Influence of Bridgman Solidification on Microstructures and Magnetic Behaviors of a Non-equiatomic FeCoNiAlSi High-entropy Alloy

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Abstract: The non-equiatomic FeCoNiAlSi alloy is prepared by the Bridgman solidification (BS) technique at different withdrawal velocities ($V = 30, 100$, and $200 \mu\text{m/s}$). Various characterization techniques have been used to study the microstructure and crystal orientation. The morphological evolutions accompanying the crystal growth of the alloy prepared at different withdrawal velocities are nearly the same, from equiaxed grains to columnar crystals. The transition of coercivity is closely related to the local microstructure, while the saturation magnetization changes little at different sites. The coercivity can be significantly reduced from the equiaxed grain area to the columnar crystal area when the applied magnetic field direction is parallel

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to the crystal growth direction, no matter what is the withdrawal velocity. In addition, the alloy possesses magnetic anisotropy when the applied magnetic field is in different directions.

Keywords: A. High entropy alloy; B. magnetic property, anisotropy; C. crystal growth;

1. Introduction

The microstructure and texture related to the processing of a metal were key factors that influence the final properties. An ever-increasing interest has been attracted to improve mechanical/physical properties by obtaining the desired microstructure and texture of materials using directional solidification [1-3] . During the directional solidification, due to the solute redistribution and texture rearrangement, solidification defects, such as lateral boundaries, are eliminated, which facilitates the formation of the columnar-crystal or single-crystal structure with the preferred crystallographic orientation, leading to the improvement of the longitudinal mechanical properties and magnetic properties of alloys [4]. Since both the grain orientation and grain size have effects on the magnetic properties of the soft magnetic materials, in which the basic requirements are high permeability, low coercivity, and small core loss. If the easy axis of magnetization is the same as the grain orientation, an external magnetic field parallel to the easy axis can increase the permeability

1 drastically [5]. As to the grain size, if it is in the magnitude of micron, the large grain
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4 size is preferred due to the reduction of the coercivity [6, 7]. Thus, for preparing the
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7 soft magnetic materials, the factors affecting the grain orientation and grain size
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13 In the past decade, high-entropy alloys (HEAs), which are defined as multi-
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16 component alloys containing several components (≥ 5) in equal or near equal atomic
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19 proportions [8], have attracted much research interest [9-11] because of their unusual
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22 properties, such as high hardness [12-14], high fracture toughness [15], high-
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25 temperature resistance [16], excellent tensile ductility [17, 18], and super-plastic
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28 behavior [19]. Existing reports show that there is the potential for HEAs to be used in
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31 heat-resistant and wear-resistant coatings, diffusion barriers [20], mould linings, and
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34 areas that need excellent magnetic properties and high-temperature performance and
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37 so on. In our precious study [21], it is found that the as-cast FeCoNiAl_{0.2}Si_{0.2} alloy
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40 shows excellent soft magnetic properties and good plasticity, although its coercivity is
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43 somewhat higher. The subsequent heat treatment can largely reduce the coercivity by
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46 decreasing the internal stress. Besides this process, other methods, which favor to
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49 form the texture or increase the grain size, can also improve the magnetic property.
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52 One technique is the directional solidification. In this study, the properties of the
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55 FeCoNiAl_{0.2}Si_{0.2} alloy prepared by Bridgman-type-solidification (BS) are investigated.
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The relationship between the microstructures and magnetic properties is explored.

2. Materials and methods

In this paper, the alloy ingot of nominal compositions of $\text{FeCoNiAl}_{0.2}\text{Si}_{0.2}$ (0.2 is in a molar ratio) was synthesized by arc-melting pure elements with a purity higher than 99.95 weight percentage (wt. %) under a high-purity argon atmosphere on a water-cooled Cu hearth. The alloy was remelted at least four times to obtain the chemical homogeneity. Cylindrical rods with a diameter of 3 mm were prepared by suction casting. Then, the cylindrical rod was placed in an alumina tube with an internal diameter of 3 mm and inductively heated to the completely melting condition by adjusting the heating power, holding for 20 min. The BS was carried out with different withdrawal velocities (V) ($V = 30 \mu\text{m/s}$, $100 \mu\text{m/s}$, and $200 \mu\text{m/s}$, and the corresponding alloy samples are simply defined as A30, A100, and A200, respectively) through a temperature gradient (G) of about 45 K/mm into the water-cooled Ga-In-Sn liquid alloys. The BS equipment is the same as reference [22].

The cylindrical samples after BS were cut open along the longitudinal direction and, then, ground, polished, and etched. The microstructure evolution of the synthesized specimens was investigated by a metallographic microscope. Crystal structures were identified, using an X-ray diffractometer (XRD) under radiation conditions of 30 kV and 20 mA, with a Cu target and a scanning speed of $10^\circ/\text{min}$.

