Segmentation and Alignment of Nd₂Fe₁₄B Platelets in Nd-Cu Eutectic Alloys Using the Electromagnetic Vibration Technique

MINGJUN LI and TAKUYA TAMURA

An anisotropic Nd₂Fe₁₄B magnet has been of particular significance in engineering, which is usually produced *via* powder metallurgy. In this study, we report on the production of an anisotropic magnet by solidifying two alloys, *i.e.*, Nd₇₀Cu₃₀-30, 50 wt pct Nd₂Fe₁₄B from the semisolid state using the electromagnetic vibration (EMV) technique. The solidification structures are observed, and the crystalline orientations of the Nd₂Fe₁₄B intermetallic compounds are revealed by electron backscatter diffraction (EBSD) patterns. It is found that the two-step EMV processing is effective in segmenting the developed Nd₂Fe₁₄B compound into fine laths and then aligning these platelets with their easy magnetization directions parallel to that of the static magnetic field. The magnetic properties measured by a vibrating sample magnetometer (VSM) indicate that the specimen with the well-aligned Nd₂Fe₁₄B platelets exhibits a strong anisotropy in magnetism. The segmentation and alignment mechanisms are discussed when considering the EMV imposition parameters, the difference of electrical resistivity between the Nd₂Fe₁₄B compound and the eutectic melt, and the role of the static magnetic field in the present processing condition. The two-step EMV processing technique is promising and expected to provide a new alternative for the simple production of anisotropic Nd₂Fe₁₄B magnets *via* solidification only instead of conventional powder metallurgy.

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I. INTRODUCTION

IN comparison with an isotropic magnet, an anisotropic magnet has attracted increasing interest from scientific and technical viewpoints. This has been of particular importance since the invention of the Nd₂Fe₁₄B magnet^[1,2] that has been witnessed a wide application in hybrid electric vehicles and electric vehicles over the past decades. The pioneering work of fabricating a bulk anisotropic Nd₂Fe₁₄B magnet may be attributed to Lee,^[3] who used a die-upset technique to press the melt-spun ribbons, during which the Nd₂Fe₁₄B platelets were well aligned and thus an anisotropic magnet was produced. From then on, there have been a number of studies^[4–6] to improve the technique to align the Nd₂Fe₁₄B platelets and nowadays, the technique, frequently termed as powder metallurgy, has been predominant in fabricating the anisotropic Nd₂Fe₁₄B

magnet, which mainly involves the preparation of fine powder, the alignment and pressing the powder in a static magnetic field, the densification of the pre-aligned bulk by sintering, and final treatment and tailoring into a product.

Here arises a basic concern; why the Nd₂Fe₁₄B phase exhibits anisotropy in magnetism? The magnetic anisotropy mainly originates from the crystalline anisotropy because of the coupling of orbital motion of the electrons, *i.e.*, spinning of electrons, with crystal electric field in a lattice unit. As far as the crystal lattice of the Nd₂Fe₁₄B phase is concerned, it has a tetragonal structure (space group P4₂/mnm)^[7] in which four Nd₂Fe₁₄B formula are included with 68 atoms. Figure 1(a) depicts the schematic of an Nd₂Fe₁₄B unit cell. One can see that along the *c*-axis direction, each Nd₂Fe₁₄B unit cell consists of an eight-layer structure, indicating that the atomic stacking sequence along the *c*-axis is more complex than that along the *a*-axis in terms of the atomic sites, occupancies, and coordinates.^[8]

The Nd₂Fe₁₄B crystal is a well-ordered stoichiometric intermetallic compound, in which each atom has its well-determined position, as depicted in Figure 1(a). The growth of the Nd₂Fe₁₄B crystal requires each atom to sort its correct position and then incorporate into the

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Fig. 1—(a) The tetragonal unit cell of the Nd₂Fe₁₄B crystal. The actual a/c ratio is 1.385 ($a = 8.80$ Å and $c = 12.19$ Å)^[7] that is exaggerated to illustrate the stacking of the hexagonal iron nets. (b) The schematic drawing of an actual Nd₂Fe₁₄B crystal exhibiting a platelet morphology when considering the pronounced difference in growth kinetics along the a and c directions.

corresponding lattice site, which is a short-range diffusion-limited process at the solid/liquid interface.^[9]

By reviewing the linear kinetic coefficients of various compounds and oxides, Li and Kuribayashi^[10] summarized that the more complex an ordered crystalline phase is, the longer the time is required for an atom to diffuse to its “correct” position and thus the more sluggish the growth kinetics will be generated at the solid/liquid interface during solidification. For the present Nd₂Fe₁₄B compound, the crystal structure along the c -axis is more complex than that along the a -axis, which will generate more sluggish growth kinetics along the former than that along the latter. For an effective Nd₂Fe₁₄B crystal nucleus in an undercooled melt, the interface undercoolings of the a and c planes should be similar, resulting in a similar driving force for crystal growth. Because the growth kinetics along the c -axis is rather sluggish, its crystal-growth velocity is very slow in comparison with that along the a -axis. This growth behavior will enable the Nd₂Fe₁₄B crystal along the a -axis to overgrow along the c -axis, and thus produce a platelet morphology with a high aspect ratio, as depicted in Figure 1(b). The platelet morphology of the Nd₂Fe₁₄B crystals has been verified.^[3,4,11,12] Moreover, Nd₂Fe₁₄B-based crystals doped by Ga^[13,14] and Co^[15] and Dy^[16] exhibit the same platelet morphology as that of the Nd₂Fe₁₄B compound due to similar growth behavior. The platelet crystals can range in a nanometer scale in melt-spun ribbons^[3,4,11–16] and in a micrometer scale in strip-casting flakes^[17] according to solidification conditions.

Along the shorter direction is the c -axis, which is the [001] direction and also the easy magnetization axis, hence its perpendicular plane is the (001) plane, *i.e.*, the c plane, as schematically depicted in Figure 1(b). When

the c -axis of each platelet is well aligned to a certain direction, an anisotropic magnet can be fabricated,^[2,18] which is expected to produce a higher magnetic remanence.

In terms of electromagnetic vibration (EMV), the production principle lies in the simple fact that a conductor is driven to oscillate centering its initial equilibrium position according to Fleming’s left-hand rule when alternating current (AC) passes through the conductor perpendicularly to the direction of the magnetic field. The earliest work using the EMV technique in solidification may be attributed to Vives^[19,20] who achieved refined structures of aluminum alloys when EMV was properly imposed. From then on, great efforts have been devoted to improving the technique that has been employed to refine solidification structures of metals,^[21,22] alloys,^[23–28] and intermetallic compounds.^[29–31] Moreover, the incorporation of the EMV technique with the continuous casting of Al-7 wt pct Si^[32] and semi-continuous casting of Al-15 wt pct Sn alloys^[33] enabled the production of refined structures and improved properties. In addition to refining solidification structures, Tamura *et al.*^[34] found that the imposition of high-frequency EMV upon a bulk Mg₆₅Cu₂₅Y₁₀ alloy could improve the glass forming ability, which may be owing to the suppression of effective nucleation events at the frequency range. Very recently, the present authors^[35] briefly reported that EMV could refine and align the Nd₂Fe₁₄B compound in Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloys.

