Nano-heterogeneity-stabilized and magnetic-interaction-modulated metallic glasses

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Because of their boundary-free and long-range-disordered microstructure, Fe-based metallic glasses (MGs) exhibit an ultra-low pinning effect on the magnetic domain and unparalleled soft-magnetic properties [1–3], and thus are increasingly used in electric devices for the energy-saving and high-efficiency requirements [4,5]. However, the conventional alloy design concept based on a homogeneous microstructure and high glass formability (GFA) has approached the limit in improving the magnetization (B_s) [6,7], due to the trade-off of GFA and B_s as shown in Fig. 1a. The Fe content limit of the high- B_s alloys for the ribbon production has been a long-standing dilemma, in the commercial FeSiB and FeSiBC alloys [2,3,8]. Recently, we developed FeSiBPC MGs with a distinctly high Fe content and a B_s up to 1.67 T [9]; yet, the knee point and reversed tendency of B_s were also unexpectedly found, as shown in Fig. 1a [7]. By enhancing the exchange interactions with Co alloying according to the Slater-Pauling curve [10], it is feasible to improve the B_s to 1.85 T in the representative $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$ alloy [11]. Nevertheless, such alloy in the industrialization suffers from both deteriorative soft-magnetic performances and poor manufacturability originating from the low GFA. Moreover, its poor thermal stability hinders the structural relaxation and stress-release processes during the heat treatment (HT). All of these are too harsh for the mass production and force us to explore new approaches to uncouple the B_s -GFA trade-off and enhance the comprehensive performances.

Tuning the nano-heterogeneities, such as short-range orders [12–15], compositional segregations [16], as well as “solid-like” and “liquid-like” regions [17,18], is recently found to be an effective route for improving the selective properties [19–28]. The formation of icosahedra-like

clusters in Zr-based MGs can impede the crystallization and stabilize the super-cooled liquid [29]. The deposited nano-globular nano-glass can exhibit kinetically ultra-stable glass-transition and crystallization behaviors [30–32]. Accordingly, we were inspired to design a nano-cluster-stabilized MG alloy with super-high content of ferromagnetic elements and a strong magnetic interaction, in order to break the B_s -GFA paradox in scalable melt-spun ribbons. However, two critical issues should be aroused: (1) how to control the nano-precipitation in an intrinsically gradient cooling process, without a high content of glass-forming elements; (2) how to reduce the magnetic anisotropy in a heterostructured MG, for superior soft-magnetic properties. These challenges are universal for all MGs and more complicated in magnetic ones [19,23,33,34], and therefore, they require revolutionary approaches.

Here, by using our novel alloy design strategies of critical formability and light metalloid multi-alloying, novel $\text{Fe}_{71}(\text{Co},\text{Ni})_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ alloys with a high B_s up to 1.86 T, superior GFA and manufacturability were developed, as shown in Fig. 1a. A unique magnetic-field-assisted HT process was employed to align the magnetic domain and soften the coercivity (H_c) to as low as 2 A m^{-1} . The microstructures and magnetic domain patterns after HT were comparatively and systematically investigated, which helps us to unveil the universal physical mechanisms of the microstructural evolution and clustering-induced stabilization in the magnetic MGs.

Alloys with nominal compositions of $\text{Fe}_{86}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ (BA), $\text{Fe}_{71}\text{Co}_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ (Co-15) and $\text{Fe}_{71}\text{Ni}_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ (Ni-15) were prepared with induction melting by mixing pure elements of Fe, Co, Si, B, pre-alloyed Fe_3P and FeC ingots under an argon atmosphere. The

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Figure 1 (a) A schematic illustration of the dependences of GFA and B_s on the ferromagnetic element (Fe(Co,Ni)) content in different alloy systems, showing the limits of the GFA and B_s in the current Fe-based metallic glasses; (b) atomic number and radius of the component elements of Fe(Co,Ni)-SiBPC alloys (inserted table shows the mixing enthalpy); (c) considerations of other properties influenced by Co/Ni alloying; (d) XRD patterns of AQ $\text{Fe}_{71}(\text{Co,Ni})_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ alloy ribbons prepared with different wheel speeds, together with the $\text{Fe}_{68}\text{Co}_{17}\text{B}_{14}\text{Si}_1$ alloy for a comparison.