The orientations of the grains were determined by the electron back-scatter diffraction (EBSD), using a CAMBRIDGE S-360 scanning electron microscope (SEM). Before the EBSD characterization, the HEA bulk sample was cross-sectioned using the electric discharge machining, and finally polished using the 1.0 μm diamond paste. In order to study the magnetic property, cylinders of 3 mm in diameter and 1 mm in thickness were prepared from the directional solidified rods and tested by an LDJ 9600 vibrating sample magnetometer (VSM) at room temperature. Then (1) the saturation magnetization, M_s , which is the largest magnetic moment that the alloy can possess when the applied field is increasing, (2) the remanence, M_r , which remains when the applied field is restored to zero, and (3) the coercivity, H_c , which is the reverse field needed to reduce the magnetization to zero, are marked on the hysteresis loop.

3. Results and discussion

Figure 1 shows the XRD patterns of the samples prepared at different withdrawal velocities. It is clear that all directional solidified samples are with a single FCC structure which is not influenced by the withdrawal velocities. However, compared with the directionally solidified samples, the as-cast sample shows a minor peak besides the (111) face-centered-cubic (FCC) peak, which proved to be a body-centered-cubic (BCC) phase. It implies that the process of directional solidification

can suppress the formation of BCC precipitates.

The optical microstructure evolution of the FeCoNiAl_{0.2}Si_{0.2} alloy prepared by BS at the withdrawal velocity of 200 $\mu\text{m/s}$ is presented in Figure 2. It is clear that the microstructure is composed of three parts, which is defined as the initial region (the bottom area, which is the unstable area), the transition zone (the middle area), and the stable phase (the top area). The growth direction is shown in the lower right corner of Figure 2. The microstructure transforms from the polycrystalline morphology at the bottom to dendrite morphology at the top, although there are some defects. Unlike the dendrites at the middle place growing to different directions, only two different grain orientations can be found at the top place, which implies that directional solidification promotes preferred grain orientation. As known, the microstructure of directional solidification mainly depends on the temperature gradient, G , and the process parameters, such as the growth velocity, V , in addition to the original solidification characteristics of the materials [3]. Since in this experiment, the temperature gradient is relatively constant, the main factor that needs to be considered is the growth rate, which is determined by the withdrawal velocity. For different withdrawal velocities, the microstructure transformation process is similar, which transfers from the polycrystalline to dendrite morphology. But the grain sizes for different withdrawal velocities are different, although there is no obvious relationship between the grain

size and withdrawal speed.

The magnetic properties of the BS samples are plotted in Figure 3. Similar to the as-cast alloy, the BS samples are ferromagnetic. But in different regions, the performances exhibit some differences. Saturation is usually regarded as being independent, to a large extent, of the microstructure. Small variations can, however, be detected for the A30 and A100 alloys in different parts of the samples. But the deviation for the A200 alloy is more obvious, since the fast withdrawal speed can lead to the instability of crystal growth. Overall, the saturation magnetization values are at the same level for different withdrawal velocities, which are in the range of 80 emu/g to 120 emu/g. Since the structure-insensitive saturation magnetization is largely dependent on the composition of the alloy, it is not changed substantially by different manufacturing process.

However, the structure-sensitive properties, such as the coercivity, permeability and hysteresis loss, are closely affected by the magnetization processes of domain nucleation, domain-wall motion, and domain rotation. These processes, in turn, are governed by the intrinsic properties, such as the saturation magnetization and magnetic anisotropy as well as microstructural details, including dislocations, grain boundaries, and precipitates [23]. It is well known that the grain boundary obstructs

the movement of magnetic domain walls. Therefore, the specimens with the greater width of grains and lower densities of grain boundaries have the lower coercivity. The coercivity depends on the grain size, as shown below [6, 24]:

$$H_c \approx 3 \sqrt{\frac{\kappa_B T_c K_1}{\alpha M_s} \frac{1}{D}} \quad (1)$$

where H_c is the coercivity, D the grain size, M_s the magnetisation saturation, K_1 the magneto-crystalline anisotropy, κ_B the Boltzmann constant, T_c the Curie temperature, and α the lattice constant. From this equation, it is clear that the larger the grain size is, the smaller the coercivity becomes.

By observing Fig. 3(e), it is clear that, at a given withdrawal velocity, the coercivity value decreases significantly from the bottom to the top areas, since the grain size increases along the direction of the crystal growth which can be seen in Fig. 2. At the unstable bottom area, the grain boundaries of the polycrystalline structure contribute greatly to the domain-wall pinning. With the growth of a columnar crystal, there is a substantial reduction in the lateral boundary, which favors the motion of magnetic domains. Besides, the variation tendency of M_r is similar to that of H_c .