There have been some reports^[36–38] that the Nd-rich layer along the Nd₂Fe₁₄B grain boundary can enhance the coercivity of hot-deformed Nd-Fe-B magnets due to the pinning force against the domain wall motion. Moreover, the Nd-rich phase can react with Fe to form compounds and thus suppress the formation of the α -Fe phase that is detrimental to the hard magnet. Simply doping the pure Nd metal into the Nd₂Fe₁₄B phase may be an alternative provided that the Nd metal can be melted to homogenize its distribution along phase boundaries above the melting point, *i.e.*, 1021 °C, at which Nd₂Fe₁₄B crystals will coarsen about 50 pct in grain size and hence result in decreased coercivity.^[18] Similarly, Liu *et al.*^[39] found that in comparison with the finer crystals and higher coercivity achieved at 750 °C, sintering at 900 °C led to the formation of larger Nd₂Fe₁₄B crystal grains and thus resulted in a lower coercivity. Therefore, an alloy system containing Nd liquid with a low melting point is desired and the CuNd-Nd eutectic system, more specifically, the Nd₇₀Cu₃₀ alloy with CuNd and α -Nd as its terminal eutectic phases meets the criteria with the eutectic temperature of 520 °C,^[40] as shown in Figure 2. Actually, by soaking the hot-pressed Nd-Fe-B specimen in the Nd₇₀Cu₃₀ eutectic melt, Sepehri-Amin *et al.*^[13] found that the coercivity of hot-deformed anisotropic Nd-Fe-B magnets was increased after the grain boundary diffusion process was accomplished to form an Nd-rich intergranular phase.

In the present study, the Nd₇₀Cu₃₀ eutectic alloy was used with two weight fractions of 30 wt pct and 50 wt pct Nd₂Fe₁₄B, *i.e.*, Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B and

Fig. 2—A partial Cu-Nd binary phase diagram showing the Nd-rich region redrawn from Ref. [40] with permission from Elsevier. The arrow indicates the eutectic composition in the present alloys.

Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloys. The master alloy was cast in a metallic mold and then heated to the semisolid state, under which the EMV processing was imposed to segment and orient the Nd₂Fe₁₄B compound. It was found that under a suitable processing condition, the Nd₂Fe₁₄B compound could be finely segmented into short laths and their *c*-axes were well aligned, which could be verified by electron backscatter diffraction (EBSD) patterns. The specimen with well-aligned Nd₂Fe₁₄B platelets exhibited a strong anisotropy in magnetism, as revealed by magnetic hysteresis loops. The segmentation and alignment mechanisms were discussed, and the future direction was outlined. The present study may open a new avenue for the production of anisotropic Nd₂Fe₁₄B magnets *via* solidification only instead of conventional powder metallurgy.

II. EXPERIMENTAL PROCEDURE

A. Preparation of the Master Alloy Ingot

Bulk metals of Fe, Cu (purity better than 99.99 pct), Nd (purity 99.9 pct), and B (purity 99.5 pct) were first cleaned to remove the oxide surface layer and then charged into a ceramic crucible that had been amounted into a high-frequency induction furnace. The chamber of the furnace was evacuated, purged, and backfilled with inert He gas with a purity greater than 99.9999 pct. A metallic mold that had been coated by spraying boron nitride (BN) was set beside the ceramic crucible. After the metals were melted, homogenized, and then the alloy melt was poured into the metallic mold with a round cavity of 3 mm in radius, *r*, and thus a cylindrical ingot was produced. Note that the entire processing at high temperature was completed in a high-purity condition,

under which contamination could be minimized. An infrared thermometer was used to monitor the alloy temperature to guarantee the same preparation condition for different batches of ingots. To well control the melt temperature could also lower the evaporation of Nd and Cu and thus improve the uniformity of ingot composition, enabling different batches of ingots comparable when analyzing experimental results. Two alloys, *i.e.*, Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B and Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B, were prepared under the same casting condition. Here, it is worth noting that the weight fraction of the Nd₂Fe₁₄B phase could be controlled by adjusting the metal weight proportion, which should be ascribed to the fact that the Fe and B atoms can be only incorporated into the compound. For instance, when preparing an alloy of Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B ingot, the mass ratio of four element metals follows as Fe:Cu:Nd:B = 21.85:11.09:66.76:0.30, and for the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy, it is Fe:Cu:Nd:B = 36.34:7.90:55.25:0.50.

B. EMV Processing

After the ingot was prepared, it was cut into a rod of 20 mm in length and then encapsulated into an Al₂O₃ tube with the same inner diameter as the ingot. The ingot was fixed by two carbon blocks that were connected with Cu electrodes so that AC could flow. A blind hole was made in the wall of the Al₂O₃ tube, in which a K-type thermocouple was embedded to monitor the temperature of the specimen. A movable arc-shaped carbon heater covered the specimen and then the setting kit was placed into a bore with the static magnetic flux density of up to $B_0 = 10$ T. Figure 3(a) shows the schematic setting of the sample in the present experiment. Note that three parameters, *i.e.*, the magnetic flux density, B_0 , the effective AC, J , and the frequency of AC, f , are included in terms of EMV imposition. In the present study, we kept $B_0 = 10$ T and $J = 90$ A as constants for EMV processing and examined the influence of vibration frequency on segmentation and alignment of the Nd₂Fe₁₄B intermetallic compound.

The specimen was heated to 700 °C, which is 180 °C higher than the melting point of CuNd-Nd eutectic alloy, and approximately 480 °C lower than the peritectic decomposition temperature of the Nd₂Fe₁₄B compound, *i.e.*, 1180 °C. One can see that the Nd₂Fe₁₄B phase is stable solid whereas CuNd-Nd eutectic is liquid, indicating that the whole sample is in a semisolid state at the temperature. The sample was kept at 700 °C for 120 s to homogenize the temperature distribution. To reveal the influence of EMV on solidification structures, a sample was first solidified from the semi solid state in the static magnetic field of $B_0 = 10$ T only without the imposition of AC. To elucidate the role of vibration frequency in segmenting and orienting the Nd₂Fe₁₄B phase, two vibration patterns were imposed, which were termed as one-step EMV and two-step EMV. After homogenization at 700 °C, the AC power was switched on to vibrate the sample at a certain frequency, *e.g.*, $f = 250$ Hz or $f = 1000$ Hz, which was one-step EMV. For two-step EMV processing, the power was switched

Fig. 3—(a) the front view with the schematic setting of a specimen for processing in the magnet bore. (b) the notching position and the sectioning plane when slicing the solidified bulk for structure observation and properties measurement. The solid arrow shows the direction of AC passing in the specimen. (c) the sliced disc after it is turned over 90 deg. The solid and dashed arrows indicate the direction of the Lorentz force when EMV is imposed. The disc is also cut along the A-A and B-B planes to reveal the structure from the top and side views. The dashed arrows beside each drawing marked by B_0 show the direction of the static magnetic field.

on to vibrate at $f = 250$ Hz for 120 second and then the frequency was increased to $f = 1000$ Hz for another 120 seconds.

C. Microstructure Characterization

After the sample was solidified, a notch was made along the longitudinal direction of the rod in the place where the thermocouple was embedded in the blind hole in the Al_2O_3 tube, as schematically shown in Figure 3(b). This was important not only in revealing the orientation distribution of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets but also in characterizing the anisotropic magnetism of the sample.

The $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase embedded in the sample could be magnetized when cooled below the Curie temperature (314°C) in the static magnetic field, which made it hard to prepare a qualified sample for metallographic examination or for characterization in a scanning electron microscope (SEM). Hence, the sample was heated in a vacuumed image furnace to 350°C , *i.e.*, approximately 36°C higher than the Curie temperature of the phase, and then kept for 30 minutes, under which the sample could be demagnetized. After the thermal demagnetization, the sample was sliced with the sectioning plane parallel to the diameter direction of the rod, as shown in Figure 3(b). According to Fleming's left-hand rule, when AC passed through the sample along the arrow direction in Figure 3(b), the Lorentz force, F , was perpendicular to the plane of the paper. After the sliced disc was turned over 90 deg, F could be schematically depicted by arrows in Figure 3(c). In addition to the front view of the round disc, it was cut along the A-A and B-B planes to reveal the structures from the top view and side view, as shown in Figure 3(c).

The specimen was mounted, ground, polished, and observed under an optical microscope to reveal the macro distribution of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The SEM image was captured mainly under backscattered electron (BSE) mode that revealed composition contrast of the

constituent phases. Meanwhile, the energy-dispersive X-ray spectroscopy (EDS) was used to analyze the chemical composition of a macro area by mapping and the micro phase by spot analysis.