$\text{Fe}_{68}\text{Co}_{17}\text{B}_{14}\text{Si}_1$ contrast alloy was also prepared. Ribbons were prepared with a single-roller melt-spinning method. Thermal parameters including crystallization temperature (T_x) and Curie temperature (T_c) were determined by differential scanning calorimetry (DSC). Ribbons were isothermally heat-treated in a special pipe furnace, as illustrated in Fig. S1b–d. Field HT (FHT) under a magnetic field of about 1.6 kA m^{-1} and normal HT (NHT) were all processed in an argon atmosphere. Magnetic properties of B_s , H_c and effective permeability (μ_e) were measured with a vibrating sample magnetometer (VSM), a direct current (DC) B–H loop tracer and an impedance analyzer under a field of 10 A m^{-1} , respectively. Thermal-magnetization curves were also measured with a VSM at a heating rate of 5°C min^{-1} . The domain structures were characterized *via* a Magneto-optical Kerr Microscope (MOKE). The microstructures of the as-quenched (AQ), NHT and FHT samples were identified by X-ray diffraction (XRD). In-detail microstructures were observed with high-resolution transmission electronic microscopy (HRTEM) and selected area electronic diffraction (SAED).

In order to achieve an unprecedented B_s enhancement, we proposed fourfold combinational alloy design concepts: (1) only small metalloid elements were selected as glass-forming constituents, in order to obtain a strong

magnetic interaction, as shown in Fig. 1b, excluding the large and heavy elements which apparently enlarge the distance of ferromagnetic atoms [9]; (2) introducing Co and Ni to enhance the intercoupling effects, according to the Slater-Pauling curve [10]; (3) approaching a critical-high total content of ferromagnetic elements in multi-component Fe(Co,Ni)SiBPC alloys [35], by using the synergistic effect for breaking the formability limit and matching the industrial requirement, as shown in Fig. 1a; (4) promoting the dense clustering (see Fig. S1a in the Supplementary information), both in the melt-spinning process by matching the critical cooling rate to the industrial parameter, and in HT process [29,36,37]. Moreover, as shown in Fig. 1c, the Co/Ni introductions would considerably improve the thermal stability and corrosion resistance, as well as tune the T_c and T_x . Accordingly, by laboriously optimizing the ratio of metalloid elements and the Co/Ni content, novel $\text{Fe}_{71}(\text{Co,Ni})_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ alloys were successfully developed and representatively studied here.

The GFA and manufacturability of the $\text{Fe}_{71}(\text{Co,Ni})_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ alloys were firstly evaluated by using a common single-roller melt-spinning method. Ribbons with excellent ductility and surface quality were readily prepared with wheel speeds of $25\text{--}40 \text{ m s}^{-1}$. XRD patterns in Fig. 1d show that fully glassy structure can be obtained

with a critical wheel speed of 30 m s^{-1} which is generally acceptable for the industry [9]. Compared with the $\text{Fe}_{68}\text{Co}_{17}\text{B}_{14}\text{Si}_1$ alloys (wheel speed $> 50 \text{ m s}^{-1}$), the as-designed alloys exhibit improved manufacturability, validating the effectiveness of the alloy design strategy.

