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Note: This paper was presented at the 64th Annual Conference on Magnetism and Magnetic Materials.

ABSTRACT
FeCoNi(Si\textsubscript{0.6}Al\textsubscript{0.2}B\textsubscript{0.2}) high entropy alloy powders with flaky shapes of 14.7–17.6 μm in mean particle size and 8.2–14.9 in aspect ratio have been prepared by melt-spun and subsequent ball-milling for 10–50 h. The powders possess a mixing structure of BCC nanocrystalline and amorphous phases with average grain sizes of 6–20 nm. The powders exhibit soft magnetic characteristic with saturation magnetization of 78.6–88.1 emu/g. The powders/paraffin (mass ratio = 3:2) composites have high permeability, matchable permittivity, and excellent electromagnetic wave absorption properties in X- and Ku-bands. The composites with thicknesses of 1.2−2.0 mm possess minimum reflection losses (RL) of -38.1 to -44.1 dB with effective absorption bandwidths (RL<10 dB) of 2.5−3.8 GHz.

I. INTRODUCTION
With the rise of the new generation of wireless communication technology, plenty of electronic devices have been applied in GHz frequency range, and the ensuing electromagnetic (EM) interference and pollution also keep increasing. Soft magnetic ferrites have been widely used as EM wave absorbents due to their high permeability ($\mu$), high resistivity and low cost, while the improvement of the EM wave absorption ability in GHz frequency is still a challenge due to their low saturation magnetization ($M_s$). Flaky FeSiAl\textsuperscript{1} and FeSiCrAl\textsuperscript{7} powders with enhanced $M_s$ and $\mu$ exhibit good EM wave absorption ability in 2−16 GHz. Soft magnetic Fe-based nanocrystalline alloys show excellent high-frequency EM wave absorption performance by virtue of their higher $\mu_s$ in high frequency along with low permittivity ($\varepsilon$) arising from the low conductivity of amorphous phase.\textsuperscript{8,9} High-entropy alloys (HEAs) containing at least five principal elements with respective concentration ranging 5−35 at.% have received much attention due to the unique corrosion and oxidation resistance, and mechanical and EM properties.\textsuperscript{10−13} FeCoNiSiAl\textsubscript{12} and FeCoNiCrAl\textsubscript{13} HEA powders have been found exhibiting effective microwave absorption in GHz range. Similar to FeSiAl, the metallic HEA powders usually have relatively high $\varepsilon$ mismatching to the $\mu$, which limits the absorption ability. Increase in the volume fraction of the amorphous phase might be a useful way to reduce the $\varepsilon$ and improve the EM wave absorption performance. In this work, with aim of improving the amorphous-forming ability (AFA) of the FeSiAl alloy and enhance the EM wave absorption ability, a B-bearing FeCoNi(Si\textsubscript{0.6}Al\textsubscript{0.2}B\textsubscript{0.2})\textsubscript{25} HEA has been designed. The HEA powders have been fabricated by melt-spin and subsequent ball-milling methods. The morphology, microstructure, EM parameters and EM wave absorption properties of the powders with different milling time ($t_m$) have been investigated.

II. EXPERIMENTAL PROCEDURES
Fe\textsubscript{25}Co\textsubscript{25}Ni\textsubscript{15}(Si\textsubscript{0.6}Al\textsubscript{0.2}B\textsubscript{0.2})\textsubscript{25} HEA ingots were prepared by arc melting Fe, Co, Ni, Si, Al, and B with a purity of ≥ 99.9 mass%
under Ti-gettered argon atmosphere. Ribbon samples with a width of 2 mm in thickness of 20 μm were prepared by melt-spinning under argon atmosphere. The ribbons were crushed and sieved to obtain powders with particle sizes of < 10 μm, and subsequently wet-milled by a planetary ball mill at a rotation speed of 350 rpm using anhydrous ethanol as process-control agent (PCA). Stainless steel pots with a capacity of 250 mL and balls with diameters of 10 and 6 mm were used, and mass ratio of the balls to powders was 20:1. The $t_m$ was 10, 30, and 50 h, respectively. The morphology and microstructure were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) (Cu Kα), and transmission electron microscopy (TEM), respectively. The $M_s$ and coercivity ($H_c$) were measured by a vibrating sample magnetometer with maximum applied field of 15 kOe at room temperature. The complex permeability ($\varepsilon'' - j\varepsilon'$) and permeability ($\mu'' - j\mu'$) in 2–16 GHz of powders/paraffin (mass ratio = 3:2) composites were measured by a vector network analyzer using coaxial reflection/transmission method. The composite samples were concentric cylinders with a thickness of 2.0 mm, inner and outer diameters of 3.0 and 7.0 mm, respectively.

