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Effect of Process Controlling Agent on the Microstructural Evolution of CoCrFeMnNi High Entropy Alloy Processed Through Mechanical Alloying

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Abstract

An innovative and distinct class of materials that have piqued the interest of metallurgists owing to their distinct characteristics generated from four major core effects i.e., sluggish diffusion effect, high entropy effect, severe lattice distortion, and cocktail effect are termed as high entropy alloys. Mechanical alloying is one of the key techniques employed to produce high entropy alloy. In this investigation, the impact of the process controlling agent (PCA) and milling time on the microstructural evolution of CoCrFeMnNi HEAs (high entropy alloys) metallic powder particles in milling is studied. Mechanical alloying has a set of attributes, such as a ball-to-powder weight ratio, milling time, process controlling agent, ambient conditions, and grinding media. The phase evolution is investigated through X-ray diffraction (XRD), particle morphology identified via field emission scanning electron microscopy (FESEM), and elemental composition and distribution analyzed via energy dispersive X-ray (EDS), and elemental mapping, respectively. The significant effect is realized with varying process controlling agents and the optimum weight % of PCA is reported as 1.5.

Keywords

Mechanical alloying, High entropy alloys, Process controlling agent, Milling time, Microstructure

Introduction

The requirement for functional materials that demonstrate exceptional qualities and fully satisfy diverse aspects, such as economic viability, availability, and essential properties, paves the way for the development of a completely new and sophisticated class of materials as technology advances [1-3]. The functional alloys that fulfill the demand for next-generation materials that exhibit superior tribological properties [4, 5], excellent hot strength without compromising ductility [6] and toughness [7], and corrosion resistance [8] are some topmost priorities of researchers. HEAs are one of the advanced alloys because of the design strategy used to enhance the performance of materials. HEAs are solid solutions made up of five or more elements with equiatomic or nearly equiatomic atomic ratios [9, 10]. Due to their low Gibbs free energy, the high entropy of mixing plays an important role in determining their characteristics, allowing the synthesis of simple phase structures such as BCC, FCC, and BCC+FCC while limiting the production of intermetallic compounds [11, 12]. The primary determinants for the generation of simple solid solutions, along with the entropy of mixing, are differences in atomic sizes, mixing enthalpies, and valence electron concentration [13, 14].

HEAs are produced using a variety of processes, including (1) solid-state processing [15], (2) liquid-state processing [16], (3) gaseous-state processing

[17], and (4) electrochemical processing [18]. Mechanical alloying is a recognized non-equilibrium solid-state synthesis technique which allows for more control over the morphology of particles and microstructural evolution, as well as the formation of metastable phases [19, 20].

In mechanical alloying, powder particles undergo continuous welding-fracture of particles [21]. These processes cause a lower diffusion distance between powder particles. Particle size decreases during fracture and particle contact surface area rise, but cold welding improves particle bonding and, as a result, interdiffusion. The presence of soft particles causes the cold-welding process to dominate [22, 23]. To deal with this issue, PCA is often used, which works as a lubricant and restricts undue cold welding of powder. These lubricating media, however, modify the microstructure variations in the alloying system [24]. In their investigation, Lu and Zhang [25] discovered that the low concentration of PCAs causes fast interdiffusion and reaction between Mg and Al in the mechanical alloying process.

Mechanical alloying was utilized to process 'CoCrFeMnNi HEA' powder particles in this investigation. The fundamental goal of this study is to examine the influence of PCA on physical characteristics and to conduct an in-depth examination of the microstructure of HEAs.

Materials and Method

As raw materials, elemental powder particles of Mn, Co, Cr, Fe, and Ni (purity concentration 99.5%) with particle sizes 40 - 60 microns were employed. The raw material was milled using a stainless-steel vial and tungsten carbide balls in a vertical-planetary ball mill. To inhibit oxidation, milling was completed at 300 RPM for 48 hours in an argon environment. For three different concentrations, isopropyl alcohol was used as a process controlling agent, and the ball-to-powder weight ratio is 10:1. At every 6-hour interval, the milled powder sample was withdrawn and examined for microstructure and morphology, as well as phase progression. Figure 1 depicts a schematic illustration of a vertical planetary ball milling setup.

The XRD is used to identify the phases of HEA particles, which used Cu-Ka radiation at λ = 1.540 A° to study the phases developed. The diffraction angle (2θ) ranged from 20 to 100 degrees. However, the nova nano FESEM 450 (FEI) was used to analyze the morphology and microstructure of powder particles using EDS and elemental mapping to determine composition distribution.

