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Effect of Cu and P on the Crystallization Behavior of Fe-Rich Hetero-Amorphous FeSiB Alloy

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The effect of simultaneously adding P and Cu on the crystallization behavior of hetero-amorphous FeSiB alloy was investigated. Thermal properties and microstructure evolution were studied by means of X-ray diffraction, transmission electron microscopy, differential scanning, and isothermal calorimetric methods. It is found that the addition of P and Cu to the FeSiB alloy changes its crystallization temperature as well as the apparent activation energy for crystallization. The crystallization process is mainly dominated by three-dimensional growth with various nucleation rates for the selected FeSiB(PCu) alloys. The phases formed during crystallization for the different alloys of Fe83Si4B12, Fe83Si4B12Cu0.7, and Fe83Si4B12P0.7Cu0.7 are similar. The refinement effect of adding P and Cu to the FeSiB alloys is observed. The mean size of α-Fe phases decreases from 200 nm to about 20 nm. [doi:10.2320/matertrans.M2009206]

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1. Introduction

Fe-based amorphous and nanocrystalline alloys have triggered much interest and research activity in both academic/research community and the industrial community due to their excellent soft magnetic properties and commercial application prospects.1,2 In recent years,3,4–13 many researchers committed to improve the soft magnetic properties by adding elements (Nb, Zr and Cu) to Fe-based alloys. Great progress6,7,11–13 had been made by simultaneously adding P and small amounts of Cu into Fe-based alloys. A series of FeSiBPCu hetero-amorphous alloys5,12 with high Fe content have been developed, which exhibited excellent soft magnetic properties compared with the typical Fe78Si4B12 amorphous alloy in practical use currently. Recent work reported that the Fe83Si4B12P0.7Cu0.7 alloy exhibits low coercivity ($H_C$) of about 7 A/m and high saturation magnetic flux density ($B_S$) of about 1.88 T (as shown in Fig. 10 of Ref. 12). As we know, controlling crystallization behaviour is the key to the realization of nanocrystalline structure. In this work three alloys with the compositions of Fe83Si4B12, Fe83Si3B12Cu0.7 and Fe83Si3B3CuP4Cu0.7 were selected. We will focus on the effects of simultaneously adding P and Cu on thermal properties and microstructure evolution for the hetero-amorphous FeSiB(PCu) alloys.

2. Experimental Procedure

Alloy ingots were prepared by arc-melting of Fe (99.98 mass%), Si (99.98 mass%), B (99.5 mass%), Cu (99.99 mass%) and pre-alloyed Fe-P (99.9 mass%) in a purified argon atmosphere. Rapidly solidified ribbons were fabricated by a single-roller melt-spinning facility in air. The melt-spin ribbons were about 1–2 mm in width and 20 μm in thickness. The structure of the ribbons was identified by X-ray diffraction (XRD) with Cu-Kα radiation and transmission electron microscopy (TEM). Thermal properties of melt-spun ribbons were measured with a differential scanning calorimeter (DSC) under flowing high purity argon. A set of DSC scans were obtained at heating rates ranging from 5 to 80 K/min. For the isothermal analysis, the melt-spun samples were first heated (at a rate of 10 K/min) to a fixed temperature, then, maintained for a certain period of time until the completion of the first exothermic process. All specimens were annealed at appropriate temperatures for 10 min in a vacuum furnace.

3. Results and Discussions

3.1 Thermal properties

3.1.1 Continuous heating

The XRD profiles for the melt-spun Fe83Si4B12, Fe83Si4B12Cu0.7 and Fe83Si4B12P0.7Cu0.7 alloys are shown in Fig. 1. All melt-spun samples were identified to be amorphous. However, a few additional weak diffraction peaks corresponding to crystalline phases were detected for the melt-spun Fe83Si4B12 and Fe83Si4B12Cu0.7 alloys. The local structure of the melt-spun Fe83Si4B12 and Fe83Si4B12Cu0.7 alloys was investigated by TEM. The rather sharp selected area electron diffraction (SAED) patterns suggest the existence of nanocrystallines in the as-quenched Fe83Si4B12 and Fe83Si3B12Cu0.7 alloys. For the Fe83Si4B12 alloy, the α-Fe with a grain size of 10–25 nm are embedded in an amorphous matrix (shown in Fig. 2(a)). The dispersion of many crystal-like clusters with a size of 5–10 nm in the amorphous matrix was observed in the HRTEM image for the as-quenched Fe83Si4B12Cu0.7 alloy (shown in Fig. 2(b)). Figure 3 presents the DSC scans of the selected compositions at a heating rate of 40 K/min. There are two
exothermic peaks for all the selected compositions, which indicates that the crystallization behavior for the alloys studied is similar and belongs to primary crystallization. Furthermore, the onset crystallization temperature ($T_{x1}$) and peak temperature ($T_{p1}$) of the first exothermic peak for the Fe$_{83}$Si$_{3}$B$_{12}$Cu$_{0.7}$ alloy (shown in Fig. 3(b)) occur at 702 K and 713 K, respectively, which are much lower than those of the Fe$_{84}$Si$_{4}$B$_{12}$ alloy. Previous investigation also indicated that $T_{x1}$ and $T_{p1}$ decreased by adding 1 at%Cu to the FeSiB alloy.

Figure 4 shows the DSC curves measured at heating rates of 5, 10, 20, 40, 60 and 80 K/min under flowing high purity argon for the Fe$_{83}$Si$_{3}$B$_{8}$P$_{4}$Cu$_{0.7}$ alloy. It is clearly seen that the $T_{x1}$, $T_{x2}$, $T_{p1}$ and $T_{p2}$ shift to higher temperatures with increasing heating rates.