III. RESULTS AND DISCUSSION

Figs. 1(a–c) shows the morphology and particle size (diameter) distributions of the milled FeCoNi(Si$_0.6$Al$_{0.4}$B$_{0.2}$) HEA powders. The powders all present a flaky characteristic due to the flattening effect of the PCA, and the particle size distributes in ranges of 1–35, 3–30, and 2.5–32 μm after milling for 10, 30, and 50 h, respectively. The mean particle size decreases from 17.6 to 14.7 μm, and the aspect ratio (diameter/thickness) increases from 8.2 to 14.9 with increasing the $t_m$ from 10 to 50 h (Fig. 1d). Fragmentation and cold welding co-exist in the process of ball milling, and the competition between the two effects determines the particle size.14–16 During the 10–50 h milling, the particle size and thickness of the powders are reduced continuously, whereas the aspect ratio keeps increasing. The reduced size is attributed to that the fragmentation is dominant comparing with the cold welding. The increased aspect ratio might be due to the flattening effect induced by the PCA plays a major role during the milling process.14

According to the XRD patterns shown in Fig. 2a, the melt-spun ribbon is mainly composed of BCC and amorphous phases, and the average grain size ($D$) calculated by Scherrer’s equation is around 30 nm. As the $t_m$ increases, the (200)$_{\text{BCC}$ peak becomes lower and broader, indicating the decreased $D$ and volume fraction of the BCC phase. The high-resolution TEM images and corresponding selected area electron diffraction (SAED) patterns further confirm the mixing structure of the BCC nanocrystalline and amorphous phases. The volume fraction of the BCC phase gets reduced and the $D$ is decreased from 20 to 6 nm with increasing the $t_m$ from 10 to 50 h (Figs. 2b, c). During milling, new dislocations and other defects are formed by impingement of the milling balls and rapidly increased due to plastic deformation. The dislocations pile up at the grain boundaries, leading to the formation of sub-grain structures, and hence the $D$ is decreased. As the milling progresses, the defects containing stored energy get increased, which enhances the free energy of the crystals. When the free energy of the crystals is greater than that in the amorphous state, spontaneous amorphization occurs. Accordingly, some of BCC phase transforms into the amorphous phase.

The hysteresis loops of the milled HEA powders suggest a typical soft magnetic characteristic. The $M_t$ exhibits a downtrend with the increase of $t_m$, i.e., 88.1, 83.6, and 78.6 emu/g for the powders with $t_m$ = 10, 30, and 50 h, respectively. The $H_c$ also get reduced from 79.5 to 63.3 Oe with extending the $t_m$ from 10 to 50 h. As the $t_m$ increases, the volume fraction of the amorphous phase is enhanced. The $M_t$ of the BCC phase is larger than that of the amorphous...
FIG. 2. XRD patterns of FeCoNi(Si$_{0.6}$Al$_{0.2}$B$_{0.2}$) HEA powders after milling for different time (a) and high-resolution TEM images inset with corresponding SAED patterns of the powders after milling for 10 (b) and 50 h (c), respectively.

phase, hence the powders milled for a longer time possess a reduced $M_s$. The nanocrystalline alloys with smaller grain sizes usually exhibit lower $H_C$. Since the $D$ decreases gradually with increasing $t_m$, the $H_C$ gets reduced as well. The enhanced volume fraction of the amorphous phase can also contribute to the lowered $H_C$ because the magnetocrystalline anisotropy of the amorphous phase is smaller.