Crystallization behaviors of the base alloy (BA), Ni-15 and Co-15 alloy ribbons were then comparatively studied by means of the DSC measurement as shown in Fig. 2a. It is interesting that the introduction of Co/Ni does not apparently change the onset temperature of the first crystallization peak (T_{x1}) corresponding to the bcc-Fe(Co, Ni) precipitation, suggesting the unchanged clustering temperature and the cluster structure. As enlarged in the inset of Fig. 2a, a T_c is clear in the curve of the BA, while no obvious transition can be detected in the Ni-15 and Co-15 curves. To understand the magnetic and structural transitions, the saturated magnetic moment (M_s) vs. temperature (M - T) curves were measured and shown in Fig. 2b, exhibiting significant differences of the magnetic state of the ribbons before the crystallization. For the BA with a super-high Fe content, M_s decreases drastically even at a low temperature, which is dangerous for the application in devices in a high-load condition. The introduction of Ni and Co can effectively improve the decrease rate of M_s at 120°C (an international standard) from 13.3% to 5.9% and 4.3%, respectively, ensuring the

safe application. In the temperature window for HT, the Ni-15 and Co-15 alloys are still in a strong ferromagnetic state, suggesting the strong influences of the spontaneous magnetic field on the multi-mode relaxation and clustering processes [36,38].

We employed a proper magnetic-field-assisted HT (FHT) and a normal HT (NHT), to modulate the magnetic domain and structural relaxation. Based on the DSC and M - T curves, FHT and NHT (schematically shown in the Fig. S1) were conducted in the temperature range of 270 – 350°C for exploring the optimal parameters. As shown in the Fig. 2c, the NHT and FHT have quite different effects on the H_c in the three alloys with different magnetic states. The H_c cannot be effectively reduced by NHT and FHT for the BA with the critical Fe content, differing from the conventional Fe-based alloys. The Ni-15 and Co-15 samples subjected to the NHT process also exhibit the obviously deteriorative H_c . On the contrary, the FHT Ni-15 and Co-15 samples result in a significantly low H_c , manifesting the effectiveness of the FHT in improving the soft-magnetic properties. As shown in Fig. 2d, the Ni- and Co-doped alloys subjected to the optimal FHT (330°C , 15 min) have the lowest H_c of 5 and 2 A m^{-1} , respectively. As shown in Fig. 2e, the μ_e under a field of 10 A m^{-1} at a large frequency range is also substantially improved. The μ_e at 1 kHz of the Co-15 alloy is

Figure 2 (a) DSC curves of the AQ BA, Ni-15 and Co-15 ribbons prepared with 40 m s^{-1} ; (b) thermal-magnetization curves of AQ samples, showing the magnetization decrease at the working temperature and the magnetic state in the HT temperature range. (c–f) Magnetic properties of the BA, Ni-15 and Co-15 alloy ribbon samples: (c) dependences of the H_c on the HT process; (d) amplified B - H loops of FHT samples; (e) dependences of μ_e on frequency measured with a field of 10 A m^{-1} ; (f) saturated magnetization curves.

up to 24×10^3 , which is much higher than that of the commercial Si-steel and Fe-based MGs [9]. Most important, the saturated magnetization curves in Fig. 2f shows that the B_s of Co-15 and Ni-15 alloys increase to 1.86 and 1.65 T, respectively, exhibiting the increases of 16% and 3% as compared with the BA. Based on these results, we can conclude that the newly developed $\text{Fe}_{71}(\text{Co,Ni})_{15}\text{B}_{9.5}\text{Si}_{2.5}\text{P}_{0.5}$ alloys exhibit superior magnetic properties and the application of the FHT is very important.

To unveil the improvement mechanisms in soft-magnetic properties, magnetic domain patterns of BA, Ni-15 and Co-15 ribbons in different states were identified systematically. As shown in Fig. 3a, irregular zig-zag and branch-like domains with a fine width of about $20 \mu\text{m}$ are detected in the BA ribbon sample after FHT, similar with the NHT and AQ samples. For the Ni-15 and Co-15 samples after FHT, as shown in Fig. 3b and c, strip domains with smooth boundaries and a large width of more than $200 \mu\text{m}$ exhibit the significantly decreased pinning effect and low magnetic anisotropy. Accordingly, the magnetic domain structures would well explicate the excellent soft-magnetic properties of the FHT treated Ni-15 and Co-15 ribbons.