D. EBSD Orientation Mapping

To reveal the crystalline orientation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets, the sample was finely polished using silica colloidal suspension, by which mechanical polishing and chemical polishing could be simultaneously accomplished. This operation was essential to generate clear Kikuchi bands, from which a high image quality and a high confidence index could be obtained. It should be noted that in the present study, as the orientation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets played a vital role in determining magnetic properties, only the magnetic phase was indexed and highlighted when decoding Kikuchi bands. During data acquisition, one-step scanning could generate a group of Kikuchi bands and thus generated an indexing point, which would be represented by one pixel in the EBSD map in data analysis. Space lattices of typical crystals were generated to show the crystalline orientation. Meanwhile, the discrete [001] inverse pole figure (IPF) of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase was generated based on the EBSD map, from which the overall orientation of the phase within the area of interest could be inferred. The scale of the neighboring bars in the IPFs was 10 deg when referring to the degrees of planes, *e.g.*, 90 deg between (001) and (100).

E. Magnetic Properties Measurement

According to the microstructure and the notch position in the sample, the sliced disc was fixed delicately into a holder that was then set in the VSM. For each sample, two magnetic hysteresis loops were achieved when the magnetic field of the VSM was imposed parallelly and perpendicularly in terms of AC direction,

i.e., along the B_0 direction and the F direction, respectively, as depicted in Figure 3(c). To ensure the VSM data of different samples comparable, a high-purity Ni (greater than 99.99 pct) disc with almost the same specification, *e.g.*, the shape, the size, the mass, and the setting condition, was used as reference to calibrate the raw data under the same measurement condition. The alloy density, $\rho_{(d)}$, was required for calibration, which was measured using Archimedes' principle in ethanol and found to be 7.311 g cm^{-3} for $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ and 7.357 g cm^{-3} for $\text{Nd}_{70}\text{Cu}_{30}$ -50 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$.

III. RESULTS

A. Structure and Phases of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 Wt Pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ Alloy Without EMV

As stated previously, the structure of the sample solidified in the static magnetic field without EMV can provide a basis for comparison with those samples subjected to EMV. Figure 4(a) shows an optical view of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified at $B_0 = 10 \text{ T}$ when no AC was imposed, in which the fine thread-like white phase is the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound and the grey matrix is the CuNd -Nd eutectic. The compound phase seems to commence to grow from the outer periphery of the sample and then encounters near the

center region, exhibiting a radiated structure from inside to outside. This is similar to that observed in the as-cast ingot, indicating that the static magnetic field at $B_0 = 10 \text{ T}$ has no detectable influence on the macro view. The radiated structure should be attributed to the crystal growth mode in the metallic mold, in which solidification begins from the mold wall and then the solid/liquid interface proceeds to encounter near the center as crystallization heat can be directionally released mainly *via* the mold.

When the red rectangle region in Figure 4(a) is magnified by the SEM, the BSE image is shown in Figure 4(b), in which the black phase is the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound and the surrounding grey phase is the eutectic. One can see that the overall morphology of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is directional and feathery with an average length of more than several $100 \mu\text{m}$.

Except for the long thread-like structure, there are a few fine isolated $\text{Nd}_2\text{Fe}_{14}\text{B}$ fragments embedded in the eutectic matrix, as highlighted by the red ellipses in Figure 4(c). When the red rectangle region in Figure 4(c) is observed in the secondary electron image (SEI) mode, both the $\text{Nd}_2\text{Fe}_{14}\text{B}$ laths and the irregular "Chinese script" eutectic structure can be clearly identified, as shown in Figure 4(d), and the latter of which is helpless in elucidating the present concern. Therefore, the SEM image in the subsequent context refers to the BES image that is better than the SEI in revealing the phase morphology and neglecting unnecessary details as

Fig. 4—(a) the optical macro view of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified in the static magnetic field at $B_0 = 10 \text{ T}$ without EMV processing. (b) the enlarged area highlighted by a red rectangle in (a) in the BES mode. (c) enlarged region in the red rectangle in (b) in the BES mode with a few isolated debris marked by red ellipses. (d) the enlarged area in the red rectangle in (c) in the SEI mode. The EDS analysis reveals that the grey and black phases are eutectic and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phases, respectively (Color figure online).

we mainly focus on the influence of EMV on the morphology change of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound.

Mapping EDS analysis of a rectangle area ($2.5\text{ mm} \times 2\text{ mm}$) reveals that the composition within the macro-region of the sample falls approximately into the following range, *i.e.*, $\text{Fe}:\text{Cu}:\text{Nd} = 22 \pm 1:10 \pm 1:68 \pm 1.5$ (in mass ratio, hereinafter), which is in accordance with the theoretical value of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy with $\text{Fe}:\text{Cu}:\text{Nd} = 21.92:11.12:66.94$. It is noted that this ratio has a minute difference with that when preparing an ingot in that B element cannot be quantified by the present EDS analysis. Moreover, EDS analysis of other samples, either prepared by metallic mold casting or processed after EMV imposition, reveals the similar composition ratio as above. For the $\text{Nd}_{70}\text{Cu}_{30}$ -50 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy, the EDS result reads $\text{Fe}:\text{Cu}:\text{Nd} = 36 \pm 1:8 \pm 1:56 \pm 1.5$, which agrees with the theoretical value of $36.53:7.94:55.53$. The EDS analysis indicates that no pronounced loss or severe contamination occurs from preparing the master ingots to processing during the EMV imposition.

Spot EDS analysis of the black phase, *e.g.*, as the arrow indicates in Figure 4(d), reveals that the ratio of $\text{Fe}:\text{Nd} = 70 \pm 1:30 \pm 1$ is near to the theoretical value in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase being of 73.05:26.95 when considering the measurement error of the technique. A similar mass ratio has been confirmed in the black phase in the $\text{Nd}_{70}\text{Cu}_{30}$ -50 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy, indicating that the phase is $\text{Nd}_2\text{Fe}_{14}\text{B}$ in SEM, whereas it is white under the optical microscope due to light reflection. The mass ratio of Nd and Cu around the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound is consistent with the nominal composition of the CuNd -Nd eutectic alloy. We also measured the composition of grey block phase and the white phase, revealing that the $\text{Cu}:\text{Nd} = 44 \pm 1:55 \pm 1$ for the grey block and $\text{Cu}:\text{Nd} = 1 \pm 1:99 \pm 1$ for the white phase. Considering the measurement error of the technique, one can say that the grey phase with block morphology is CuNd compound and the white phase is Nd, consistent with the phase constituent in Figure 2.

B. Microstructures of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 Wt Pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ Alloy by One-Step EMV Processing

Our previous studies^[24,31,41,42] revealed that there exists an optimum vibration frequency range in refining solidification structures, usually from about 500 Hz^[31] to 1000 Hz.^[24] Considering the weight fraction of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound and our preliminary work, a low vibration frequency of $f = 250\text{ Hz}$ is applied for one-step EMV processing.

Figure 5(a) shows the optical view of the alloy when EMS was imposed at $f = 250\text{ Hz}$ for 120 s and then cooling water with a flow rate of 6 L min^{-1} was sprayed onto the Al_2O_3 tube from two sides to quench the sample. The peripheral and central areas highlighted by two red rectangles of (I) and (II) are magnified in SEM, as shown in Figures 5(b) and (c), respectively. One can find that in contrast to directional and long $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase observed in Figure 4(b), no directional characteristic can be discerned, and moreover the black magnetic laths become much shorter, indicating that

refinement occurs during EMV processing. In addition, the distribution of the compound laths exhibits somewhat a whirl-like pattern in both regions.

