradian, H.; Shabani, A. Synthesis of FeCrCoNiCu high entropy alloy through mechanical alloying and spark plasma sintering processes. *Mater. Chem. Phys.* **2022**, *289*, 126433. [CrossRef]
- Cui, Z.Q.; Qin, Z.; Dong, P.; Mi, Y.J.; Gong, D.Q.; Li, W.G. Microstructure and corrosion properties of FeCoNiCrMn high entropy alloy coatings prepared by high speed laser cladding and ultrasonic surface mechanical rolling treatment. *Mater. Lett.* 2020, 259, 126769. [CrossRef]

- 19. Otto, F.; Yang, Y.; Bei, H.; George, E.P. Relative effects of enthalpy and entropy on the phase stability of equiatomic high-entropy alloys. *Acta Mater.* **2013**, *61*, 2628–2638. [CrossRef]
- 20. Gali, A.; George, E.P. Tensile properties of high- and medium- entropy alloys. Intermetallics 2013, 39, 74–78. [CrossRef]
- 21. Gludovatz, B.; Hohenwarter, A.; Catoor, D.; Chang, E.H.; George, E.P.; Ritchie, R.O. A fracture-resistant high-entropy alloy for cryogenic applications. *Science* 2014, 345, 1153–1158. [CrossRef] [PubMed]
- Zhang, Z.J.; Mao, M.M.; Wang, J.W.; Gludovatz, B.; Zhang, Z.; Mao, S.X.; George, E.P.; Yu, Q.; Qitchie, R.O. Nanoscale origins of the damage tolerance of the high-entropy alloy CrMnFeCoNi. *Nat. Commun.* 2015, *6*, 10143. [CrossRef] [PubMed]
- Otto, F.; Dlouhý, A.; Somsen, C.; Bei, H.; Eggeler, G.; George, E.P. The influences of temperature and microstructure on the tensile properties of a CoCrFeMnNi high-entropy alloy. *Acta Mater.* 2013, *61*, 5743–5755. [CrossRef]
- 24. He, J.Y.; Zhu, C.; Zhou, D.Q.; Liu, W.H.; Nieh, T.G.; Lu, Z.P. Steady state flow of the FeCoNiCrMn high entropy alloy at elevated temperatures. *Intermetallics* 2014, 55, 9–14. [CrossRef]
- 25. Wu, Z.; Bei, H.; Pharr, G.M.; George, E.P. Temperature dependence of the mechanical properties of equiatomic solid solution alloys with face-centered cubic crystal structures. *Acta Mater.* **2014**, *81*, 428–441. [CrossRef]
- Stepanov, N.; Tikhonovsky, M.; Yurchenko, N.; Zyabkin, Y.D.; Klimova, M.; Zherebtsov, S.; Efimov, A.; Salishchev, G. Effect of cryo-deformation on structure and properties of CoCrFeNiMn high-entropy alloy. *Intermetallics* 2015, 59, 8–17. [CrossRef]
- Park, N.; Li, X.; Tsuji, N. Microstructure and mechanical properties of Co<sub>21</sub>Cr<sub>22</sub>Cu<sub>22</sub>Fe<sub>21</sub>Ni<sub>14</sub> processed by high pressure torsion and annealing. *JOM* 2015, 67, 2303–2309. [CrossRef]
- Hsu, Y.J.; Chiang, W.C.; Wu, J.K. Corrosion behavior of FeCoNiCrCu<sub>x</sub> high-entropy alloys in 3.5% sodium chloride solution. *Mater. Chem. Phys.* 2005, 92, 112–117. [CrossRef]
- Oh, S.M.; Hong, S.I. Microstructural stability and mechanical properties of equiatomic CoCrCuFeNi, CrCuFeMnNi, CoCrCuFeMn alloys. *Mater. Chem. Phys.* 2018, 210, 120–125. [CrossRef]
- Ren, B.; Liu, Z.X.; Li, D.M.; Shi, L.; Cai, B.; Wang, M.X. Effect of elemental interaction on microstructure of CuCrFeNiMn high entropy alloy system. J. Alloys Compd. 2010, 493, 148–153. [CrossRef]
- 31. Huang, L.; Wang, X.J.; Huang, B.X.; Zhao, X.C.; Chen, H.; Wang, C.Z. Effect of Cu segregation on the phase transformation and properties of AlCrFeNiTiCu<sub>x</sub> high-entropy alloys. *Intermetallics* **2022**, *140*, 107397. [CrossRef]
- 32. Zhang, K.B.; Fu, Z.Y.; Zhang, J.Y.; Wang, W.M.; Lee, S.W.; Niihara, K. Characterization of nanocrystalline CoCrFeNiTiAl high-entropy solid solution processed by mechanical alloying. *J. Alloys Compd.* **2010**, *495*, 33–38. [CrossRef]
- 33. Fogagnolo, J.B.; Velasco, F.; Robert, M.H.; Torralba, J.M. Effect of mechanical alloying on the morphology, microstructure and properties of aluminium matrix composite powders. *Mater. Sci. Eng. A* **2003**, *342*, 131–143. [CrossRef]
