Improving electromagnetic properties of FeCoNiSi_{0.4}Al_{0.4} high entropy alloy powders via their tunable aspect ratio and elemental uniformity

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Abstract

Mechanical milling and melting-strip casting-milling have been used to prepare FeCoNiSi_{0.4}Al_{0.4} high entropy alloy (M-HEA and C-HEA respectively) powders. Both techniques have different solution and phase formation rules. The M-HEA powders have more FCC, and the opposite is true for C-HEA powders. In addition, the C-HEA powders have better elemental uniformity and a larger aspect ratio. Because of this, the C-HEA powders have a smaller $M_s$ and a larger $H_c$; the $M_s$ range from 93.6 emu/g to 104.4 emu/g, and the $H_c$ vary from 81.5 Oe to 159.6 Oe. As the milling time increases, the variety of aspect ratios and uniformity give rise to the change of electromagnetic (EM) parameters for both HEA powders. Versus the EM parameters of M-HEA powders (ranging from 7.5 to 16 and from 0 to 1.4 for $\varepsilon'$ and $\varepsilon''$, respectively), these C-HEA powders have larger values (ranging from 11 to 26 and from 0 to 8 for $\varepsilon'$ and $\varepsilon''$, respectively). At the same time, the $\mu'$ (varying from 1.78 to 1.90 at 2 GHz) and the $\mu''$ (up to 0.52) of C-HEA powders are larger than the M-HEA powders.

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HIGHLIGHTS

• The mechanical milling method and melting-strip casting-milling method have been designed to prepare FeCoNiSi_{0.4}Al_{0.4} HEA powders.
• During this two kinds of technologies, the rules of dissolution and phase formation are different.
• It has been proven that the C-HEA powders possess better uniformity and larger aspect ratio than M-HEA powders.
• The variety of aspect ratio and uniformity lead to the change of electromagnetic parameters for both kinds of HEA powders.

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1. Introduction

Due to the rapid developments of microwave electronic technology and the increasingly serious EM pollution problems, many EM wave-absorbing materials have been studied in recent years because they can fundamentally eliminate EM pollution. The frequency range in the S—Ku band (2–16 GHz) has many significant applications, such as communication, electric equipment, and radar. Consequently, alloy powders are widely applied in the development of EM wave absorbers. The alloys have a higher electric conductivity and permeability that consumes EM waves by interacting with the electric and magnetic field vectors of the EM wave \[1,2\]. Thus, ferromagnetic alloys containing Fe, Co, and Ni elements have received significant attention. While most of these alloys (carbonyl iron, FeSi and FeSiAl) can easily achieve strong absorption and a wide absorption band, they are also susceptible to corrosion and...
oxidation [1–4]. Alkaline environments like seawater and high-temperature conditions like high-speed aircraft preclude the widespread use of traditional absorbent materials [5,6]. Environmental adaption and multi-spectrum stealth are evolving trends for future EM wave-absorbing materials [7].

High entropy alloy (HEA) has received much attention in recent years due to its good corrosion and oxidation resistance, extraordinary mechanical properties, and combinations of two or more properties [8–15]. HEA powders are likely the next generation of EM wave-absorbing materials [16–19]. In contrast to traditional metallurgical theory and the Gibbs phase rule, HEA containing five to sixteen elements with each elemental concentration between 5 and 35 at. % tends to form a single crystal structure, such as face-centered-cubic (FCC) and/or body-centered-cubic (BCC) solid solution due to the high configurational entropy [20–24]. It has four unique “core effects”: high entropy of mixing in thermodynamics, sluggish diffusion in dynamics, severe lattice distortions and cocktail effects in performance [20].

HEAs such as FeCoNiCrAl, and FeCoCrAlCu–X alloys have much better corrosion resistance than SS304 alloy [11,12]. Many studies have shown that the addition of Al and AlO can increase the corrosion and oxidation resistances of alloys [25–28]. At the same time, the addition of Al and Si elements to NbCrMoAl HEAs can effectively improve the high temperature oxidation resistance [26]. Therefore, we concluded that HEAs with Si and Al elements would likely have good corrosion and oxidation resistance in the light of the presence of the “cocktail effects” for HEAs.