Figure 5(d) depicts the optical structure of the alloy solidified under the same EMV processing condition when cooled in flowing Ar gas. One can see that when the peripheral area of (I') in Figure 5(d) is magnified in Figure 5(e), the overall feature of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is similar to that in Figures 5(b) and (c), *i.e.*, refined short laths show no directionality, but exhibit a whirl-like pattern. However, when the central area (II') is observed under the SEM, the broken short laths exhibit a certain directional feature, *i.e.*, the laths are primarily oriented with their longitude directions perpendicular to the B_0 direction, like a swarm of ordered sardines with a good directionality. Hence, it is clear that one-step EMV processing at $f = 250\text{ Hz}$ can completely segment the thread-like long $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound into short laths and partially align those platelets in the central position with a good directionality.

In addition to the low frequency of 250 Hz, a high frequency of 1000 Hz has been imposed upon the alloy. Figure 6(a) shows the macro view of the alloy when EMS was imposed at $f = 1000\text{ Hz}$ for 600 s and then naturally cooled in flowing inert Ar gas. The structure can be classified into two categories of (I) and (II), as separated by the dashed curve. When the inner region (I) is magnified in Figure 6(b) in SEM, one can see that the microstructure is similar to Figure 4(b) with long and feathery compounds, indicating that no refinement occurs at this region. When the outer area (II) is magnified in Figure 6(c), one can find that the compounds are finely segmented and well aligned, similar to that in Figure 5(f) with their longitude direction perpendicular to the B_0 direction. When the area in the red rectangle in Figure 6(c) is further magnified in Figure 6(d), one can clearly see that the segmented laths are almost horizontal and usually less than $100\text{ }\mu\text{m}$ in length except a rather long one highlighted by a red ellipse. Both the unrefined structure in Figure 6(b) and the long magnetic lath in Figure 6(d) indicate that the segmentation at the vibration frequency of $f = 1000\text{ Hz}$ is not sufficient with a partial refinement and alignment. We actually imposed EMV at $f = 1000\text{ Hz}$ for 120 seconds and found that only about 10 pct peripheral area of the sample could be refined and highly oriented. When the imposition time, t , is extended to 600 seconds, the fraction of the refined and aligned area increased to about 50 pct, as shown in Figure 6(a). Further extending the imposition time may increase the fraction area of segmented and aligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase with a high directionality, while leaving some developed and thick laths, similar to that highlighted in Figure 6(d).

Here, it is clear that the one-step EMV processing of the alloy at a low frequency of $f = 250\text{ Hz}$ results in a complete segmentation within the entire sample and the partial alignment of the compound phase in the sample central area, whereas at a high frequency of $f = 1000\text{ Hz}$, a partial of compounds can be segmented and aligned even when the EMV imposition is substantially extended.

Fig. 5—Structures of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified in the one-step EMV processing at $f = 250$ Hz. (a) the optical macro-view when sample is quenched during EMV processing. (b, c) the enlarged SEM structures of the respective region highlighted by the red rectangles near the periphery with (I) and the center with (II) in (a). (d) the optical macro view when sample is naturally cooled during EMV processing. (e, f) the enlarged structures of the periphery (I') and center (II') in (d), respectively (Color figure online).

Fig. 6—(a) the optical view of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified by the one-step EMV processing at $f = 1000$ Hz. Two subregions can be separated by the dashed curve and marked by (I) and (II). (b) the SEM structure of the red rectangle in region (I). (c) the SEM structure of the red rectangle in region (II). (d) the enlarged structure of the area highlighted by the red rectangle in (c) (Color figure online).

C. Microstructures of the $\text{Nd}_{70}\text{Cu}_{30-30}$ and 50 Wt Pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ Alloys by Two-Step EMV Processing

Based on the results achieved by one-step EMV processing at two frequencies, one can infer that a two-step EMV processing may be effective and efficient in segmenting and aligning $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound, *i.e.*, to segment long compounds into short laths at a low frequency and then to align the short platelets with a high directionality at a high frequency.

Figure 7(a) shows the optical macro view of the $\text{Nd}_{70}\text{Cu}_{30-30}$ wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified under such a processing condition; EMV was imposed at $f = 250$ Hz for 120 seconds and then the frequency was increased to $f = 1000$ Hz for another 120 seconds, *i.e.*, two-step EMV processing. One can see that the macro structure is uniform without the directional feature. When the area highlighted by the red rectangle is magnified in Figure 7(b), the SEM microstructure exhibits the same feature as that in Figures 5(f) and 6(c), *i.e.*, the segmented compounds align well with their longitude direction perpendicular to B_0 . When the central region in the red rectangle is further magnified, one can find that most all laths are horizontal with a little deviation, and moreover, they are around $50\text{ }\mu\text{m}$ along their longitude direction, indicating that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound is finely segmented and highly oriented under the two-step EMV processing condition.

When the sample is cut along the A-A direction in Figure 7(a) and observed from the top position, as schematically depicted in Figure 3(c), the optical macro view is depicted in Figure 7(d), in which the white particles are randomly distributed. When the area

marked by the red rectangle is revealed in SEM, one can see that different from the slim and slight feature in Figure 7(b), the compound phase exhibits block-like morphology and distributes randomly without directionality. Further magnification of the red rectangular region in Figure 7(e) shows that most of the blocks are small, while a few are large with the contour lines longer than $100\text{ }\mu\text{m}$, as depicted in Figure 7(f). Considering the orthogonality characteristic of two cutting planes for structure observation, one can readily tell that the compound has a platelet morphology, which is consistent with our previous analysis and others' observations.^[3,4,11–17]

The two-step EMV processing is also used to solidify the $\text{Nd}_{70}\text{Cu}_{30-50}$ wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy with the same processing parameters. Figure 8(a) depicts the optical structure that is homogenous. When the peripheral and central areas, marked by two red rectangles, are observed in the SEM, one can find that the microstructures of both regions are homogenous with well-aligned short laths that are the same as those in the $\text{Nd}_{70}\text{Cu}_{30-30}$ wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy with their longitude directions perpendicular to B_0 , as shown in Figures 8(b) and (d). In comparison with Figure 7(b), the short laths are more densely populated due to an increased weight percentage of the compound. When two inner regions are further magnified in Figures 8(c) and (e), one can find that the black phase is segmented into short laths and aligned to exhibit a good directionality, indicating the technique works well in refining and orienting the intermetallic compound phase in both alloys when processed with suitable EMV parameters.

Fig. 7—Structures of the $\text{Nd}_{70}\text{Cu}_{30-30}$ wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified by the two-step EMV processing. (a) the optical macro view of the specimen. (b) the SEM structure of the red rectangle area in (a). (c) the further enlarged morphology in the red rectangle in (b). (d) the optical top view when the sample is cut along the A-A plane. (e) the SEM structure of the red rectangle area with individual blocks. (f) the further enlarged structure in the red rectangle in (e) (Color figure online).

Fig. 8—Structures of the $\text{Nd}_{70}\text{Cu}_{30}$ -50 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified by the two-step EMV processing. (a) the optical macro view of the specimen. (b, d) the SEM structures of the red rectangle areas in periphery and center in (a), respectively. (c, e) the further enlarged morphology in the red rectangles in (b) and (d), respectively (Color figure online).

D. Crystalline Orientation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ Phase in Alloys with EMV Processing

Microstructure observation indicates that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound can be segmented into short laths and then well aligned, whereas it cannot reveal the crystalline orientation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Hence, the EBSD mapping is used to clarify the orientation distribution of the phase subject to various EMV processing conditions.

Figure 9(a) is the ESM structure of the $\text{Nd}_{70}\text{Cu}_{30}$ -50 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified in the one-step EMV processing at $f = 250$ Hz, showing no preferred directionality of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ laths. Figure 9(b) depicts the EBSD pattern of the intermetallic compound in the red rectangle in Figure 9(a), revealing the crystalline orientation of the platelets. Note that each point is colored according to an automatically color-coded unit triangle of the inverse pole figure. For the present $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, the color red is assigned to the [001] crystal direction, green to [100] and blue to [110], as depicted by the color unit triangle at the bottom right corner of Figure 9(b), which applies to all EBSD maps hereafter. This also applies to discrete [001] inverse pole figure (IPF) when referring to the crystal direction. One can see that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is colorful, indicating that the crystalline orientations of the laths are random. To give more intuitive illustrations, six crystal lattices are depicted beside the EBSD map, showing the crystalline orientations of the typical crystals with different colors from pink to blue. It is easy to tell that the direction of the c plane of individual crystal is random without preference. When the highlighted phase

is projected to produce a discrete [001] IPF, as shown in Figure 9(c), one can see that the points shaded in the orientation map distribute randomly within the triangle, consistent with the colorful laths in Figure 9(b).

