Influence of Fe and Co Content on Crystallization and Magnetic Property of FeZrB Alloys

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Substituting Fe with Co in Fe-based alloys to adjust the composition and optimize properties is a hot topic. Amorphous Fe84−xCo7xB3 (x = 0, 7, 14, 21, 28, 35, 42) ribbons were prepared and annealed at their first exothermic peak temperature. The crystallization and magnetic properties of the alloys can be divided into two regions. The first region corresponds to the Fe84−xCo7xB3 (x = 0, 7, 14, 21) alloys, and the second region corresponds to the Fe84−xCo3Zr7B3 (x = 28, 35, 42) alloys. There are four exothermic peaks for Fe84−xCo7xB3 (x = 0, 7, 14, 21) alloys, and there are three crystallization exothermic peaks for Fe84−xCo3Zr7B3 (x = 28, 35, 42) alloys during crystallization. Only a single phase precipitates from the amorphous matrix for all alloys after annealing. With the increase in Co content, the lattice constant first increases up to 21 at.% Co and then decreases. The crystallization volume fraction (Vm) and the grain size (D) continue to decrease. When the Co content is 21 at.%%, there is little change in Co concentration between the nanocrystal and the remaining amorphous matrix. When the Co content is 42 at.%, the Fe content in the remaining amorphous matrix is significantly less than that in the nanocrystal, and the Co content in the remaining amorphous matrix is slightly higher than that in the nanocrystal. The content of Fe in the nanocrystal is higher than that of Co in the nanocrystal. The specific saturation magnetization Ms of as-quenched alloys and annealed alloys increases sharply up to 28 at.% Co and then decreases with a further increase in the Co content. The Ms values of annealed alloys are greater than those of as-quenched alloys. The coercivity Hc values of annealed alloys are lower than those of as-quenched alloys. For Fe84−xCo7xB3 (x = 0, 7, 14, 21) alloys, the higher the Co content, the higher the difference between the Hc values of as-quenched and annealed alloys. For Fe84−xCo3Zr7B3 (x = 28, 35, 42) alloys, the difference between the Hc values of as-quenched and annealed alloys is small.

1. Introduction

Fe(Co)-based alloys have higher Curie temperatures and higher magnetization compared to other Fe-based alloys without Co, resulting in potential applications at higher operating temperatures, which have been widely reported [1–7]. Furthermore, scholars have paid attention to the effect on structure [4–9], thermal property [9, 10], magnetic property [10–17], and application [18, 19] of using Co to replace Fe in the alloys.

For Fe3.2−xCo7B10CoCu0.8 (where x = 0–10) alloys [10], the doping of Co can effectively regulate the Curie temperature and magnetic properties of alloys. For (Fe1−xCo)x80Hf7B9Cu1 (x = 0–1) alloys [14], the lattice parameter of nanoscale precipitation decreased with increasing Co content because of the high solubility of Co in the a(α′)-Fe(Co) solid solution. For Fe80Co2B14−xSi2P3Cu1 (x = 0, 2, 4, 6) alloy ribbons [16], the addition of Co decreased the thermal stability of the alloy to crystallization and expanded the heat treatment temperature region of this family of alloy. For Fe61+2xCo10−2xY8W1B20 (x = 0, 1, 2) bulk amorphous alloys [17], a change in the Co content resulted in measurable effects on the Curie temperature and the value of the coercive field but had little effect on the saturation of the magnetization. For (Fe1−xCo)x80Zr3.5Nb3.5B8Cu1 (x = 0.0–0.8) alloys [20], the crystallization temperature Tc of the amorphous alloy decreased with increasing Co content, whereas the Curie temperature Tc of the amorphous alloy was enhanced by the increase in the Co content.

The magnetic properties of Fe-based amorphous-nanocrystalline alloys are closely related to their microstructure. It is very important to explore the
effect of Co content on the crystallization and magnetic properties of Fe-based amorphous alloys. Especially after adding Co into the Fe-based alloy, the distribution ratios of Fe and Co in the crystalline phase and in the remaining amorphous phase are different, which further affects the crystallization of the alloys and results in differences in the structure and properties of FeCo-based nanocrystalline alloys with different Fe and Co ratios. Substituting Fe with Co in Fe-based alloys to adjust the composition and optimize properties is still a hot topic.