Figure 4 presents the magnetic hysteresis loops and the variation tendency of H_c of the sample prepared by the BS process at a withdrawal velocity of 100 $\mu\text{m/s}$, when

the applied magnetic field direction is parallel or perpendicular to the growth direction of the alloy. It is obvious that, when the applied magnetic field direction is perpendicular to the crystal growth of the alloy, the slope of the magnetic hysteresis loop before saturation is higher, which implies that the magnetization is much easier in this condition. Since in the single crystal, there is magnetic anisotropy, which means that the magnetization curve and the difficulty of saturation magnetization measured along the different crystal axis direction are different. If the direction of the applied magnetic field is close to or the same as the easier magnetization axis of the alloy, the magnetization process will be rapid. For the FCC-structured FeCoNiAl_{0.2}Si_{0.2} alloy, the easier magnetization axis is along the <111> direction, and the difficult magnetization axis is along the <100> direction. From Figure 5, the EBSD maps of the crystal orientation of this alloy prepared by the BS process at a withdrawal velocity of 100 $\mu\text{m/s}$, it is evident that at the bottom area, which is the equiaxed crystal zone, the grains are with different crystal orientations, and the grain boundaries all belong to high-angle grain boundaries. As the crystal grows, there are only two grains at the top area of the sample, and their crystal orientations are close to <100> and <101>, respectively, which deviate from the easier magnetization axis. It can be the good interpretation for why the slow magnetization can occur.

The variation tendency of H_c of the sample prepared by the BS process at the

withdrawal speed of 100 $\mu\text{m/s}$ is different, when the applied magnetic field direction is parallel or perpendicular to the growth direction of the alloy. Compared with the former condition (the applied magnetic field direction is parallel to the growth direction), when the applied magnetic field direction is perpendicular to the growth direction, the H_c value increases along the crystal growth which presents the opposite change tendency. Since both the grain orientation and grain size have effects on the magnetic properties of the soft magnetic materials. In the bottom area, the H_c values are nearly the same, since the grains in this area are in the different orientation, and the impeding effects of grain boundaries in all directions are almost equal. As the crystal grows, although the grain orientation has become increasingly deviating from the preferred direction, the horizontal grain boundary is eliminated, which present less resistance on the magnetic domain wall movement. So when the applied magnetic field direction is parallel to the growth direction, the H_c value decreases. In contrast, when the applied magnetic field direction is perpendicular to the growth direction, the influence of the longitudinal grain boundary on the magnetization process is more significantly than the crystal orientation, and the H_c value rises dramatically. However, the saturation magnetization of the specimens changes slightly with different applied magnetic field directions because it is insensitive to the texture and microstructure. It is indicated that controlling the texture and microstructure has little

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4 **4. Conclusions**

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8 In summary, the directional solidification technology can be applied to improve
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10 the soft magnetic properties of the FeCoNiAl_{0.2}Si_{0.2} alloy by controlling the grain
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12 morphology and crystallographic texture. The results suggested that a
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14 FeCoNiAl_{0.2}Si_{0.2} alloy with columnar grains can be produced by the directional
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16 solidification with the proper processing parameter, and its corecivity can be greatly
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18 reduced to 3.97 Oe (≈ 315 A/m) at the withdrawal velocity of 200 $\mu\text{m/s}$ when the
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20 applied magnetic field direction is parallel to the crystal growth direction, which is
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22 much smaller than the value obtained for the as-cast sample ($H_c \approx 1400\text{A/m}$),
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24 although the saturation magnetization changes slightly. However, when the applied
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26 magnetic field direction is different, the alloy possesses magnetic anisotropy. The
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28 crystallographic texture obtained by directional solidification at the withdrawal speed
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30 of 100 $\mu\text{m/s}$ deviates from the easier magnetic axis $\langle 111 \rangle$. Both the grain size and
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32 crystal orientation influence the corecivity value. An excellent comprehensive
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34 magnetic performance can be obtained when the withdrawal rate is very slow (30
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36 $\mu\text{m/s}$) or fast (200 $\mu\text{m/s}$).
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Figure 1

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Figures caption

Fig. 1 The XRD patterns of the samples prepared by arc melting and by BS with different withdrawal velocities

Fig. 2 The optical microstructure evolution of the sample prepared by BS process at the withdrawal velocity of 200 $\mu\text{m/s}$ and the schematic diagram of crystal growth

Fig. 3 Magnetic hysteresis loops and the variation tendency of M_s , H_c , and M_r of samples prepared by BS process at different withdrawal velocities.

Fig. 4 Magnetic hysteresis loops of (a) top area, (b) middle area, (c) bottom area, and the variation tendency of H_c of the sample prepared by BS process at the withdrawal velocity of 100 $\mu\text{m/s}$ when the applied magnetic field direction is parallel or perpendicular to the growth of the alloy.

Fig. 5 EBSD IPF maps of the crystal orientation of $\text{FeCoNiAl}_{0.2}\text{Si}_{0.2}$ HEA by BS at withdrawal velocity of 100 $\mu\text{m/s}$ (a) the bottom area (b) the top area; the grain orientation schematic diagram is shown on the right side.