Figure 9(d) shows the unrefined SEM structure of the alloy solidified at $f = 1000$ Hz in one-step EMV processing. When the crystalline orientation of the compound in the rectangular region is revealed by the EBSD pattern as shown in Figure 9(e), one can find that except for several long laths colored in green, *i.e.*, the observed crystal planes are near to (100), other crystals are colorful, from orange to blue. Similarly, six typical crystal lattices are generated from the respective Kikuchi bands of crystals, as depicted beside the EBSD map, showing no preferred directionality. This characteristic can also be identified from the [001] IPF, as indicated in Figure 9(f), in which the points are projected randomly. A difference can be discerned in that the number of projected points in Figure 9(f) is less than that in Figure 9(c), which should be ascribed to the fact that the latter is the refined structure with more platelets whereas the former is the unrefined structure with less platelets that are long and developed even within almost the same area.

Figure 10(a) depicts the SEM structure of the alloy solidified by two-step EMV processing, in which the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is finely segmented and well aligned. When the crystalline orientation of the intermetallic compound in the red rectangular area is mapped in Figure 10(b), one can see that the color of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase ranges from green to deep blue, *i.e.*, the crystal planes of these platelets vary from (100) to (110) when referring to the unit triangle for color decoding. Similar

Fig. 9—(a, d) the SEM structures of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified when the one-step EMV processing is imposed at $f = 250$ Hz and $f = 1000$ Hz, respectively. (b, e) the EBSD patterns of the area marked by the red rectangle in (a) and (d), respectively, when the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is indexed only. Beside each map are the space lattices of six $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains showing their crystal orientation in space. (c, f) the [001] IPFs of the indexed $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. The automatically color-coded unit triangle is included for referring to the orientations of gains in the EBSD maps (Color figure online).

to that operated in Figures 9(b) and (e), six crystal lattices are presented beside the EBSD map, with the longitude direction of the tetragonal crystals being almost vertical. Referring to the crystal structure of the compound in Figure 1, one can see that the c -axes of these crystals are highly oriented to be parallel to the B_0 direction, as shown by the arrows beside Figure 10(a). As the direction of c -axis is also the normal direction of the c -plane, it is equally to say that the c planes of the well-aligned phases are perpendicular to the B_0 direction. The c -axes are highly aligned, which does not follow that the a -axes should be aligned as (100) and (010) are equivalent in crystallography. In addition to the (100) crystal plane colored in green, *e.g.*, marked by (i) in Figure 10(b), when the vertical tetragonal crystal lattice rotates approximately 45 deg in the horizontal direction along its c axis, the observed plane will be (110) with deep blue, as marked by (ii) in the right side. The other four crystal lattices represent different angles when the individual crystal rotates along its c -axis. Figure 10(c) shows the discrete [001] IPF generated from the EBSD pattern. In contrast with the random distribution of the points in Figures 9(c) and (f), the crystal planes are biasedly projected along the arc from the green (100) to the blue (110). It is noted that the (100) and (110) planes are perpendicular to the (001) plane, hence the angle difference between two

neighboring bars is 10 deg in the present figure. Theoretically, the crystals whose c -axes are exactly vertical will be projected onto the arc from (100) to (110). A point will be projected to leave the arc when the c -axis of the crystal deviates from the vertical direction. The larger the angle is formed between the c axis and vertical direction, the longer the distance will be covered from the dot to the arc. For easy identification, we arbitrarily insert a dashed red arc connecting two bars adjacent to (100) and (110), as illustrated in Figure 10(c). One can see that almost all data are projected into the partial sector region, within which the c -axes of these crystals deviate less than 10 deg from the vertical direction. This is consistent with the representative crystal lattices in Figure 10(b), in which one can find, for example, lattice (iii) leans toward the left side with certain degrees.

Figure 10(d) shows the top-view SEM structure observed along the B_0 direction, similar to that in Figures 7(e) and (f). When the crystalline orientation of the blocks in the rectangular region is indexed, as shown in Figure 10(e), only unique red color can be observed. Considering the color unit triangle, it is easy to tell that all the observation planes are the (001) c planes of the compound. Similarly, all six crystal lattices are depicted beside the EBSD map, in which their c planes with a regular square in the lattice drawing can be identified.

Fig. 10—The front-view (a) and top-view (d) SEM structures of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified when the two-step EMV processing is imposed. (b, e) the EBSD patterns of the area marked by the red rectangle in (a) and (d), respectively when the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is indexed only. Beside each map are the space lattices of six $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains showing their crystal orientation in space. (c, f) the [001] IPFs of the indexed $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. The automatically color-coded unit triangle is included for referring to the orientations of grains in the EBSD maps (Color figure online).

When the [001] IPF is generated, as illustrated in Figure 10(f), one can see that all points are projected to concentrate to (001), showing a highly intensified texture.

The EBSD analysis of the front view in Figure 10(b) shows that the crystal planes are near (100) to (110) and that of the top view in Figure 10(e) reveals that the observed planes are the c planes of the compound phase. When referring to the schematic platelet morphology of a macro crystal in Figure 1(b), one can readily infer that as the front view, *e.g.*, Figures 7(b) and (c), and the side view as depicted in Figure 3(c) from B-B direction, are equivalent, the microstructures from these two directions should be identical. The top views of a macro area, *e.g.*, in Figure 7(d), and a micro area, *e.g.*, in Figures 7(f) and 10(d), show no preference in orientation in terms of the (100) or (110) planes. We actually observed the microstructures from the B-B direction, showing the similar structure as in Figure 7(b). To avoid massive repetition, we omit to present the microstructures here.

Both the EBSD patterns and IPFs, together with representative space lattices, observed from the front and top directions demonstrate that these platelets are well aligned with their c axes parallel to the B_0 -direction, no matter they are formed in one-step or two-step EMV processing.

E. Magnetic Properties of Alloys with Various Distributions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ Phase

To provide a comparable criterion to show the influence of refinement and alignment of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase on magnetic properties, Figure 11(a) depicts the magnetic hysteresis loops of the $\text{Nd}_{70}\text{Cu}_{30}$ -30 wt pct $\text{Nd}_2\text{Fe}_{14}\text{B}$ alloy solidified in the static magnetic field, *i.e.*, $B_0 = 10$ T, without EMV processing. One can find that both the coercive force and the magnetic remanence, M_r , are less than 0.1 T in two directions, showing very poor magnetic properties and typical isotropy in magnetism. The properties can be readily understood when considering the radial macro structure with long and developed $\text{Nd}_2\text{Fe}_{14}\text{B}$ laths, as depicted in Figures 4(a) and (b). A minute difference arises in that the saturation magnetization, M_s , parallel to B_0 is slightly larger than that perpendicular to B_0 , which will be interpreted in the discussion section later.