In this paper, Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys were prepared and annealed at their respective first exothermic peak temperature. The thermal behavior, microstructure, and magnetic properties of alloys have been investigated. The effect of Co content on the crystallization and magnetic properties of FeZrB alloys was studied in detail. Especially after adding different Co content into the alloy, the distribution ratios of Fe and Co in the crystalline phase and in the remaining amorphous phase were investigated. The crystallization and magnetic properties of the Fe-CoZrB alloys can be divided into two regions. By exploring the law of the microstructure change of the primary crystallization phase of the FeZrB amorphous alloy caused by the change in Fe and Co content, we can purposefully guide the research and development of this kind of alloy materials.

2. Experimental details

Alloy ingots with nominal compositions Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) were prepared by induction melting the mixtures of high-purity Fe (99.98 wt%), Co (99.99 wt%), Zr (99.92 wt%), and B (99.999 wt%). High-purity Ti of high-purity Fe (99.98 wt%), Co (99.99 wt%), Zr were prepared by induction melting the mixtures and results in differences in the structure and magnetic properties of alloys have been investigated. The thermal behavior, microstructure, and magnetic properties of alloys were investigated. The effect of Co content on the crystallization and magnetic properties of FeZrB alloys was studied in detail. Especially after adding different Co content into the alloy, the distribution ratios of Fe and Co in the crystalline phase and in the remaining amorphous phase were investigated. The crystallization and magnetic properties of the Fe-CoZrB alloys can be divided into two regions. By exploring the law of the microstructure change of the primary crystallization phase of the FeZrB amorphous alloy caused by the change in Fe and Co content, we can purposefully guide the research and development of this kind of alloy materials.

3. Results and discussion

Figure 1 shows the XRD patterns of the Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) as-quenched alloys. No crystalline diffraction peaks are observed, indicating that the as-quenched alloys are all fully amorphous.

The DSC traces of Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys are shown in Fig. 2. For Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21$) alloys, there are four exothermic peaks during the crystallization. For Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 28, 35, 42$) alloys, there are three crystallization exothermic peaks during the crystallization. With the increase in Co content, the intensity of the first ($T_{p1}$) and the third ($T_{p3}$) crystallization exothermic peaks is slightly enhanced, and the values of a peak temperature shift to the low-temperature direction. The second ($T_{p2}$) exothermic crystallization peak temperature decreases up to 21 at.% Co and then increases with the increase in Co content. When the atomic percent of Co is between 0 to 21, the fourth ($T_{p4}$) crystallization peak temperature shifts to the high-temperature direction. Three or four exothermic peaks were observed in the DSC curves of FecCoZrB series alloys, indicating that the crystallization processes of the series alloys were multistage crystallization.

XRD patterns of Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys annealed at the first exothermic peak temperature are shown
Fig. 2. DSC traces of Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys: (1) Fe$_8$Zr$_7$B$_9$, (2) Fe$_{77}$Co$_7$Zr$_7$B$_9$, (3) Fe$_{70}$Co$_{14}$Zr$_7$B$_9$, (4) Fe$_{63}$Co$_{21}$Zr$_7$B$_9$, (5) Fe$_{56}$Co$_{28}$Zr$_7$B$_9$, (6) Fe$_{49}$Co$_{35}$Zr$_7$B$_9$, and (7) Fe$_{42}$Co$_{42}$Zr$_7$B$_9$.

Fig. 3. XRD patterns of Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys annealed at the first exothermic peak temperature (a); local area magnification (b); (1) Fe$_8$Zr$_7$B$_9$, (2) Fe$_{77}$Co$_7$Zr$_7$B$_9$, (3) Fe$_{70}$Co$_{14}$Zr$_7$B$_9$, (4) Fe$_{63}$Co$_{21}$Zr$_7$B$_9$, (5) Fe$_{56}$Co$_{28}$Zr$_7$B$_9$, (6) Fe$_{49}$Co$_{35}$Zr$_7$B$_9$, and (7) Fe$_{42}$Co$_{42}$Zr$_7$B$_9$.

Fig. 4. Grain size and lattice constant of Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys annealed at first exothermic peak temperature.

In Fig. 3. It can be seen that only α-Fe phase precipitates from the amorphous matrix for all alloys. With the increase in Co content, the diffraction peak (110) first shifts to the low angle up to 21 at.% Co and then slightly to the high angle. The crystallization volume fraction ($V_{\text{cry}}$) decreases. The FWHM (full width at half maxima) of the diffraction peak increases gradually, which indicates that the average grain size decreases with the increase in Co content.