Yang et al. prepared FeCoNiCrAl, (x = 0, 0.8, 1) HEA powders by mechanical milling and investigated the EM wave-absorbing properties [16–18]. In addition, Zhang et al. prepared the FeCoNiCrAl HEA powders and studied the EM interference shielding effectiveness [19]. The results indicate that the FeCoNiCrAl, HEA powders exhibit good EM wave absorbing performance. Nevertheless, the FeCoNi(Si)Al, HEA with different SiAl contents was prepared. Later work showed that FeCoNi(Si)Al, is a much better candidate than FeCoNiCrAl, for soft-magnetic application [29]. Zhang et al. also showed that Mn decreases and electrical resistivity increases with the addition of Si or Al content for FeCoNi alloy, which can suppress the eddy current effect [30]. In addition, a smaller magnetostrictive coefficient can be achieved by adding a small amount of Si, which leads to a higher permeability material. Thus, FeCoNiSi0.4Al0.4 HEA powder with good magnetic properties was selected as the EM wave-absorbing materials. The effects of milling time on the structure, magnetic and EM properties of the FeSiAl, FeCoNi and FeSiCr alloys have been investigated before. The flake-shaped magnetic particles with a larger planar anisotropy can be prepared with mechanical milling by adding anhydrous ethanol as process control agent. This leads to a reduced eddy current loss, increased permeability, and a higher resonance frequency above Snoek’s limit [31–38].

Much attention has been focused on the microstructure, mechanical, and magnetic properties of HEAs; however, few studies have reported the effects of milling time on the aspect ratio and uniformity, or the relationship between these factors and EM properties for the HEA powder/paraffin composite materials. Here, FeCoNiSi0.4Al0.4 HEA powders were prepared by two methods: one is a mechanical alloying method using pure metal powders as the initiation materials and the other is the combination technology of melting, strip casting, and milling. The tunable crystal structure, aspect ratio, uniformity, and the magnetic and EM properties of the alloy powders were researched by changing the preparation technologies and milling time.

2. Experiments

2.1. Synthesis

The raw powders (Fe, Co, Ni, Si and Al) with 99% purity were processed by ball milling in a planetary ball mill QM-QX4. The FeCoNiSi0.4Al0.4 (at. %) HEA powders were prepared by wet milling with a moderate amount of anhydrous ethanol as a process-control agent. The powder-to-ball (10 mm and 6 mm in diameter) weight ratio was 1:20, and the stainless steel pot rotation speed was 300 rpm. The milling time ranged from 0 to 70 h (0, 10, 30, 50, and 70 h). This was used to investigate the magnetic- and EM wave-absorbing properties of the powders. The alloy powders (M-HEA powders) were denoted as M0, M10, M30, M50, and M70, respectively. In addition, a pause of 4 min was done to avoid excessive heating during milling, and the direction of the rotation was changed every half an hour.

The other methods include melting, strip casting, and ball milling; these were used to create HEA powders here. Metallurgy of the alloy ingots with nominal composition of FeCoNiSi0.4Al0.4 were initially prepared by arc melting in a 2r-gottered high-purity argon atmosphere. The ingots were remelted four times to obtain a homogeneous composition. The ribbons were prepared via liquid quenching from the melted ingots, and the rotation speed of the copper wheel was 3500 rpm. To reduce the hardness of the alloy and release the internal strain generated in the melt-spinning process, the ribbons were annealed at 1023 K for 1 h in argon. The ribbons were then milled into alloy powders (powder-to-ball mass ratios were 1:30) for 50, 60, 70, 80, and 90 h in QM-QX4 at 300 rpm upon addition of anhydrous ethanol. The powders (C-HEA powders) were denoted as C50, C60, C70, C80, and C90, respectively.

2.2. Characterization

The morphology and microstructure of the powders were characterized by scanning electron microscopy (SEM, SUPRA55) equipped with energy-dispersive spectrometry and X-ray diffractometer (XRD, Empyreal) using a Co Kα radiation (λ = 1.78901 Å) in the 2θ range from 30° to 120°, respectively. The size distribution of alloy powders was tested

![Fig. 1. XRD patterns of (a) M-HEA and (b) C-HEA FeCoNiSi0.4Al0.4 powders. The enlarged picture from 48°–58° is shown in the inset. The change in integral area ratio (A_{bcc}/A_{fcc}) for the C-HEA powders is also presented.](Image)
by laser scattering particle size distribution analyzer (LA960WET). A vibrating sample magnetometer (VSM7404) was employed to research the magnetic properties, e.g. saturation magnetization ($M_s$) and coercive force ($H_c$) with a maximum applied field of 10,000 Oe at room temperature. The electrical conductivity was tested with a four-point probe measurement tool (RTS-9), and the resulting cylinders were pressed using powders at 10 MPa.