Figure 11(b) shows the hysteresis loops of the alloy solidified by one-step EMV processing at $f = 250$ Hz with water quenching, in which the $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets are not aligned or oriented to a certain direction, *i.e.*, Figures 5(b) and (c). Although the magnetic compound is completely segmented into short laths, both loops in Figures 11(a) and (b) measured perpendicular to the B_0 direction seem almost identical with no remarkable

Fig. 11—The hysteresis loops of the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloy solidified (a) in the static magnetic field at $B_0 = 10$ T only without EMV processing, (b) when one-step EMV is imposed at $f = 250$ Hz with water quenching, (c, d) the hysteresis loops when two-step EMV is imposed for the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B and Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloys, respectively.

difference. For the properties parallel to the B_0 direction, the coercivity and the remanence increase greatly to about 0.91 T and 0.28 T. A simple approximation^[43,44] has been proposed to characterize the degree of alignment of Nd₂Fe₁₄B phase, α , which is defined as follows:

$$\alpha = M_r/M_s. \quad [1]$$

For a completely isotropic magnet having the same remanence in all directions, $\alpha = 0.5$, while for a perfectly oriented anisotropic magnet having the remanence in only one direction, $\alpha = 1$. In Figure 11(b), $M_s = 0.38$ T, hence it is calculated to be $\alpha = 0.74$, which is less than unit but larger than 0.5, indicating that although the overall structure seems to be “random” with whirl-like Nd₂Fe₁₄B platelets in Figures 5(b) and (c), the magnetic properties indicate that the magnetic platelets are not *completely* random, but with a certain anisotropy in magnetism. This will be elucidated in the next section when discussing the segmentation and alignment mechanism.

Figure 11(c) shows the hysteresis curves of the alloy solidified by two-step EMV processing, by which the Nd₂Fe₁₄B platelets are finely segmented and highly oriented as observed in Figures 7 and 10. One can see that the remanence and the coercivity acquired along the easy magnetization direction of c -axis of the platelets,

i.e., parallel to the B_0 direction, are 0.36 T and 0.78 T, respectively, whereas they are almost naught when measured perpendicular to the c -axis, similar to that confirmed by Sagawa *et al.*^[2] in the Nd₁₅Fe₇₇B₈ alloy. The magnetization saturation reaches approximately 0.38 T along the easy direction, whereas it is 0.12 T along the hard direction. These two loops indicate clearly that the alloy processed under the condition exhibits a strong anisotropy in magnetism, revealing that the two-step EMV technique is effective in producing an anisotropic magnet. Moreover, the degree of alignment of the platelets can be assessed by calculating α using Eq. [1], *i.e.*, $\alpha = 0.36/0.38 = 0.93$, quite near to unit and consistent with the [001] IPFs, in which the discrete dots are projected into the sector belt less than 10 deg in Figure 10(c) and highly intensified to (001) in Figure 10(f).

Figure 11(d) shows the measured hysteresis loops of the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy solidified by two-step EMV processing, whose structures are depicted in Figure 8. As the Nd₂Fe₁₄B platelets are well aligned, it is sensible to find that both curves exhibit a typical feature with a strong anisotropy, similar to that in Figure 11(c). As the weight fraction in the alloy is increased to 50 pct, the M_r and M_s along the easy magnetization c -axis correspondingly increase to 0.70 T and 0.76 T, respectively. However, the degree of alignment, *i.e.*, $\alpha = 0.92$, is almost the same as that

Fig. 12—The magnified SEM structure of the area marked by the red rectangle (a) in Fig. 7(c) of the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloy and (b) in Fig. 8(e) of Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy (Color figure online).

for the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloy in Figure 11(c). Another feature is that the increased weight fraction results in an increased magnetization along the hard direction, *i.e.*, perpendicular to the B_0 direction, to 0.27 T compared with 0.12 T in the alloy with 30 wt pct of the Nd₂Fe₁₄B phase.

In contrast to the increase of M_r and M_s along the easy magnetization axis in the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy, the coercivity along the c -axis is approximately 0.59 T in Figure 11(d), which is lower than that of 0.78 T in the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloy. Although the coercivity mechanism of hard magnets has not been well understood^[43,45,46] as a number of factors are involved in controlling the nucleation and formation of magnetic domains, their movement and rotation, and pinning, it has been phenomenologically confirmed that the finer the grain size of the magnetic phase is, the higher the coercivity will be, which has been confirmed in alloys with the nanometer-sized magnetic compound.^[18,39,47] For the present Nd₂Fe₁₄B grains in a micrometer scale, it might be plausible to infer that this rule still operates. To validate the relation, we have used a Cu mold to solidify the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy, by which the solidification rate is higher and thus finer Nd₂Fe₁₄B compounds have been observed in the master ingot. Further work on the issue is under way.

For the alloys with 30 wt pct and 50 wt pct Nd₂Fe₁₄B phases, when their respective microstructures, *e.g.*, two red rectangles in Figures 7(c) and 8(e), are magnified to show in Figure 12, it can be discerned that the compound phase in the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy is averagely larger and thicker in c -axis than that in the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloy. This may be why a higher weight fraction of the magnetic phase cannot produce a higher coercivity. Another possible reason is that with the increase of weight fraction of the Nd₂Fe₁₄B phase to 50 pct, the amount of remaining eutectic liquid becomes less, making the viscosity of the semisolid slurry increase and thus impeding the orienting of Nd₂Fe₁₄B platelets, which may bring the c -axes of some platelets to deviate from the theoretical orientation and thus lower the coercivity.

As far as the formation of the coarse compound phase in the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloy is concerned, it should be attributed to a lower cooling rate in the alloy during casting. The Nd₂Fe₁₄B intermetallic compound has a poor thermal conductivity^[48] that is usually less than 10 W m⁻¹ K⁻¹ at ambient temperature, much lower than that of Cu-based and Cu liquid melts, ranging from about 50 to 130 W m⁻¹ K⁻¹.^[49] Once a layer with a higher weight fraction of the Nd₂Fe₁₄B compound is formed near the wall of the metallic mold, it becomes a thermal barrier to the release of heat during crystallization and thus the subsequent cooling rate becomes lower in comparison with that having a lower fraction of the intermetallic compound. Hence, the compound laths in the Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B ingot can fully develop, and the growth along their c -axes becomes pronounced to form thick platelets.

In comparison with a commercial Nd-Fe-B magnet produced by powder metallurgy,^[18] the properties of the alloys solidified by two-step EMV processing in the present study are low. To achieve better properties with a higher coercivity and a larger remanence of the magnet, further work is required to refine the Nd₂Fe₁₄B compound from preparing an ingot with refined structures to tuning the EMV processing parameters, which is under way.

In addition to magnetic properties that are, of course, the most important properties for the alloy, other properties should also be considered in engineering. From the present processing procedure, it is readily to infer that the technique is expected to produce the alloy with improved mechanical properties and thermal stability superior to the polymer-bonded magnets, which can expand the application of the magnet when tailoring a smart device in engineering.

IV. DISCUSSION

A. The Segmentation of Nd₂Fe₁₄B Compounds During EMV Processing

The present results indicate that the EMV processing is effective in segmenting the long thread-like Nd₂Fe₁₄B compound into short laths at a lower frequency, *e.g.*,

$f = 250$ Hz and in aligning the segmented platelets with their c axes parallel to B_0 at a higher frequency, *e.g.*, $f = 1000$ Hz for both Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B and Nd₇₀Cu₃₀-50 wt pct Nd₂Fe₁₄B alloys.

It is noted that in the magnesium-based^[50] and 7xxx aluminum alloys,^[51] the weight fraction of the primary solid solution phase increases continuously from naught to unit once the alloys are cooled from liquidus to solidus.^[24,41,42,52] Therefore, the primary solid phase crystallized just below the liquidus immerses and floats freely within the liquid pool. However, in the present alloys, the weight fraction of the Nd₂Fe₁₄B phase remains as high as 30 and 50 pct when the alloys are cooled from 700 °C up to the eutectic temperature. Moreover, the developed Nd₂Fe₁₄B trunks intersect and/or overlay each other to form networks with certain strength when crystallizing in the metallic mold. Different from the isolated primary solid particles floating freely in the melt pool, the Nd₂Fe₁₄B network immersing in the eutectic melt is pushed to collide onto the crucible wall upon the imposition of EMV, *i.e.*, the mechanical collision of the network against the wall occurs, which may break the network into pieces and the “hard” collision plays a major role in segmenting the long feathery Nd₂Fe₁₄B phase into short laths in the initial EMV processing stage.