Grain size ($D$) and lattice constant of Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) amorphous alloys annealed at their first exothermic peak temperature are given in Fig. 4. With the increase in Co content, the grain size of α-Fe continued to decrease. According to the works by A. Takeuchi et al. [21], the heat of mixing of Co–Fe is $-1$ kJ/mol. The heat of mixing of Co–B ($-24$ kJ/mol) is close to that of Fe–B ($-26$ kJ/mol), but the heat of mixing of Co–Zr ($-41$ kJ/mol) is larger than that of Fe–Zr ($-25$ kJ/mol). Therefore, substituting Fe with Co increases the density and viscosity of liquid atoms, which leads to atom rearrangement. After crystallization, the distribution ratio of element atoms in the crystallization phase is different, which leads to a difference of the lattice constant. The crystallization phase α-Fe has a body-centered cubic structure (bcc). The lattice constants of pure α-Fe and pure α-FeCo are 2.8664 and 2.8550 Å, respectively. For Co-free alloys, the lattice constant of the α-Fe phase is much lower than that of pure α-Fe. It shows that some B atoms enter the α-Fe lattice to form the α-Fe(B) solid solution for Fe$_8$Zr$_7$B$_9$ alloy. With the increase in Co content, the lattice constant first increases up to 21 at.% Co and then decreases. The increase in lattice constants shows that the increase in Co content inhibits the solid solubility of the B atom in α-Fe. When the ratio of Co is 21 at.%, the lattice constant is close to that of pure α-Fe. That is to say, few Co/B atoms dissolve in α-Fe, and Co/B atoms are mainly distributed into the residual amorphous matrix. With the further increase of Co content, the lattice constant decreases and is lower than that of pure α-Fe, indicating that some Co dissolves in α-Fe gradually.
Fe is distributed in the remaining amorphous matrix. For Fe$_{44}$Co$_{42}$Zr$_7$B$_9$ alloy, Zr is also enriched in the remaining amorphous phase. The nanocrystal does not contain Zr and contains lots of Fe and some Co. The Zr and the other part of Fe and Co are distributed in the remaining amorphous matrix. There is little change in Co concentration between the nanocrystal and the remaining amorphous matrix. For Fe$_{42}$Co$_{12}$Zr$_7$B$_9$ alloy, Zr is enriched in the remaining amorphous phase. The nanocrystal does not contain Zr and contains many Fe and Co. The content of Fe in the remaining amorphous matrix is significantly less than that in the nanocrystal. The content of Co in the remaining amorphous matrix is slightly higher than that in the nanocrystal. This is similar to the study of the result by Ping et al. [5]. These authors reported that for Fe$_{44}$Co$_{42}$Zr$_7$B$_9$Cu$_4$ alloy, Co was preferentially partitioned in the remaining amorphous phase, which was attributed to the large negative heat of mixing between Co and Zr atoms.

The specific saturation magnetization ($M_s$) and coercivity ($H_c$) of the as-quenched Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 0, 7, 14, 21, 28, 35, 42$) alloys and the annealed alloys are given in Fig. 7. The saturation magnetization $M_s$ of the as-quenched alloys increases sharply up to 28 at.% Co and then decreases with a further increase in the Co content. The variation in $M_s$ of the annealed alloys is similar to that of the as-quenched alloys. All the $M_s$ values of the annealed alloys are greater than those of the as-quenched alloys. It is worth noting that a high Co content does not necessarily ensure a high $M_s$ value. The $M_s$ values first increase with increasing Co content and then decrease with a further increase in the Co content. Similar results were obtained for other FeCo-based alloys [15, 22].

The coercivity $H_c$ of the as-quenched alloys varies negligibly with increasing Co content. The variation in $H_c$ of the annealed alloys is remarkably different — $H_c$ decreases rapidly up to 21 at.% Co and changes only negligibly with further increase in the Co content. For the amorphous nanocrystalline two-phase alloy, the intergranular magnetic coupling between adjacent nanocrystals through the residual amorphous phase suppresses the magnetocrystalline anisotropy, affording excellent soft magnetic properties. Suzuki et al. [23] revealed that $H_c$ is directly proportional to $D^3$ and $V_{cry}$. In addition to grain size $D$ and crystallization volume fraction $V_{cry}$, the value of $H_c$ is also related to the uniformity of grain distribution. For the Fe$_{83}$Zr$_7$B$_9$ alloy, $D$ and $V_{cry}$ are relatively large. Moreover, grain agglomeration is evident, and therefore, $H_c$ is large. Both $D$ and $V_{cry}$ decrease with increasing Co content, thereby leading to a decrease in $H_c$. However, the magneto-crystalline anisotropy constant of $\alpha$-Fe(Co) is greater than that of $\alpha$-Fe [24]. For Fe$_{84-x}$Co$_x$Zr$_7$B$_9$ ($x = 28, 35, 42$) alloys, the decrease in $H_c$ is small, even if the grain size continues to decrease with increasing...
Fig. 6. TEM image (a–c), and STEM-EDS line-scan (d–f) of three kinds of amorphous alloy after annealing — (a, d) Fe₈₄Zr₇B₉; (b, e) Fe₆₃Co₂₁Zr₇B₉; (c, f) Fe₄₂Co₄₂Zr₇B₉.