2.3. Electromagnetic performance testing

The EM parameters ($\varepsilon(f)$ and $\mu(f)$) were measured with an Agilent vector network analyzer (8720B) using coaxial reflection/transmission from 2 GHz to 16 GHz. The milled powders were blended with paraffin at a weight ratio of 6:4. Concentric cylinders with 3.00 mm inner diameter, 7.00 mm outer diameter, and 2.00 mm thicknesses were prepared with this mold.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD patterns of both FeCoNiSi0.4Al0.4 HEA powders under various milling times. The HEA powders were successfully prepared with two methods. The peak height, main diffraction peak angle position, grain size, and internal stress of XRD patterns at different milling time are expressed in Fig. 2. Of these, the grain size and internal stress after different milling time were calculated by the Williamson-Hall equations: $\frac{\delta \cdot \cos \theta \cdot \lambda}{\lambda} = K \cdot D + \frac{4 \cdot \sin \theta}{\lambda}$, where $\delta$ is the FWHM of the peaks, $K = 0.9$, $D$ is the grain size, and $\varepsilon$ is the internal strain. Then, the $\frac{\delta \cdot \cos \theta}{\lambda}$ and $\frac{4 \cdot \sin \theta}{\lambda}$ were the y-axis and x-axis, respectively. The average grain size and the internal strain can be obtained from the slope of the line and the intercept of the Y axis [33]. Fig. 1(a) presents the change of the crystal structure for the process of preparing the M-FeCoNiSi0.4Al0.4 HEA powders using pure metal powders as initial materials by ball milling. The diffraction peaks of the raw pure metal powders are presented in the M0 sample. The circulation of cold welding and crushing promotes mutual dissolution between different elements during the milling process and facilitates the formation of a solid solution. After 70 h, the alloy powders have an abundant FCC phase (corresponding to (111), (200), (220) crystal face); they lack a BCC phase (corresponding to (110), (200), (211) crystal face). This indicates the formation of complete solid solution (high entropy alloy). However, the peak of Si at 33.2° and 55.5° remain because the crystal structure of Si differs from the other elements. The alloying rate depends on the crystal structure and melting point, and elements with same crystal structure and lower melting point are easily dissolved [16,17]. The Si will not be completely dissolved with prolonged milling time to 150 h (in Fig. S1). This may be because the Si possesses a diamond-type structure that is difficult to disrupt. The sequence of dissolution in the milling process can be concluded from the disappearance order of the peak. The peak of Al at...
45.01° disappears first after 30 h milling, and then the peaks of Co at 48.74° and 55.55° vanish after 70 h of milling. The direction of the main peak shift can also reflect the dissolution order of the element. The dissolution of the elements with different atomic radii leads to lattice distortion, and a larger atomic radius causes the peak to shift to a lower angle and vice versa. In addition, the diffraction peaks broaden, and the intensity weakens with increased milling time. This is due to the reduction in grain size, the growth of internal strain, and the formation of an amorphous structure (Fig. 2(a) and Fig. S2).

Fig. 1(b) shows the XRD patterns of the C-FeCoNiSi0.4Al0.4 HEA powders milled for different times. The C-HEA powders also have a simple solid solution structure (FCC and BCC) similar to the crystal structure of the M-HEA powders. The difference is that the peaks of Si disappear in all powders. This is because all elements completely dissolve during milling.

Fig. 3. Backscatter electron images of (a–e) M- and (f–j) C-FeCoNiSi0.4Al0.4 HEA powders with different milling times. The inset shows the corresponding enlarged image. The aspect ratio of C-HEA powders is larger than M-HEA powders.
melting. The milling process only grinds the alloy strips into powders. The XRD pattern of the HEA ribbon is shown in Fig. S3. It has the same crystal structure, except that the diffraction peaks are sharp. As the milling time increases, the diffraction peaks have a similar trend in terms of width and intensity (in Fig. 2(b)). The main diffraction peak shifts rightwards slightly, and this may be due to the miscibility of the elements between FCC and BCC phases and the precipitation of elements from the FCC phase matrix. A two-phase nanocrystalline alloy may be prepared with this approach because the amount of amorphous phase gradually increases, and the crystal phase decreases with increased milling time. In addition, the relative content of FCC to BCC phase ($A_{\text{BCC}}/A_{\text{FCC}}$, integral area ratio) for the C-HEA powders changes with the milling time (see Fig. 2(b) insert).

