

Paragraph Ran in the Queries

Paper Title:Effect of AlCrCuFeNi high entropy alloy reinforcements with and without B₄C on powder characteristic, mechanical and wear properties of AA5083 metal-metal composites

Content :

Characterization of HEA powders

The XRD patterns of AlCrCuFeNi HEAPs with and without B₄C ceramic particles at different mechanical alloying times (5, 15, 25 h) are shown in Fig. 2. Fig. 2a represents the XRD pattern of the AlCrCuFeNi HEA, while Fig. 2c shows the XRD pattern of the AlCrCuFeNi-B₄C HEA. As the milling time increases, the diffraction intensity gradually decreases, and some diffraction peaks even disappear. For the raw powders examined after 25 h of milling in the XRD device, the specific peak values for the appropriate elements are provided. In the XRD patterns after 25 h of milling, distinct BCC and FCC peaks are observed. The BCC phase peaks appear at three different angles: $2\theta = 44.51^\circ$, 64.62° , and 82.35° , while the FCC phase peak appears at a single angle of $2\theta = 51.7^\circ$. After the initial 5 h of milling, as shown in Fig. 2a, the peak intensity is higher compared to other milling times, and the individual peaks of the elements within the AlCrCuFeNi HEA are still distinguishable. After 15 h, many of the individual element peaks that were clear at 5 h have disappeared, leaving behind very low intensity and significant peak broadening. This can be attributed to the repeated collisions and cold welding of particles, causing elements to diffuse into each other's lattice. In other words, elements with lower melting points have higher diffusion rates, leading to the formation of a solid solution. This phenomenon has been explained in various studies [48], [49]. After 25 h, the presence of individual element peaks completely disappears, and the complete formation of FCC and BCC peaks, indicative of solid solution formation, is evident. Additionally, the peaks after 25 h of milling are broader compared to those after 15 h. The formation time of BCC and FCC phases is shorter compared to other studies in the literature, which is attributed to the rotational speed. The rate of the solid solution formation is directly proportional to the rotational speed. Higher rotational speed increases the energy imparted to the particles, accelerating element diffusion, and thus solid solution formation occurs in a shorter time [50], [51]. The changes in milling time shown in Fig. 2c are almost identical to those in Fig. 2a. Due to the very low amount of B₄C, no distinct peak for B₄C is observed in the XRD patterns. This is a common occurrence in studies where the reinforcement used is below 4 % by weight.

The crystallite sizes and lattice strains of AlCrCuFeNi and AlCrCuFeNi-B₄C HEAPs with BCC and FCC crystal structures after different milling times are shown in Figs. 2b and 2d. In both figures, the crystallite sizes continuously decrease with increasing milling time, while the lattice strains continuously increase. For AlCrCuFeNi HEAPs, the crystallite sizes decrease from 16.7 nm to 10.2 nm as the milling time increases from 5 to 25 h, while for AlCrCuFeNi-B₄C HEAPs, the crystallite sizes decrease from 15.9 nm to 9.7 nm. The lattice strains of AlCrCuFeNi HEAPs increase from 0.51 % to 1.07 % with increasing milling time, while for AlCrCuFeNi-B₄C HEAPs, the lattice strains increase from 0.62 % to 1.31 %. As noted in many studies, severe plastic deformation occurring in the powders during the milling process leads to an increase in lattice strain. This significantly increases structural defects (such as dislocations and voids), resulting in higher lattice strain. Additionally, the rearrangement of dislocations within low-angle grain boundaries leads to smaller fracture areas, thereby reducing crystallite size [52], [53], [54]. The presence of a hard phase like B₄C in the HEAPs leads to more severe plastic deformation, which explains both the smaller crystallite sizes and the higher lattice strains observed in the AlCrCuFeNi-B₄C HEAPs.

Through the mechanical alloying method, two distinctive types of high-entropy alloy powders (HEAPs), namely AlCrCuFeNi and AlCrCuFeNi -B₄C, were synthesized, revealing significant differences in their structural characteristics. As depicted in Fig. 3, these powders underwent milling for durations of 5, 15, and 25 h, showcasing varied morphologies, average powder sizes, and particle size distributions. The mechanical milling process subjects the powders to intense plastic deformation through ball-powder-ball and ball-powder-container collisions, which not only leads to work hardening but also to the fracturing of particles [55], [56]. Consequently, this considerable deformation dramatically transforms both the morphology and size of the powder. The essence of the mechanical alloying process encapsulates flattening, cold welding, fracturing, and the subsequent re-welding of elemental powders [57], [58], [59]. Initially, after 5 h of milling, the AlCrCuFeNi HEAPs exhibited a tendency toward flattening, signaling severe deformation and fracturing. This was evident alongside the emergence of irregularly shaped, smaller-sized particles adjacent to larger, flake-like structures. The persistence of larger particles that are prone to flattening underscores their resilience to plastic deformation, whereas the smaller particles underscore the efficacy of the fracturing mechanism. It is plausible that the ongoing deformation, fracturing, and cold welding during the mechanical alloying process amplifies the diffusivity of elements, thereby facilitating the formation of the HEA [58], [59]. Subsequent to the initial 5 h of milling, the average particle size of the AlCrCuFeNi HEAPs was determined to be 36.6 μm . Incorporating 1 wt% of the hard and brittle B₄C into the HEA powders resulted in an even greater reduction in powder size. Specifically, after 5 h, the average size of the AlCrCuFeNi-B₄C HEAPs was recorded at 32.5 μm , marking a roughly 8 % diminution in comparison to the AlCrCuFeNi HEAPs. This