The microstructures and their evolution processes were

then investigated to understand the different magnetic performances. The typical XRD patterns of MG in Fig. 3d shows that the NHT and FHT do not cause obvious crystallization in the XRD detectable scale. In HRTEM images of the AQ ribbons (Fig. 3f), the short (medium)-range orders for the Co-15 ribbon are very small and of a high density, as proved by the diffused ring in the inserted SEAD picture. According to Fig. 3g, dense clusters with a diameter of about 5 nm formed during the NHT process. Compared with the NHT samples, the cluster size in FHT samples decrease apparently. We can therefore declare that the HT considerably promotes the growth of the short (medium)-range orders to clusters, the applied magnetic field would slow down the growth rate. Since it was hard to determine the exact microstructure of the short-range orders and clusters [12,13,39], we performed an indirect analysis by identifying the bcc-Fe(Co,Ni) initial phase (in Fig. 3e), based on the embryos and nucleation concepts. It is reasonable to deduce that the short (medium)-range orders and clusters are enriched with Fe(Co,Ni) atoms and would be the nuclei for the subsequent crystallization [29,39], all of which enhance the magnetic inter-coupling and result in high B_s .

Based on above results, we are in the position to discuss

Figure 3 (a–c) Magnetic domain patterns of the BA, Co-15 and Ni-15 alloy ribbons identified without applying a magnetic field after the optimal FHT; (d, e) XRD patterns of AQ, NHT and FHT treated $\text{Fe}_{71}\text{Co}_{15}\text{Si}_{2.5}\text{P}_{0.5}$ alloy ribbons in the stress released state and partially crystallized state; (f–h) TEM images and diffraction patterns (insets) of Co-15 alloy ribbons in AQ, NHT and FHT states.

the formation mechanism and origins of the superior performances in these high- T_c $\text{Fe}_{71}(\text{Co,Ni})_{15}\text{Si}_2\text{B}_{9.5}\text{P}_2\text{C}_{0.5}$ alloys. Except the synergistic enhancement and entropy stabilization mechanisms [35] described in the design part, the excellent manufacturability should be attributed to the cluster stabilization mechanism. The dense short-range orders and clusters (shown in Fig. 3f–h) in the alloys made with critical parameters not only decrease the energy state of the glassy structures for a higher energy barrier of the crystallization (shown in Fig. 4d), but also kinetically slow down the nucleation and crystallization processes *via* pinning effects [29,31,40]. With respect to the unusual modulation mechanisms of the microstructure and magnetic domain for the superior soft-magnetic properties, we focus on the effects of spontaneous and applied magnetic fields in the HT process. As illustrated in Fig. 4a, MGs commonly include loose-packed regions and short (medium)-range orders, which should be of higher densities in the present MGs [33]. According to the well-known models of the structure relaxation during the HT [23,31,34], the loose-packed region (shown in Fig. 4b) will relax to an atomic homogeneous structure and some ordered clusters (shown in Fig. 4c) will grow *via* the atomic diffusion. Since the local fields with different magnetization directions will affect the interface energy as well as the energy states of the disordered structure and clusters, the relaxed homo-

geneous structures and grown clusters in different domains would possess diverse sub-states [41,42], as shown in Fig. 4d. In the BA sample with a low T_c , the matrix is in a paramagnetic state during the HT and relaxes freely like the conventional Fe-based and the non-magnetic MGs, while the clusters with a high T_c are in magnetic states and grow tendentially under the field environment. As shown in Fig. 4e, the clusters magnetically aligned at the beginning of the FHT would be magnetic heterogeneities in the re-magnetized matrix after the FHT, which apparently increases the magnetic anisotropy and accounts for the poor soft-magnetic properties. For the Co-15 sample shown in Fig. 4f, the matrix and the clusters relax and grow diversely in different domains during the NHT, which more intensively increase the magnetic and structural anisotropies, resulting in the deteriorative magnetic properties. During the FHT, the matrix and the clusters are magnetically aligned by the applied field, leading to the conformably microstructural evolution and a domain modulation to the easy-magnetization direction. The above discussions show that the FHT and Co/Ni addition-enhanced magnetic interaction are crucial for the co-modulations of the relaxed microstructure and the magnetization directions in the matrix and nano-heterogeneities, which is the origin of the superior soft-magnetic properties in these special cluster-stabilized MGs [5,10]. We should also mention that the applied