The mechanical collision strength and frequency are important factors in influencing collision efficiency that determines the breakdown of the Nd₂Fe₁₄B network. In the present study, the crucible wall is still, and the semisolid specimen is movable, whose velocity, v , in the time of half circle, $t = 1/2f$, can be calculated according to the equation below, as presented elsewhere in detail.^[24]

$$v = (\sqrt{2}B_0 \times J) / (\pi^3 \times r^2 \times \rho_{(d)} \times f) = k_1/f. \quad [2]$$

where k_1 is a constant determined by the specimen and experimental conditions. Hence, the velocity at $f = 250$ Hz is four times of that at $f = 1000$ Hz, resulting in a higher collision strength when the specimen is driven to crash against the crucible wall. This makes it understandable that the imposition at $f = 250$ Hz for 120 seconds leads to a full segmentation as shown in Figure 5, whereas that at $f = 1000$ Hz for 600 seconds results in a partial segmentation as depicted in Figure 6. The collision strength at $f = 1000$ Hz is comparatively lower, leaving some trunks unchanged with several hundred micrometers, *e.g.*, the lath by the red ellipse in Figure 6(d).

From the analysis and observations, it may be inferred that a lower frequency may be sufficient to segment within a shorter imposition time. Moreover, there may exist a certain high frequency, *e.g.*, $f = 1000$ Hz, at which the Nd₂Fe₁₄B network may be fully segmented and well aligned provided that the imposition time is sufficiently long because the lowered collision strength with more collision cycles seems to be effective in segmentation although the efficiency is low and homogeneity is poor when referring to Figure 6(d).

B. The Movement of Segmented Nd₂Fe₁₄B Platelets During EMV Processing at $f = 250$ Hz

After the Nd₂Fe₁₄B networks are broken down and the long compounds are segmented into fine and short laths, an individual platelet becomes isolated and is enveloped by liquid layer, which can be readily inferred from the SEM structures.

The movement behavior of the Nd₂Fe₁₄B platelets wrapped by the liquid layer can be analyzed when considering the electrical resistivity that is approximately 1350 nΩ m,^[53] similar to the value given by Sagawa *et al.*^[2] who found it to be 1400 nΩ m for the Nd₁₅Fe₇₇B₈ bulk alloy (near to Nd₂Fe₁₄B in composition) and almost remains constant up to 1000 K.^[54] For the Nd₇₀Cu₃₀ eutectic melt, no electrical resistivity data have ever been reported, which can be estimated from the that of Nd, *ca.* 650 nΩ m^[55] and of Cu, *ca.* 210 nΩ m^[56] at the melting temperature when assuming a proportional relation with the alloy composition to be about 518 nΩ m. Hence, the electrical resistivity of the Nd₂Fe₁₄B solid compound is about twice of that liquid phase, which makes the solid compound sluggish while the liquid phase mobile, similar to the primary compound in 3xxx aluminum alloys.^[31]

As the detailed deduction has been presented elsewhere,^[24] here we only show the equation of the distance, s , of a volume phase (i) covered within a half cycle, $t = 1/2f$ as follows:

$$s_{(i)} = (\sqrt{2}B_0 \times J_{(i)}) / (4\pi^3 \times r^2 \times \rho_{(i)} \times f^2) = k_2/f^2, \quad [3]$$

where k_2 is a constant. Using the present experimental parameters and considering the relation of electrical resistivity between the Nd₂Fe₁₄B compound and eutectic melt, one can calculate the distance covered by the two phases as a function of vibration frequency, f , as depicted in Figure 13. It can be found that the distance is about 3200 and 1200 μm for the liquid eutectic and solid compound at $f = 250$ Hz, which can result in uncoupled movement between the mobile liquid and the sluggish solid in the semisolid slurry.

According to Fleming's left-hand rule and the experimental condition, one can see that the Lorentz force has a constant direction provided that the AC direction remains its sign unchanged. Assuming an ideal condition under which the Lorentz force pushes the fluid to collide against the crucible wall and then form vortex flow, one can infer that the axis of the vortex should be parallel to the direction of AC, indicating that the streamlines of the vortex should be centered on the axis. Theoretically, the platelets are driven to float along the streamlines and rotated with their short axes parallel to the normal direction of the vortex, under which the resistance from the melt can be minimized.

When the sample solidified at $f = 250$ Hz is sectioned perpendicularly to the axis of the vortex, *i.e.*, the direction of AC, as shown in Figure 3(b), the platelets of their short axes with slim and slight sides should be observed and the macro view of platelets exhibits a vortex-like pattern, which can be verified in Figures 5(b) and (c). However, in comparison with an ideal fluid

Fig. 13—The calculated movement distance of the eutectic liquid and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound as a function of vibration frequency within the time interval of $t = 1/2f$. Two shaded areas are the frequency range of interest in the present study.

vortex, the platelets with various length scales may collide each other during EMV processing and thus make the actual vortex stream deviate more or less from the ideal one, resulting in the pattern somewhat irregular, as shown in Figures 5(b) and (c).

When the sample is sectioned parallel to the axis of the flow vortex, *e.g.*, the A-A plane, in the cutting plane may contain *c* planes of $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets if the deduction above stands. The specimen of Figure 5(a) was cut along the A-A direction, and Figure 14 depicts SEM structures of the specimen captured from the top view. A belt can be found in Figure 14(a) in which the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phases are coarse. The magnified structure of the region in the red rectangle shows that the morphology of the magnetic phase is similar to that in Figures 7(f) and 10(d), indicating that the crystal planes of these coarse blocks should be the *c* planes. Beside the belt are the platelets showing their short axes, similar to that in Figures 5(b) and (c). These structures reveal that the flow vortex due to the Lorentz force exhibits a certain directional feature. Although the platelets in Figures 5(b) and (c) are not well aligned, they are *not completely* random in terms of the orientation of the *c* planes, *e.g.*, only one coarse block can be identified as circled in the upper left corner in Figure 5(c) whereas a number of platelets with their *c* planes can be inferred in Figure 14(a). This should be why the degree of alignment in Figure 11(b), *i.e.*, $\alpha = 0.74$, is larger than 0.5 that is for a completely random distribution of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

C. The Alignment of Segmented $\text{Nd}_2\text{Fe}_{14}\text{B}$ Platelets During EMV Processing at $f = 1000$ Hz

The leading distance covered by the mobile liquid decreases to approximately 100 μm when f increases to 1000 Hz from Figure 13, which is almost equivalent to the length scale of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets along their

longitudinal direction. Considering that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets float and move sluggishly within the semisolid slurry, the leading amplitude of the mobile liquid is around hundred micrometers. As the Lorentz force is always perpendicular to the B_0 direction, those platelets whose *c* axes are not parallel to the B_0 suffer from the drag force due to the mobile liquid, which can drive the platelets to rotate certain degrees, at which their *c* planes are always pushed to be parallel to direction of the Lorentz force, as schematically depicted in Figure 15(b). In this case, the platelets subject to the minimum shear force from the surrounding liquid and thus they are energetically stable.

Here, it is noted that to rotate a platelet to its stable direction requires that the leading distance covered by the liquid should be in a proper range; *i.e.*, a long-leading distance produces macro flow vortex that disturbs the direction of *c*-axes of platelets, as shown in Figures 5(b) and (c) whereas a rather short distance, *e.g.*, about 6 nm at $f = 50,000$ Hz, may not produce effective impact to enable the platelet to rotate in the viscous melt within microseconds. In other words, the leading amplitude of the mobile liquid should be small enough not to give rise to macro flow to form a whirl-like pattern of the platelets, and meanwhile, it should be large enough to drive the platelet to rotate instead of vibration in a nanometer scale. Further work to optimize the vibration frequency for platelet rotation is under way.