addition of B₄C notably enhances the mechanical milling's efficiency by intensifying the plastic deformation applied, which in turn, promotes more effective fracturing and cold-welding mechanisms, leading to a finer powder size [60]. Moreover, the morphology of the AlCrCuFeNi-B₄C HEAPs after 5 h of milling bore similarities to that of the unreinforced HEA powders, with a notable increase in the concentration of small, irregularly sized particles, a change attributed to the shearing effect of B₄C. As the milling time extended, both types of HEAPs experienced a decrease in powder size. Specifically, the size of the AlCrCuFeNi HEAPs was reduced to 19.2 μm and 11.9 μm after 15 and 25 h of milling, respectively, whereas the AlCrCuFeNi-B₄C HEAPs saw their average sizes diminish to 12.3 μm and 7.9 μm , respectively. This consistent trend in morphology change, observed in both powders, indicates that increased milling leads not only to particle fragmentation and size reduction but also to cold welding, which introduces larger particles within the structure, culminating in a bimodal particle size distribution. Therefore, the powder morphologies after 25 h of milling encompassed very small particles alongside larger, agglomerated spherical and flaky powders in both HEAPs varieties. This pattern suggests that the initial breakdown of larger particles contributes to a reduction in the average particle size and distribution range, followed by the fragmentation of relatively finer particles. In tandem, the particles undergo alloying, indicating that particle fragmentation, along with an increased relative surface area and enhanced diffusivity on particle surfaces, plays a crucial role in the formation of the alloy.

To investigate the distribution of elements within HEAPs subjected to the mechanical alloying process, EDS compositional surface mapping was performed. This analysis focused on two specific HEA formulations: AlCrCuFeNi and AlCrCuFeNi-B₄C, with their resulting characteristic maps showcased in Fig. 4 and Fig. 5 after a milling duration of 25 h. The EDS mapping utilized a color-coded system where red, brown, purple, green, and turquoise respectively signified the presence and distribution of Al, Fe, Cr, Ni, and Cu within the HEAPs. Furthermore, the introduction of B, as indicated by the blue color in the EDS analysis of Fig. 5, highlights the dispersion of B₄C within the alloy. The examination of these EDS analyses reveals a crucial finding: the uniform distribution of each constituent element post 25 h of milling, showcasing an absence of heterogeneity. This uniformity suggests that all elements were successfully and evenly integrated into the primary lattice, culminating in the synthesis of homogeneous HEAPs. To substantiate this observation and verify the composition, a detailed EDS-SEM semi-quantitative analysis was meticulously carried out on five different areas (or powders) for each HEA composition. The insights derived from this comprehensive analysis, depicted in Fig. 4 and Fig. 5, affirm that the average weight ratios of the constituent elements, initially added in equal weight proportions, closely mirror the original composition after 25 h of mechanical alloying. This consistency effectively maintains the desired 20 wt% for each element, reinforcing the homogeneity achieved in

the alloying process across both HEA systems. Thus, these findings not only validate the compositional integrity of the HEAPs but also underscore the effectiveness of the mechanical alloying method in achieving a uniform elemental distribution, which is pivotal for the properties and performance of HEAs.

The change in particle hardness of AlCrCuFeNi and AlCrCuFeNi-B₄C HEAPs over the duration of mechanical alloying is depicted in Fig. 6. It is evident from XRD analyses in Fig. 2 that the chemical structure of the starting elemental powders and the phases formed within them undergo changes dependent on the milling time when subjected to mechanical alloying. This process facilitates the formation of nanocrystalline phases or the transition from one crystal structure to another, significantly influencing the mechanical properties. The presence of nanocrystalline phases or a tendency towards nanocrystallization typically results in smaller grain sizes, higher dislocation densities, and altered grain boundaries, all contributing to increased hardness [61]. Furthermore, as milling time progresses, the accumulated deformation and dislocations generated during the mechanical alloying process can cause variations in the material's mechanical behavior [62]. Transformations in certain phases, as the duration of mechanical alloying increases, lead to changes in the mechanical properties of the powders, as observed in Fig. 6 through the variation in microhardness with the alloying time. For AlCrCuFeNi HEAPs, the microhardness values obtained for 5, 15, and 25 h were 182 HV, 376 HV, and 485 HV, respectively. Concurrently, the lattice strains were recorded at 0.51 %, 0.79 %, and 1.07 %, respectively (Table 4). The increase in grinding time reduces the crystallite size, thereby promoting the formation of nanocrystalline phases within the powders. Additionally, the high level of plastic deformation experienced by the powders during milling enhances lattice strains, leading to an increase in dislocation density, which in turn enhances material hardness by impeding slip movement within the material. The microhardness values for AlCrCuFeNi-B₄C HEAPs at 5, 15, and 25 h were respectively 231 HV, 421 HV, and 544 HV, which are higher than those of AlCrCuFeNi HEAPs. Examination of the XRD patterns (Fig. 2) reveals similar phases in both types of HEAPs, indicating that the B₄C reinforcement does not lead to the formation of a different phase that could increase hardness. The higher hardness of AlCrCuFeNi-B₄C HEAPs can be attributed to the accelerative effect of B₄C on the milling process during mechanical alloying, resulting in more intensive work hardening of the powders, which ultimately leads to smaller particle sizes and higher lattice strains.