While both HEA powders can have a simple solid solution structure (FCC and BCC), the M-HEA and C-HEA powders are FCC- and the BCC-based structure, respectively. This is because the rule of phase formation is different between these two processes for preparing HEA powders. During milling, the whereabouts of the elemental dissolution is related to the crystal structure and atomic radius. Elements with the same crystal structures and atomic radii are easily dissolved into each other. The elemental mapping (Fig. S5) and EDS (Fig. S6) shows that Al and Si are mainly dissolved into FCC Ni, while Co is mainly dissolved into BCC Fe. The amount of dissolved elements determines the phase content. Thus, the two phases co-exist in the M-HEA powders, and the amount of FCC phase is larger than BCC phase.

During melting, the phase structure of the alloy (BCC or FCC) is determined by the covalent electron concentration ($\text{VEC}, \text{VEC} = \sum_{i=1}^{N} c_i (\text{VEC}_i)$) at $\text{VEC} < 6.87$, FCC phase; at $\text{VEC} \geq 8.0$, FCC phase; at $6.87 \leq \text{VEC} < 8.0$, two phase co-existence [23], where $c_i$ is the molar content of each element. The VEC number of Fe, Co, Ni, Si, and Al are 8.9, 10.4, 3, respectively. Therefore, the VEC of the FeCoNiSi0.4Al0.4 C-HEA is 7.84, and we predict that the alloy coexists between the two phases (FCC and BCC). While the VEC value (7.84) promotes the formation of a FCC-based phase according to this rule, the two phase co-existent interval becomes smaller for these system because the larger Al atoms and smaller Si atoms introduce a larger lattice distortion energy. The BCC-based phase can then be formed when the VEC is large. Thus, the two phases co-exist in the C-HEA powders, and the amount of BCC phase is larger than FCC phase. This is similar to the literatures [29,30].

3.2. Morphology analysis

The morphologies and particle size distribution of different HEA powders are characterized by SEM and a laser particle size distribution analyzer. Fig. 3 shows the back-scattered images of the (a–e) M- and (f–j) C-FeCoNiSi0.4Al0.4 HEA powders with different milling times. All of the alloy powders present a flake structure with alcohol as the grinding media. The aspect ratios of C-HEA powders are larger than that of the M-HEA powders due to the different preparation techniques. Furthermore, the larger aspect ratio can simultaneously magnify the surface polarization, reduce the eddy current loss, and increase the permeability [31–38].

Figs. 3(a–e) and 4(a) show that the particle size distribution and shapes of the M-HEA powders are uneven. The five initial particles are spherical, and the particles possess larger aspect ratio after milling for 10 h. The particles will be flattened because the effect of cold welding plays the main role in the earlier milling time. In the following milling process, the crushing effect makes the alloy particles broken and refined. These two effects co-exist throughout milling process. Figs. 3(f–j) and 4(b) show that the particle sizes of the C-HEA powders grow with increasing milling time, and get the maximum value at C60, then decrease. And the thickness reduces continuously. This is because the impingement of the ball first makes the strip thinner and then breaks it. Thus, the aspect ratio first increases and then decreases—it varies from 10 (C60) to 5 (C0), and the HEA powders with a tunable aspect ratio are available via this technology.

Fig. 5 presents elemental mapping date for Fe, Co, Ni, Si, Al, Cr, O and Cr in M70 and C60. The elements are better dispersed in the C-HEA powders than the M-HEA powders—especially the Si element. The presence of undissolved Si particles in sample M70 is consistent with the XRD date. The O and Cr are introduced into the system via milling (Table S1), and there is inevitable particle surface oxidation.

Fig. 6 shows TEM and HRTEM images of M70 and C60 HEA powders. The HRTEM and the corresponding SAED patterns were collected on the marked region. The patterns confirmed the XRD results, and verified that the alloy powders consist of nanocrystalline grains with an amorphous structure. In addition, the SAD pattern is indexed to FCC [10T] and FCC [01T] zone axis patterns for M70 and C60 respectively, the lattice fringe spacing agrees nicely with the calculated lattice constant from SAD patterns.