- Zhao, R.F.; Ren, B.; Zhang, G.P.; Liu, Z.X.; Zhang, J.J. Effect of Co content on the phase transition and magnetic properties of Co<sub>x</sub>CrCuFeMnNi high-entropy alloy powders. *J. Magn. Magn. Mater.* 2018, 468, 14–24. [CrossRef]
- Zhao, R.F.; Ren, B.; Zhang, G.P.; Liu, Z.-X.; Cai, B.; Zhang, J.J. CoCr<sub>x</sub>CuFeMnNi high-entropy alloy powders with superior soft magnetic properties. J. Magn. Magn. Mater. 2019, 491, 165574. [CrossRef]
- Huang, S.R.; Wu, H.; Zhu, H.G.; Xie, Z.H. Effect of niobium addition upon microstructure and tensile properties of CrMnFeCoNi<sub>x</sub> high entropy alloys. *Mater. Sci. Eng. A* 2021, 809, 140959. [CrossRef]
- Wei, R.; Jiang, Z.; Gao, Q.Y.; Chen, C.; Zhang, K.S.; Zhang, S.; Han, Z.H.; Wang, T.; Wu, S.J.; Li, F.S. The effect of Co substitutions for Ni on microstructure, mechanical properties and corrosion resistance of Fe<sub>50</sub>Mn<sub>25</sub>Cr<sub>15</sub>Ni<sub>10</sub> medium-entropy alloy. *Intermetallics* 2022, 149, 107654. [CrossRef]
- Yeh, J.W.; Chang, S.Y.; Hong, Y.D.; Chen, S.K.; Lin, S.J. Anomalous decrease in X-ray diffraction intensities of CuNi–Al–Co–Cr–Fe– Si alloy systems with multi-principal elements. *Mater. Chem. Phys.* 2007, 103, 41–46. [CrossRef]
- Wang, N.R.; Wang, S.R.; Gou, X.X.; Shi, Z.C.; Lin, J.X.; Liu, G.Q.; Wang, Y. Alloying behavior and characterization of (CoCrFeNiMn)<sub>90</sub>M<sub>10</sub> (M=Al, Hf) high-entropy materials fabricated by mechanical alloying. *Trans. Nonferrous. Met. Soc. China* 2022, 32, 2253–2265. [CrossRef]
- Kumar, A.; Singh, A.; Suhane, A. Mechanically alloyed high entropy alloys: Existing challenges and opportunities. J. Mater. Res. Technol. 2022, 17, 2431–2456. [CrossRef]
- 41. Takeuchi, A.; Inoue, A. Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element. *Mater. Trans.* **2005**, *46*, 2817–2829. [CrossRef]
- 42. Kittel, C. Introduction to Solid State Physics, 7th ed.; John Wiley&-Songs, Inc.: New York, NY, USA, 1996; p. 673.
- 43. Cantor, B. Stable and metastable multicomponent alloys. Ann. Chim. Sci. Mat. 2007, 32, 245–256. [CrossRef]
- 44. Zhang, Y.; Zhou, Y.J.; Lin, J.P.; Chen, G.L.; Liaw, P.K. Solid-solution phase formation rules for multi-component alloys. *Adv. Eng. Mater.* **2008**, *10*, 534–538. [CrossRef]
- Yang, X.; Zhang, Y. Prediction of high-entropy stabilized solid-solution in multi-component alloys. *Mater. Chem. Phys.* 2012, 132, 233–238. [CrossRef]
- 46. Wang, J.C.; Liu, C.T. Atomic-size effect and solid solubility of multicomponent alloys. Scr. Mater. 2015, 94, 28–31. [CrossRef]
- 47. Guo, S.; Ng, C.; Lu, J.; Liu, C.T. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloy. *J. Appl. Phys.* **2011**, *109*, 103–105. [CrossRef]
- Fu, Z.Q.; Chen, W.P.; Xiao, H.Q.; Zhou, L.W.; Zhu, D.Z.; Yang, S.F. Fabrication and properties of nanocrystalline Co<sub>0.5</sub>FeNiCrTi<sub>0.5</sub> high entropy alloy by MA-SPS technique. *Mater. Des.* 2013, 44, 535–539. [CrossRef]

- 49. Varalakshmi, S.; Kamaraj, M.; Murty, B.S. Processing and properties of nanocrystalline CuNiCoZnAlTi high entropy alloys by mechanical alloying. *Mater. Sci. Eng. A* 2010, 527, 1027–1030. [CrossRef]
- 50. Praveen, S.; Murty, B.S.; Kottada, R.S. Alloying behavior in multi-component AlCoCrCuFe and NiCoCrCuFe high entropy alloys. *Mater. Sci. Eng. A* **2012**, 534, 83–89. [CrossRef]
- 51. Fu, Z.Q.; Chen, W.P.; Wen, H.M.; Chen, Z.; Lavernia, E.J. Effects of Co and sintering method on microstructure and mechanical behavior of a high-entropy Al<sub>0.6</sub>NiFeCrCo alloy prepared by powder metallurgy. *J. Alloys Compd.* **2015**, *646*, 175–182. [CrossRef]

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