Characterization of composite powders

To achieve a uniformly dispersed mix of HEAP reinforcing powders within the AA5083 matrix, while also preserving their chemical content and structural integrity, the mechanical grinding method was employed for a duration of two hours. The rationale behind the limited milling time stems from the AA5083 alloy's inherent high

formability, which readily accommodates the incorporation of hard reinforcement materials, thus obviating the necessity for protracted mechanical grinding. Moreover, this approach circumvents the adverse effects of excessive plastic deformation potentially induced by extended milling periods, such as an unwelcome increase in matrix hardness that could, in turn, impede sintering capability and promote high porosity.

Fig. 7a displays the AA5083 alloy powders' initial morphology, illustrating a variety of shapes including spherical, irregular, and ligamental morphologies. The starting powders, averaging $27.8\text{ }\mu\text{m}$ in size, exhibit a particle size distribution ranging from 5 to $150\text{ }\mu\text{m}$. Fig. 7b reveals the SEM images, average particle size, and particle size distribution of the A-HE composite powders, which were synthesized by adding 10 wt% AlCrCuFeNi HEAPs to the Al matrix powders. It is evident from the figure that the addition of HEAPs prompts the matrix powders to adopt a flaky morphology, a transformation attributable to the extensive plastic deformation experienced by the soft Al matrix during the mechanical milling process. Nonetheless, the occurrence of irregularly shaped and spherical morphology powders remains noteworthy. Additionally, the inset image in Fig. 7b illustrates how composite powders undergo agglomeration due to cold welding. This phenomenon manifests as smaller matrix and/or reinforcement powders becoming welded atop relatively larger powders, thereby engendering the formation of larger aggregates and an overall increase in powder size. Consequently, the A-HE composite powders' average particle size reaches $38.1\text{ }\mu\text{m}$, marking a significant enlargement, approximately 37 % greater than the matrix alloy's original size. A noteworthy aspect illustrated in Fig. 7b' is the bimodal particle size distribution of the A-HE composite powders, further attesting to the cold-welding mechanism's pronounced efficacy throughout the milling process.

A parallel scenario unfolds for A-HE-B composite powders, albeit with a lesser degree of size augmentation due to the presence of B_4C , culminating in an average particle size of approximately $31.5\text{ }\mu\text{m}$ —about 13 % larger than the matrix alloy (Fig. 7c and c'). In alignment with the A-HE composites, the potency of the cold-welding mechanism facilitated the adhesion of small reinforcement powders and fractured small matrix powders around larger particles, thus amplifying the powder size. The composite powders' lack of particles smaller than $2\text{--}3\text{ }\mu\text{m}$ signifies that the reinforcement powders are either encapsulated within the matrix or have been cold welded onto the matrix powders, highlighting the intricate interplay of mechanical forces and material properties during the alloying process.

Hardness and tensile strength

As seen in Fig. 12, the lowest hardness values are observed in unreinforced samples, while the addition of high entropy alloy and B_4C particles separately has led to increases

in hardness values. Upon examining the graph, it is evident that adding only the high entropy alloy has resulted in an approximately 60 % increase in hardness, while adding both the high entropy alloy and B₄C particles together has led to a hardness increase of up to 100 %. To examine separately, the hardness of the aluminum alloy used in this study is lower than that of the alloy elements forming the HEA. In other words, the hardness of the reinforcing element added to the structure is higher than that of the matrix phase. Therefore, according to the rule of mixtures, due to the high hardness of the secondary phase added to the structure, an increase in the hardness of the total mass is expected. Additionally, as mentioned in the examination of powder hardness, the reinforcing powders added to the structure have caused a significant increase in powder hardness. This increase in powder hardness has directly increased the hardness of bulk samples. When comparing the hardness of only the HEA-reinforced sample with the sample containing 1 % B₄C, it is observed that even a small amount of B₄C reinforcement leads to a significant increase in hardness value. In studies related to B₄C-reinforced metal matrix composites, it has been stated that B₄C reinforcement acts as a grinding element, especially during the grinding process, and increases powder hardness more effectively by subjecting alloy powders to plastic deformation. Based on this statement and powder hardness data, the effect of B₄C reinforcement on hardness has become more pronounced due to both its direct addition to the structure and its increase in powder hardness during grinding.

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