As shown in Figs. 3(a, b), the $\varepsilon'$ and $\varepsilon''$ of the powders/paraffin composites change slightly in 2–16 GHz in addition to small fluctuant peaks of the $\varepsilon''$, while they show uprends with increasing the $t_m$. The $\varepsilon'_{\text{max}}$ and $\varepsilon''_{\text{max}}$ rise from 11.9 and 0.22 to 23.2 and 2.33, respectively. There are essentially four basic polarization mechanisms contributing to the $\varepsilon$: space charge (interfacial), dipolar, atomic, and electronic polarizations. In the microwave frequency range, the $\varepsilon$ might be mainly associated with the interfacial polarization due to small contributions of the atomic and electronic polarizations and free of permanent dipoles in the present alloy powders/paraffin composites. The particle size decreases gradually with milling progressing, and the continuous increase in specific surface area causes an enhancement of interfacial polarization at the particles/paraffin interfaces, resulting in enhanced $\varepsilon'$. The decreased particle size shortens the distance between the particles, which facilitates to establish conductive paths, leading to increased overall conductivity. The larger conductivity induces a higher $\varepsilon''$. The higher aspect ratio of the flaky particles also enhances the surface polarization and dielectric loss, which contributes to higher $\varepsilon'$. The $\mu'$ exhibit a downtrend with the increase of frequency (Fig. 3c), which is caused by eddy current loss and ferromagnetic resonance. The $\mu''$ increases in 2.0–3.7 GHz, and then decreases at higher frequencies (Fig. 3d). The $\mu$ does not change significantly with the $t_m$, i.e., $\mu'_{\text{max}}$ is 1.73–1.84 at 2 GHz and $\mu''_{\text{max}}$ is 0.69–0.82 at resonance frequencies of around 3.7 GHz. In the 2–16 GHz range, the
natural resonance and eddy current effect are critical factors affecting the $\mu$. It is presumed that the wide resonant peaks of $\mu''$ originate from the distributions of the particle sizes and grain sizes and the random orientation of particles in composites, which result in the distribution of magnetic anisotropy fields, leading to the distribution of natural resonances. As listed in Table I, although the $\mu''_{\max}$ of the present HEAs is lower than that of the Fe$_{12.3}$Si$_{12.3}$Al$_{10.1}$ due to the decreased Fe content, the $\mu''_{\max}$ is comparable and even higher. In comparison with the FeCoNi$_{0.6}$Al$_{0.4}$, the present HEAs have much lower $\varepsilon'_{\max}$ and $\varepsilon''_{\max}$ values, which might be due to that the addition of B improves the AFA of the HEA, and the high volume fraction of amorphous phase contributes to decreased conductivity, and accordingly lowered permittivity.

Reflection loss (RL) can be calculated from the following equations to characterize the EM wave absorption properties:

$$Z_{in} = Z_0 \sqrt{(\mu/\varepsilon) \tanh[(2\pi f d/c)\sqrt{\mu\varepsilon}]}$$  \hspace{1cm} (1)

$$RL = 20 \log (Z_{in} - Z_0) / |Z_{in} + Z_0|$$  \hspace{1cm} (2)