It should be pointed out that a platelet with its *c* plane parallel to the direction of Lorentz force does not follow that its *c*-axis should be parallel to B_0 in a three-dimensional space, as depicted in Figure 15(b). For the $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelet with the volume of V in the static magnetic field, the anisotropic magnetization energy, alternatively, the magnetization torque, ΔE , can be estimated^[57–59]:

$$\Delta E = V \times (\chi_c - \chi_a)(B_0)^2 \times \sin(2\theta)/(2\mu_0), \quad [4]$$

where θ is the angle between B_0 and the direction of the easy magnetization *c*-axis, μ_0 is the permeability in free space, and χ_c and χ_a are the magnetic susceptibility along the *c* and *a*-axis, respectively. When $\chi_c > \chi_a$ ^[60] and the *c*-axis of a platelet has a certain degree with B_0 , the magnetization torque occurs and turns the platelet to orient with its *c*-axis parallel to the magnetic field, by which the magnetization energy can be minimized so that the platelet becomes thermodynamically stable. Here, it is worth noting that Courtois *et al.*^[61] confirmed that the equation could be applicable for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase up to 1100 °C in the paramagnetic state. Hence it plausible to infer that this equation may be applicable over the temperature range provided that there is a difference between χ_c and χ_a regardless of the state of the solid phase, ferromagnetic or paramagnetic, when $\chi_c > \chi_a$. When the alloy is cooled below the Curie temperature, although this equation applies to the magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, this anisotropic magnetization torque is rather small in comparison with the eutectic alloy strength in the solid state and thus cannot rotate or move the discrete $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets. At the

Fig. 14—(a) The SEM structure of the specimen of Fig. 5(a) when it is sectioned along the A-A plane and captured from the top view. A belt with coarse blocks can be discerned, which is separated by dashed curves. (b, c) the enlarged structures of the areas highlighted by two red rectangles in and out of the belt, respectively (Color figure online).

Fig. 15—A schematic to illustrate (a) independent $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets after the network is segmented into fine laths at a low vibration frequency, (b) the directional Lorentz force pushing the platelets to rotate to the direction at which their c planes get parallel to the force in order to minimize the resistance due to the mobile liquid, and (c) for those platelets whose c -axes have certain degrees with B_0 , the magnetization torque aligning the platelets with their c -axes parallel to B_0 to minimize the magnetization energy.

semisolid state, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is paramagnetic, while this principle works not only in aligning the segmented $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelets in the present study, *e.g.*, the platelets can be well aligned in the central area after one-step EMV processing at $f = 250$ Hz during cooling in the static magnetic field in Figure 5(f), but also in orienting fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles to form a large anisotropic magnet and large $\text{Nd}_2\text{Fe}_{14}\text{B}$ compounds in a eutectic liquid^[61] without EMV processing. More

examples can be found in aligning the anisotropic crystals to form highly oriented textures during solidification, *e.g.*, the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ oxide,^[62] SmCo magnets,^[63] and AZ91D magnesium alloys.^[64] This may be applied to account for the slight larger value of M_s acquired along the B_0 direction in Figure 11(a), which is achieved after the specimen is solidified $B_0 = 10$ T without EMV. The isolated debris, *e.g.*, marked by the red ellipses in Figure 4(c), may be

oriented with their c -axes parallel to B_0 and thus yield a larger M_s .

It should be noted that the static magnetic field also takes into effect to orient segmented platelets provided that the sample can be kept in the semisolid for a sufficiently long interval. This can be verified from Figure 5(f) that is taken near the central area of the specimen when it is naturally cooled. In comparison with the peripheral area, the central area has a longer time in the semisolid state, in which segmented platelets that are subject to the magnetization torque only can be rotated with their c axes parallel to B_0 . In contrast, the peripheral region should solidify first once the specimen is cooled and thus have a shorter interval in the semisolid state. In this case, there may be not enough time for discrete platelets to be rotated as to overcome the viscous resistance from the eutectic melt may be a sluggish process when driving the compound to move and rotate. This should be why the structure near the sample periphery exhibits a vortex pattern in Figure 5(e) whereas the platelets near the sample center are well aligned in Figure 5(f).

Here, it is noted that this type of the structure should not be induced by the skin effect owing to the imposition of AC. The skin depth, δ , can be calculated *via* the equation below:

$$\delta = [2\rho_{(r)}/(2\pi f \times \mu)]^{1/2}, \quad [5]$$

where $\rho_{(r)}$ and μ are the electrical resistivity and magnetic permeability of the conductor, respectively. Using the Nd₇₀Cu₃₀-30 wt pct Nd₂Fe₁₄B alloy as an example, one can calculate that $\rho_{(r)} = 374$ nΩ m for the eutectic alloy when these two phases are considered to form a parallel circuit. Here, δ can be calculated using the typical permeability of the Nd₂Fe₁₄B phase, *i.e.*, 1.281×10^{-6} H/m at ambient temperature according to Sagawa *et al.*^[2] and found to be 19.3 mm at $f = 250$ Hz and 9.6 mm at $f = 1000$ Hz, which are larger than the sample diameter. Moreover, the permeability can be inferred from the temperature-dependent magnetization behavior that decreases up to the Curie temperature^[65] and eventually becomes paramagnetic when the compound is heated above the Curie temperature. In this case, the permeability is almost similar to that of vacuum, *i.e.*, 1.256637×10^{-6} H/m. Hence, one can find that the skin depth is still larger than the sample diameter and, thus, the skin effect can be negligible in the present study with regard to the vibration frequency and sample temperature of the interest.

In terms of the platelet alignment, there are two kinds of forces, *i.e.*, the Lorentz force that rotates the platelets with their c planes parallel to the force and the anisotropic magnetization torque in the static magnetic field. Although we presented here separately, these two forces work simultaneously upon the segmented platelet and the final crystalline orientation distribution should be resulted from the coherent addition of these two vectors that eventually align the c -axis of the platelet parallel to the B_0 direction.

V. CONCLUSIONS

We solidified the Nd₇₀Cu₃₀-30, 50 wt pct Nd₂Fe₁₄B alloys using the EMV technique and observed the structures formed at one-step EMV processing, *i.e.*, a low frequency of $f = 250$ Hz and a high frequency of $f = 1000$ Hz, and two-step EMV processing. The results can be summarized as follows:

- (1) The mechanical collision of the semisolid specimen upon the ceramic holder at a low vibration frequency of $f = 250$ Hz is effective to break down the Nd₂Fe₁₄B network and thus segment the developed feathery intermetallic compounds into fine laths. The pronounced difference in electrical resistivity between the compound phase and the eutectic liquid enables the production of uncoupled movement. The directional Lorentz force makes the viscous flow of the semisolid slurry exhibit a whirl-like pattern due to the directional feature of the vortex.
- (2) The EMV processing at $f = 1000$ Hz is effective in rotating segmented platelets with their c planes parallel to the direction of the Lorentz force. The Nd₂Fe₁₄B compound in semisolid slurry has anisotropic magnetic susceptibility along c and a axis even at the paramagnetic state, which produces the magnetization torque in the static magnetic field. Both the Lorentz force and the magnetization torque contribute to aligning the platelets with their c -axes parallel to the B_0 direction.
- (3) The structural observation and EBSD mapping, together with the IPFs, reveal that using two-step EMV processing, the developed long Nd₂Fe₁₄B compounds can be effectively segmented into fine laths and well aligned with their c -axes parallel to the direction of the static magnetic field. This technique works well not only for the alloy with a low fraction weight of 30 wt pct Nd₂Fe₁₄B but also for the one with a high fraction weight of 50 wt pct Nd₂Fe₁₄B compound.
- (4) The magnetic properties demonstrate that the specimen with well-aligned fine platelets exhibits a strong anisotropy in magnetism, indicating that the two-step EMV technique with a kit of suitable processing parameters is promising in fabricating a bulk magnet with a strong anisotropy in magnetism *via* solidifying the semisolid slurry only instead of conventional powder metallurgy.

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