Figure 4 Schematics of the microstructural and magnetic domain evolution processes of the MGs under the magnetic field. (a) The microstructure and domain structures (marked with different background colors), showing the loose-packed regions (free volume) and ordered structures (Fe(Co, Ni)-rich short (medium)-range orders and clusters) in different magnetic domains; (b) microstructural evolutions of the loose-packed regions during FHT and NHT processes; (c) diffusion process of magnetic atoms in the cluster interface under a magnetic field; (d) multi-states in the potential energy profiles of the magnetic MG, showing the effects of the magnetic field on structural relaxation and clustering processes. Magnetic domains of the clusters and matrix: (e) in the BA with a low T_c , during the FHT process; (f) in the Co-15 alloy with a high T_c , during the NHT and FHT processes.

magnetic field would meanwhile deter the growth rate of the clusters and improve the crystallization resistance, by changing the interface energy and slowing the diffusion rate of the magnetic atoms [43]. All these new mechanisms have not been involved in the low- T_c magnetic MGs and non-magnetic MGs.

In summary, novel $\text{Fe}_{71}(\text{Co,Ni})_{15}\text{B}_{9.5}\text{Si}_2\text{P}_2\text{C}_{0.5}$ MGs were developed with a unprecedented synergy of high magnetization (1.86 T), superior soft-magnetic properties ($H_c = 2 \text{ A m}^{-1}$, $\mu_e = 24 \times 10^3$) and excellent manufacturability (can be made with 30 m s^{-1}). The interlocking strategies of the multi-metalloid component design, the compositional adjustment under the new concept of critical formability as well as the proper Co/Ni alloying enable the approaching of super-high ferromagnetic element contents and strong magnetic interactions for the high B_s . The manufacturability is well balanced by the critical formability concept and enhanced by the cluster stabilization and synergistic effect of multi-metalloids. The FHT approach co-modulates the microstructural evolution and the magnetization processes, resulting in the superior soft-magnetic properties. These special composition and process design approaches can be widely utilized to develop scalable MGs with superior magnetic performances and enhanced thermal stability. The heterostructured modulation concepts should be also applicable to many other MGs, by replacing the FHT with ultrasound, microwave and thermal-cycling approaches.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting materials are available in the online version of the paper.

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纳米级不均匀性稳定和磁相互作用调控的金属玻璃

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摘要 在金属玻璃中可控地引入不均匀性通常能大幅改善其性能, 甚至能突破传统合金设计方法的限制. 本文中, 我们发现在临界非晶形成能力条件下能获得高密度团簇, 且其强交换耦合作用可用于调控磁性能. 基于这些新理念, 我们开发了 $\text{Fe}_{71}(\text{Co}, \text{Ni})_{15}\text{B}_{9.5}\text{Si}_{2}\text{P}_{2}\text{C}_{0.5}$ 新合金. 由于钴/镍元素添加、团簇析出强化和少量多种类金属元素组合添加等四重强化机制, 合金的饱和磁感应强度达到1.86 T. 同时, 磁场热处理工艺的采用, 可以有效调控结构不均匀和磁畴取向的各向异性, 从而明显改善软磁性能. 此外, 由于临界条件制备平衡了非晶形成能力, 纳米团簇提高了非晶态的稳定性, 我们首次获得了兼具高磁感应强度、优异软磁性能和非晶形成能力等优异综合性能的软磁非晶合金.