where $Z_{in}$ is input impedance at the absorber/free space interface, $Z_0$ is impedance of free space, $f$ is frequency, $d$ is sample thickness, and $c$ is light speed. The contour maps of RL depending on thickness and frequency of the composites are shown in Figs. 4(a–c). The effective absorption bandwidth ($\Delta f_{RL<10\ dB}$) is defined as the frequency range with RL < -10 dB, indicating that 90% of the EM wave is absorbed. It is seen that all samples possess wide $\Delta f_{RL<10\ dB}$ in X- and Ku-bands by varying the sample thickness, and obtain large RL valley ($RL_{\min}$) values in their respective impedance matching condition with specific matching thickness $(d_m)$ and frequency $(f_m)$, which indicates their excellent EM wave absorption properties. The $d_m$, $f_m$, $RL_{\min}$, and $\Delta f_{RL<10\ dB}$ can be adjusted by $t_m$. Fig. 4d shows the frequency dependence of the RL in the impedance matching condition. The $t_m = 10$ h sample with the $d_m$ of 2.0 mm gets the $RL_{\min}$ of -44.1 dB at 11.5 GHz, and the $\Delta f_{RL<10\ dB}$ is 3.8 GHz in X-band. For the samples with $t_m = 30$ and 50 h, the $d_m$ decreases to 1.2–1.3 mm, the $RL_{\min}$ is -38.1 to -39.3 dB at 14.8 and 14.9 GHz, and the $\Delta f_{RL<10\ dB}$ is 2.5–3.1 GHz in Ku-band. The $RL_{\min}$, $f_m$, $\Delta f_{RL<10\ dB}$ with corresponding frequency range, and $d_m$ are summarized in Table I. Compared with the Fe$_{7.7}$Si$_{12.3}$Al$_{10.1}$, the present HEA powders ($t_m = 30–50$ h) possess larger $RL_{\min}$ but smaller $d_m$.

IV. CONCLUSION

Flaky FeCoNi$_{0.6}$Al$_{0.4}$B$_{0.2}$ HEA powders with a BCC nanocrystalline/amorphous mixing structure have been fabricated by melt-spin and subsequent ball-milling methods. As the $t_m$ increases from 10 to 30 h, the $D$ of the BCC phase decreases from

| Absorbent | $\mu'_{\max}$ | $\mu''_{\max}$ | $\varepsilon'_{\max}$ | $\varepsilon''_{\max}$ | $RL_{\min}$ (dB) | $f_m$ (GHz) | $\Delta f_{RL<10\ dB}$ (GHz) | $d_m$ (mm) |
|-----------|---------------|----------------|---------------------|--------------------|----------------|-----------|----------------------|-----------|
| FeCoNi(Si$_{0.6}$Al$_{0.2}$B$_{0.2}$) ($t_m = 10$ h) | 1.78 | 0.69 | 11.9 | 0.22 | -44.1 | 11.5 | 3.8 (9.2–13.0) | 2.0 |
| FeCoNi(Si$_{0.6}$Al$_{0.2}$B$_{0.2}$) ($t_m = 30$ h) | 1.73 | 0.73 | 19.2 | 1.21 | -38.1 | 14.8 | 3.1 (13.2–16.3) | 1.3 |
| FeCoNi(Si$_{0.6}$Al$_{0.2}$B$_{0.2}$) ($t_m = 50$ h) | 1.84 | 0.82 | 23.2 | 2.33 | -39.3 | 14.9 | 2.5 (13.5–16.0) | 1.2 |
| Fe$_{0.2}$Co$_{0.2}$Ni$_{0.2}$Al$_{0.4}$B$_{0.2}$ | 2.20 | 0.76 | - | - | -22.2 | 12.6 | 6.0 (9.5–15.5) | 2.0 |
| FeCoNi$_{0.6}$Al$_{0.4}$B$_{0.2}$ | 1.90 | 0.52 | 26 | 8 | - | - | - | - |
20 to 6 nm, the mean particle size lowers from 17.6 to 14.7 μm, and the aspect ratio increases from 8.2 to 14.9. The soft magnetic HEA powders possess high \( M_s \) of 78.6–88.1 emu/g. The powders/paraffin composites have \( \mu'_{\text{max}} \), \( \mu''_{\text{max}} \), \( \varepsilon'_{\text{max}} \), and \( \varepsilon''_{\text{max}} \) values of 1.73–1.84, 0.69–0.82, 11.9–23.2, and 0.22–2.33, respectively. The composites with \( d_m \) of 1.2–2.0 mm possess large RL_{min} of -38.1–44.1 dB with \( \Delta f_{\text{RL}} \geq 10 \) dB of 2.5–3.8 GHz in X- and Ku-bands.

ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (Grant Nos.: 51771039, 51571047).

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