As a consistency of all of the above experimental results, a flow schematic chart detailing the formation of HEA powders and the change in aspect ratio and uniformity of the two technologies is depicted in Fig. 7. One technology is direct milling. The particles from the initial powders have a ball-like shape with different sizes. These are flattened at the beginning of the milling time, and various elements are dissolved into each other at subsequent times. The HEA powders are prepared successfully after 70 h of milling, and the undissolved Si particles are present in the alloy particles.

The other method is a composite technology. The metal powders mixture are manufactured into an alloy ingot, and the alloying is completed during this process. Strip casting and milling are used to obtain alloy powders. During milling, the impingement of the ball first makes the strip thinner and then breaks it. The particles of the alloy powders
Fig. 5. Elemental mapping of M₇₀ and C₆₀ alloy powders.

Fig. 6. (a, d) TEM and (c, f) HRTEM images of (a-c) as-milled (M₇₀) and (d-f) as-annealed (C₆₀) FeCoNiSi₀.₄Al₀.₄ HEA powders. The SAED patterns (b) and (e) for the samples.
3.3. Magnetic properties

Fig. 8 shows the hysteresis loops of (a) M0–70 and (b) C50–90 HEA powders measured at room temperature under magnetic fields up to 10,000 Oe, and the change in saturation magnetization ($M_s$) and coercivity ($H_c$) as a function of milling time are presented in the illustration. All samples present a typical soft magnetic characteristic. The $M_s$ of the C-HEA powders is smaller than the M-HEA powders—this proves that the Si element of C-HEA powders has been dissolved completely, which is consistent with the XRD and elemental mapping. Another reason why the $M_s$ of the C-HEA powders is smaller than the M-HEA powders might be that there is more amorphous phase in the C-HEA powders than the M-HEA powders. The $M_s$ of amorphous structure is smaller than that of the crystal structure. In addition, the C-HEA powders are much easier to magnetize to saturation than M-HEA powders. This represents a reduction in the magnetic anisotropy field and makes this system suitable for interaction with an EM wave.

Fig. 8(a) clearly shows that the milled powders are more easily magnetized to saturation versus the raw materials. The $M_s$ first decreases and then increases. It varies from 93.6 emu/g to 113.1 emu/g, and achieves a minimum value after 30 h of milling; the $H_c$ first increases and then decreases while varying from 65.6 Oe to 159.6 Oe. The maximum value occurs after 50 h milling. The $M_s$ is primarily decided by the composition and atomic-level structure, and the $H_c$ is sensitive to grain size ($D$), impurities, and the heat-treatment [29]. Thus, at the early stage of milling, the obvious reduction in $M_s$ is due to the dissolution of Si and Al elements—the 3d electrons of magnetic elements transfer to the 2p electron layer of Si and Al. The slight acclivity with milling time indicates the dissolution of Co.

The $H_c$ continues to increase because of the growth of defects and internal strain caused by the circulation of crushing and cold welding. The enlargement in $H_c$ is more obvious because the initial powders are pure metal powders rather than alloy powders. The declension in $H_c$ results from a reduction in grain size after the elements have been dissolved adequately with 70 h milling. For a nanocrystalline material, magnetic anisotropy constant ($K_{eff}$) and $H_c$ is proportional to $D^6$:

$$K_{eff} = \frac{K_1^3}{A^3} D^6$$

$$H_c = \frac{p_e K_{eff}}{\mu_0 M_s}$$

Here, $K_1$, $A$, and $p_e$ are the magnetocrystalline anisotropy constant, exchange coupling constant, and a constant associated with coercive force, respectively.

As shown in the inset of Fig. 8(b), the $M_s$ decreases from 92.1 emu/g to 85.8 emu/g, and $H_c$ presents a downtrend from 173.1 Oe to 111.1 Oe. The decrease in $M_s$ is explained by the following three reasons. First, the amount of the amorphous structure rises with increased milling time. Second, EDS shows that the degree of oxidation increases, which decreases the $M_s$ (Table S1). Third, the relative content of BCC phase...
diminishes, and the $M_0$ of the BCC phase is larger than the FCC phase. The reduction in $H_s$ is attributed to the decreased magnetocrystalline and stress anisotropy caused by the reduced grain size and formation of an amorphous structure. The magnetization and demagnetization are accomplished via rotation of the magnetization vector. The resistance of rotation comes from various forms of anisotropy energy (magnetocrystalline, shape, and stress anisotropy). The formulae are expressed separately:

$$H_{c2}^f = \frac{P_s (1 - V_{am})^2 K_{am} \rho_{10}}{\mu_0 M_s A^2}$$

(3)

$$H_{c2}^b = 0.497 (N_2 - N_1) M_s$$

(4)

$$H_{c2}^d = \frac{3 \lambda_s \sigma}{\mu_0 M_s}$$

(5)

$$\lambda_s = V_{am} \chi_{am} + (1 - V_{am}) \chi_{cr}$$

(6)

Here, $V_{am}$, $\lambda_{am}$, and $\chi_{cr}$ are the volume of the amorphous phase, the effective magnetostriiction coefficient, and the magnetostriiction coefficient of amorphous and crystal phases ($\lambda_{am} > 0$ and $\chi_{cr} < 0$), respectively. The decrement of $D$ and the increment of $V_{am}$ can result in the reduction of $H_s$. One outlier at $C_70$ (164.3 Oe) might be due to the increase in magnetocrystalline and stress anisotropy corresponding to the larger relative BCC phase content (Fig. 1(b)).

### 3.4. EM parameter analysis

The relative complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and the relative complex permeability ($\mu_r = \mu' - j\mu''$) are generally used to evaluate the EM wave absorbing properties of a material. Of these, the real parts ($\varepsilon'$ and $\mu'$) and the imaginary parts ($\varepsilon''$ and $\mu''$) are related to the storage and loss (or dissipation) of electrical and magnetic energy, respectively. When the EM wave enters the particles, the energy is consumed by conduction loss, dielectric loss, and magnetic loss.

Fig. 8 shows the $\varepsilon'$ (a, e) and the $\varepsilon''$ (b, f) of the M-HEA (a, b) and C-HEA (e, f) powders in a time-dependent experiment in the frequency range of 2–16 GHz. The $\varepsilon'$ for both alloy powders change only slightly across the entire frequency range. For $\varepsilon''$, the samples of $M_{30}, M_{50},$ and $M_{70}$ gradually rise and the others decline with increasing frequency. During the alloying process, the milling time has a pronounced effect on the $\varepsilon'$ and $\varepsilon''$ for M-HEA powders. The $\varepsilon'$ of the alloy powders increases from $M_0$ ($\approx 10$) to $M_{10}$ ($\approx 16$). It then decreases to $M_{50}$ ($\approx 7.5$) and increases to $M_{70}$ ($\approx 8.2$). The $M_0$ sample does not have an obvious polarization effect, and the larger conductivity ($\sigma$) induces a larger $\varepsilon'$.

This can be explained via Debye relaxation [39]:

$$\varepsilon' = \sigma/\omega\varepsilon_0 + \varepsilon_m$$

(7)

$$\varepsilon'' = \sigma/\omega\varepsilon_0, \omega = 2\pi f$$

(8)

Here, the $\varepsilon'$ and $\varepsilon''$ have a positive correlation with $\sigma$. For $\varepsilon''$, there is less polarization loss due to fewer polarization sites. This results in a smaller value that is close to zero in the low frequency range. The larger conductivity causes a larger value in the high frequency range [40]. At the early stage of milling, the $M_{10}$ sample has a larger value of $\varepsilon'$ and $\varepsilon''$, which can be explained by the following three reasons.

First, the surface polarization and relaxation loss increase because flaky particles are generated. In addition, the polarization sites present an uptrend with the enhancement of defects, and as the mutual solubility of elements induces more defects. Moreover, sample $M_{10}$ has a larger conductivity than other alloy powders ($M_{30-70}$), which leads to the increment of $\varepsilon'$ and $\varepsilon''$ (Eqs. (7) and (8)). During the milling period of 10 h to 50 h, the $\varepsilon''$ gradually reduces as the particle size declines (transformation from flake to sphere (in Figs. 3(c–e) and 4(a))). When the milling time is over 70 h, there are more defects with more uniformity, which augments point polarization and enhances $\varepsilon'$ and $\varepsilon''$. Interestingly, the change of $\varepsilon''$ ($M_0$-$M_{70}$) in the high frequency regime agrees with the variation in electrical conductivity (Fig. S7). We reached a similar conclusion in our previous studies: The conduction loss and polarization loss play a major role in the high frequency and low frequency areas, respectively.