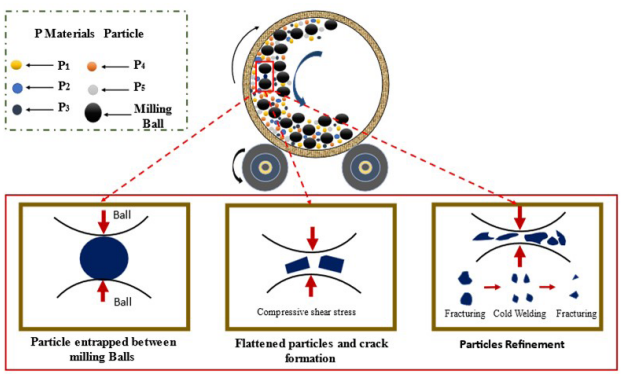


Figure 1: Representation of vertical planetary ball milling and mechanism involved.

Results and Discussion

Phase evolution

In contrast to typical alloys, the growth of solid-solution phases evolved in HEAs defies physical metallurgy rules. So, the high entropy effect increases solid solution solubility limitations, simple solid solutions occur in HEAs. An atomic size difference, the entropy of mixing, enthalpy of mixing, and valence electron concentration is the theoretical requirement for predicting phase change in solid solution HEAs (VEC) [26]. The calculated values of these attributes are listed in table 1. The values confirm the stable solid solution formation of HEAs.

Figure 2 represents XRD plots for raw materials and milled powder samples that were taken every 6 hours. The XRD plot confirms the formation of the FCC phase and also reveals the dissolution order element in the process of HEA formation i.e., Mn → Ni → Co → Fe → Cr.

Governing mechanism in milling

Mechanical alloying substantially controls the microstructure and morphology of HEA powder particles. Milling can be divided into three stages: cold welding zone, fracture dominant zone, and dynamic equilibrium region. Figure 3 depicts the variation of morphology and size of CoCrFeMnNi HEA particles. The size of the powder particle quickly increases, and uneven shape is observed in the first stage, i.e., cold welding dominating zone 0 to 6 hours powder particles are comparably soft in which plastic deformation is apparent.

The second stage is fracture dominated zone which is in between 6 hours and 24 hours grain refined however strain in the lattice increased. Severe lattice distortion is the result of the atoms' diffusion and dissolution. These are some reasons that produced the milled HEAs' metallic powder particles to harden and become brittle. The HEA particle size stabilized at the tertiary stage, which is the dynamic equilibrium stage (24 to 42 hours), as the balance between cold welding and fracture is recognized, and the spherical shape of particles is noticed. As milling rises, it has a negative impact on morphology and phase identification, as well as the undesirable phases

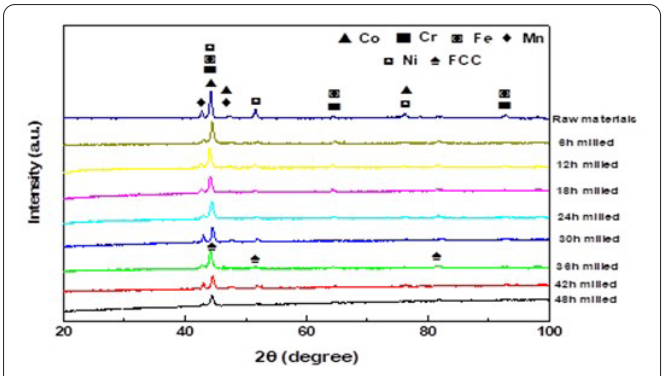


Figure 2: XRD plots of CoCrFeMnNi HEA powder particles at different milled times.

Table 1: Different thermodynamic properties and their calculated values.

Thermodynamic Parameters	Equations	CoCrFeMnNi HEA
Enthalpy of Mixing	$\Delta H_{mix} = 4\sum_{i=1,i\neq j}^{n} x_i x_j \Delta H_{i-j}^{mix}$	$-4.16\ \frac{KJ}{mol}$
Entropy of Mixing	$\Delta S_{mix} = -R\sum_{i=1}^{n} x_i \ln x_i$	$13.38\ \frac{J}{mol\ K}$
Ω	$\Omega = \frac{T_m \Delta S_{mix}}{\lvert\Delta H_{mix}\rvert}$	5.77
Atomic Size Mismatch	$\delta(\%) = 100\sqrt{\sum_{i=1}^{n} x_i\left(1-\frac{r_i}{r_{avg}}\right)^2}$	0.92
Valence Electron Concentration	$VEC = \sum_{i=1}^{n} x_i (VEC)_i$	8.33

and contamination caused by grinding media. The best milling time, according to the findings, is 42 hours. Figure 4 shows different regions formed and particle size of HEA particles in that region.

Effect of process controlling agent

To study the impact of the PCA's content over the morphology and microstructure of mechanically alloyed materials during the milling process, three PCA concentrations of 0.5 wt.%, 1.5 wt.%, and 2.5 wt.% were applied. Interdiffusion, cold welding, and fracture are the most important regulating factors in milling. During the impact of the ball-to-ball or ball-to-vial in cold welding and fracture, the HEA particles always come into contact, reducing the diffusion distance of elements [27].