Fig. 7. (a) Specific saturation magnetization ($M_s$) and (b) coercivity ($H_c$) of as-quenched Fe₈₄−ₓCoₓZr₇B₉ (x = 0, 7, 14, 21, 28, 35, 42) alloys and the annealed alloys.

Co content. All the $H_c$ values of the annealed alloys are lower than those of the as-quenched alloys. For Fe₈₄−ₓCoₓZr₇B₉ (x = 28, 35, 42) alloys, the difference between the $H_c$ values of the as-quenched and annealed alloys changes little.

4. Conclusions

1. Fe₈₄−ₓCoₓZr₇B₉ (x = 0, 7, 14, 21, 28, 35, 42) nanocrystalline alloys consisting of bcc nanograins embedded in the residual amorphous matrix were produced by crystallization of amorphous alloys. The crystallization and magnetic properties can be divided into two regions.

2. There are four exothermic peaks for Fe₈₄−ₓCoₓZr₇B₉ (x = 0, 7, 14, 21) alloys, and there are three crystallization exothermic peaks for Fe₈₄−ₓCoₓZr₇B₉ (x = 28, 35, 42) alloys during the crystallization.

3. The α-Fe(B) phase precipitates from amorphous matrix for Fe₈₄Zr₇B₉ alloy after annealing. With the increase in Co content, the lattice constant first increases up to 21at.% Co and then decreases. For Fe₈₄−ₓCoₓZr₇B₉ (x = 0, 7, 14, 21) alloys, the increase in Co content inhibits the solid solubility of B atom in α-Fe. For Fe₈₄−ₓCoₓZr₇B₉ (x = 28, 35, 42) alloys, Co dissolves in α-Fe gradually. With the increase in Co content, the crystallization volume fraction and grain size continue to decrease.

4. The grain size decreases significantly with the increase in Co content observed by TEM. For Fe₈₄Zr₇B₉ alloy, Zr is enriched in the remaining amorphous phase. The primary
nanocrystal contains lots of Fe, and the other part of Fe are distributed in the remaining amorphous matrix. For Fe$_{68}$Co$_{21}$Zr$_{7}$B$_{4}$ alloy, the nanocrystal does not contain Zr and contains lots of Fe and some Co. There is little change in Co concentration between the nanocrystal and the remaining amorphous matrix. For Fe$_{12}$Co$_{62}$Zr$_{7}$B$_{4}$ alloy, the content of Fe in the remaining amorphous matrix is significantly lower than that in the nanocrystal, and the content of Co in the remaining amorphous matrix is slightly higher than that in the nanocrystal. The content of Fe in the nanocrystal is higher than that of Co in the nanocrystal.

5. The saturation magnetization $M_s$ of both the as-quenched alloys and the annealed alloys increases sharply up to 28 at.% Co and then decreases with a further increase in the Co content. All the $M_s$ values of the annealed alloys are greater than those of the as-quenched alloys.

6. The coercivity $H_c$ of the as-quenched alloys changes little with the increase in Co content. $H_c$ of the alloys after annealing decreases rapidly up to 21 at.% Co and changes little with the further increase in Co content. $H_c$ values of the alloys after annealing are all lower than those of the as-quenched alloys. For Fe$_{84-x}$Co$_x$Zr$_7$B$_4$ ($x = 0, 7, 14, 21$) alloys, the higher the Co content is, the higher the difference in $H_c$ between alloys as-quenched and after annealing is. For Fe$_{84-x}$Co$_x$Zr$_7$B$_4$ ($x = 28, 35, 42$) alloys, the difference in $H_c$ between alloys as-quenched and after annealing changes little.

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