The $\varepsilon'$ and $\varepsilon''$ of C-HEA powders are larger than the M-HEA powders. For example, the $C_{50-70}$ sample has a value that ranges from 20 to 26; the value for $C_{90}$ reaches 11. For $\varepsilon''$, the values of $C_{50-70}$ vary from 1 to 8, and those of $C_{50-90}$ are <1. The most fundamental reasons are the C-HEA powders possess larger aspect ratio, less defects, and better uniformity. First, the larger aspect ratio results in the growth of surface polarization and a dielectric loss. Second, the conductivity of C-HEA powders should be larger because it has fewer defects according to the formula of metallic resistivity:

$$\rho = \frac{m}{ne^2} \left( \frac{1}{\tau_T} + \frac{1}{\tau_R} \right)$$

(9)

Here, $\tau_T$ and $\tau_R$ are the scattering relaxation times caused by the lattice thermal vibration and the lattice defects, respectively. The increase in $\tau_R$ is caused by a decrease in defects that in turn decreases resistivity and increases conductivity. However, the measured conductivity of C-HEA powders are smaller than that of the M-HEA powders (Fig. S7). This is because the density of the pressed cylindrical tablets for C-HEA powders is smaller than those for M-HEA powders, i.e., the particle sizes of C-HEA powders are larger. Finally, the polarization sites (dipoles) grow with increased homogeneity. Similar to the change of $\varepsilon'$ in
the milling process of alloying, the $\varepsilon'$ of C-HEA powders present an up-trend first with increasing milling time with a maximum value at C60 ($\approx 26$) followed by a decrease. During this process, the surface polarization controls $\varepsilon'$ and $\varepsilon''$ due to the change in aspect ratio. Similarly, the change of $\varepsilon''$ in the low frequency is the same as $\varepsilon'$ and that in the high frequency is the same as the conductivity. When the milling extends to 80 h and 90 h, the increase in amorphous content and defects decrease the conductivity. This results in a $\varepsilon''$ that is smaller than M70.

Fig. 9 shows the $\mu'$ (c, g) and the $\mu''$ (d, h) of the M-HEA (c, d) and C-HEA (g, h) powders at time-dependent experiments from 2 to 16 GHz.
The $\mu'$ at 2 GHz increases from 1.26 ($M_0$) to 1.70 ($M_{10}$) and then decreases to 1.54 ($M_{30}$). It gradually increases to 1.59 ($M_{70}$). The $\mu'$ of the milled alloy powders is larger than the initial powders, or more sensitive to the milling time increase, the $C_{90}$ and $C_{70}$ samples possess higher shape anisotropy and lower $K_1$ and $\lambda_0$ corresponding to higher $A_{BCC}$/A_{HCP}, respectively. The decrease in $\mu'$ results from the decrease of aspect ratio, $M_0$, and $A_{BCC}$/A_{HCP} corresponding to lower $K_1$ and $\lambda_0$. The $\mu'$ has a change that is similar to $\mu''$.

4. Conclusion

FeCoNiSi$_{0.4}$Al$_{0.4}$ HEA powders have been prepared by two kinds of methods: mechanical ball milling method and melting-strip casting-milling method. The relation between milling time, crystal structure, particle size, uniformity and magnetic and EM properties have been researched. Different solutions and phase formation rules are seen in these two technologies. We concluded that the C-HEA powders have better elemental dispersion, fewer defects, and a larger aspect ratio than M-HEA powders. The C-HEA powders possess smaller $M_s$ and larger $H_c$. Versus the M-HEA powders, the C-HEA powders possess smaller magnetocrystalline stress anisotropy as well as larger shape anisotropy. The $\epsilon'$ and $\mu'$ for M-HEA powders have roughly the same change rule with prolonged milling time. They reach 8.2 and 1.59 at 2 GHz, respectively. The $\epsilon'$ and $\mu''$ for C-HEA powders increase first, and then decrease. They reach a maximum at $C_{90}$ (26 for $\epsilon'$, 1.90 at 2 GHz for $\mu''$). The EM parameters of the C-HEA powders are obviously larger than those of the M-HEA powders, and the conduction loss plays a major role in the high frequency range.

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Appendix A. Supplementary data

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