When PCA concentration increases, it creates a PCA layer on the particle's surface that acts as a lubricating as well as a cooling agent, delaying the alloying process by reducing the rate of fracture and cold welding [28].

Excessive heat is created during milling with a low concentration of PCA, which promotes alloying but negatively affects the microstructure due to contamination with grinding media. While the ideal PCA concentration was found to be 1.5 wt.%. Figure 5 depicted the milled powder condition at vial for different PCA concentrations.

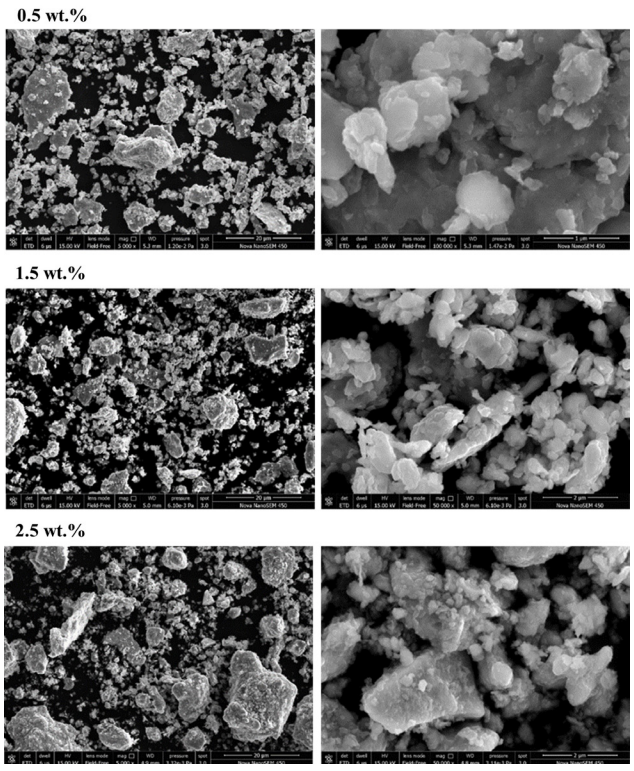


Figure 3: FESEM images of CoCrFeMnNi HEA particles at varying PCA concentration.

Conclusion

The CoCrFeMnNi HEA was effectively developed via mechanical alloying at 300 RPM milling speed. The following conclusion is derived from the study.

- It was observed that a single-phase FCC solid solution

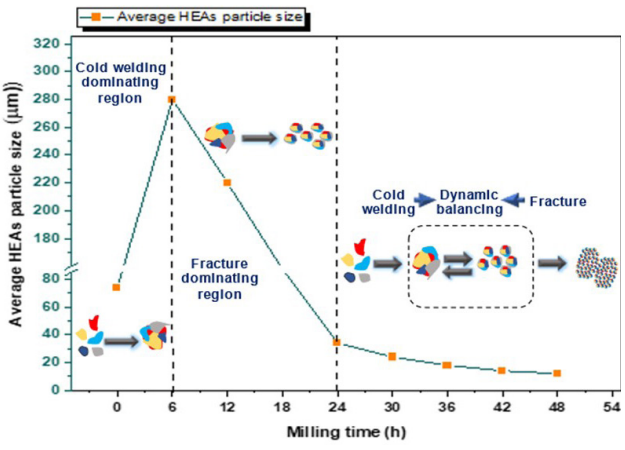


Figure 4: HEA particle size variation during milling and different regions.

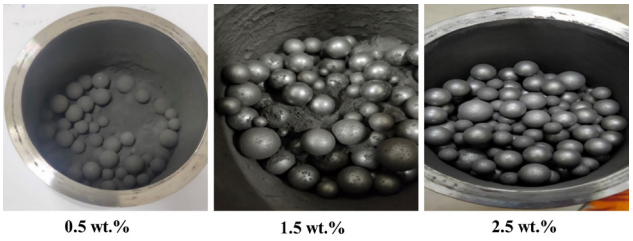


Figure 5: Milled powder at varying PCA concentration.

formed after 42-hour milling.

- At higher PCA content alloying process gets delayed whereas at lower concentration contamination problem is observed, the best result was obtained at 1.5 wt.% PCA.
- Irregular shape morphology is realized at lower concentrations of PCA, spherical morphology is reported at medium PCA content while flat plate morphology is reported for higher PCA content.

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Conflict of Interest

The authors have no conflict of interest.

Credit Author Statement

Akshay Kumar: Conceptualization, Methodology, Data collection, Data analysis, Writing - original draft preparation, Writing - review and editing; Alok Singh: Methodology; Amit Suhane: Methodology; Ashish Kumar Singh: Data collection, Writing - review and editing; Pradip Kumar Verma: Data collection, Writing - review and editing. All the authors read and approved the manuscript.

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