The apparent activation energy of the first exothermic peak can be calculated by the Kissinger’s equation:

$$\ln \left( \frac{T^2}{\beta} \right) = \ln \left( \frac{E_a}{R} \right) - \ln \nu + \frac{E_a}{RT}$$  (1)

where $\beta$ is the heating rate, $E_a$ is the activation energy, $\nu$ is the frequency factor, and $R$ is gas constant. Plotting $\ln(T^2/\beta)$ versus $1/T$, a straight line can be fit with the slope of $E_a/R$, thus the apparent activation energy could be calculated (shown in Fig. 5).

Another method is also introduced to calculate the crystallization activation energy using Doyle-Ozawa’s method with the following equation:

$$\lg \beta = \lg \left[ \frac{AE_a}{RF(\alpha)} \right] - 2.315 - \frac{0.4567E_a}{RT}$$  (2)

where the definitions of $\beta$, $E_a$ and $R$ are the same as those in eq. (1), $A$ is a constant, and $F(\alpha)$ is the crystallization fraction. The apparent activation energy (shown in Table 1) can be calculated from the $-0.4567E_a/R$, which is the slope of a straight line plotted $\lg(\beta)$ versus $1/T$ (shown in Fig. 6). Table 1 lists the results of the apparent activation energy.
crystal-like clusters with a size less than 3 nm. Thus, the FeSiBPCu has a hetero-amorphous structure including nucleation and growth, respectively. The value of activation energies deduced from the onset crystallization alloys, which is associated with the decreasing of calculated using the above methods, in which \( E_x \) and \( E_p \) are the apparent activation energy for the onset crystallization temperature and the peak temperature of the first exothermic peak, respectively.

It is well known that the onset crystallization temperature of an amorphous alloy refers to the beginning of phase precipitation from the amorphous matrix, while the peak temperature corresponds to the impingement of the crystals. Therefore, the onset crystallization temperature is considered to be associated with the nucleation process, and the peak temperature with the growth process. Thus, the activation energies deduced from the onset crystallization temperatures and the peak temperatures correspond to nucleation and growth, respectively. The value of \( E_x \) is lower than that of \( E_p \) in the FeSiB alloy, implying that the nucleation process of the FeSiB alloy is easier than the growth process. It is clearly seen that \( E_x \) and \( E_p \) increase with the addition of Cu and the combination of Cu and P to the FeSiB alloy. The crystallization process becomes much harder in the FeSiB alloy and FeSiB alloys, which is associated with the decreasing of \( T_x \) and \( T_p \). The mobility of elements strongly decreases at lower temperatures. It is known that the crystallization process is related to the microstructure of the alloy in as-quenched state. As shown in Fig. 2, the FeSiB alloy consists of crystalline phases detected by TEM observations. However, FeSiBPCu has a hetero-amorphous structure including crystal-like clusters with a size less than 3 nm. Thus, the embedded crystallites in the as-quenched FeSiB alloy may reach the critical size of crystal nucleus, and directly grow since the value of \( E_x \) and \( E_p \) is lower. Due to the adverse interactions among the constituent elements, crystal-like clusters formed in the FeSiB alloy with addition of P and Cu. The formed crystal-like clusters would serve as the nucleation sites for the \( \alpha \)-Fe phase. This similar effect has already been reported in a representative nanocrystalline soft magnetic alloy named as "Nanoperm". The size of the crystal-like clusters is much smaller than the critical size for nucleation because of the higher \( E_x \) for the FeSiB alloy. It is helpful to form a high number of crystal nuclei. The higher \( E_p \) contributes to suppression of grain growth, which is helpful to produce nanocrystalline structure for FeSiB alloys during annealing.

Moreover, amorphous alloys with a large \( \Delta T \) are likely to form a uniform nanocrystalline structure when annealed between the two crystallization peaks. Also, the resulting microstructure will not have any compounds with large magnetocrystalline anisotropy. Early work also pointed out that larger \( \Delta T \) is favorable to obtain good soft magnetic properties.

### 3.1.2 Isothermal annealing

The isothermal crystallization kinetics of the first exothermic peak for the FeSiB alloy and FeSiB alloys were further studied using DSC. As shown in Fig. 7, all the DSC scans exhibit a single exothermic peak corresponding to the first crystallization event after an incubation period. The isothermal crystallization kinetics are usually interpreted in terms of the standard nucleation-growth model formulated by Johnson-Mehl-Avrami (JMA). As shown below, it gives a relationship between the crystallized volume fraction and the time.

\[
\chi(t) = 1 - \exp[-k(t - \tau)^n]
\]  

where \( \chi(t) \) is the crystallized volume fraction at time \( t \), \( k \) is a reaction rate constant, \( \tau \) is the incubation period before the crystallization begins, \( t \) is the annealing time, and \( n \) is the Avrami exponent, which indicates the crystallization mechanism. Figure 8 shows the calculated crystallized volume fraction as a function of annealing time for the FeSiB(PCu) alloys. The value of \( n \) can be determined using the following relationship:

\[
\ln \left( \frac{1}{1 - \chi} \right) = \ln k + n \ln(t - \tau)
\]
Plotting $\ln[\ln(1/(1 - \chi))]$ versus $\ln(t - \tau)$ for the selected alloys annealed at different temperatures, we obtained the JMA plots as shown in Fig. 8. The value of $n$ is the slope of the straight line fitted by the least squares method for the data ($5\% < \chi < 95\%$) in the curves of Fig. 9. The value of $n$ is about 3.0 for Fe$_{84}$Si$_4$B$_{12}$ annealed isothermally at 660 K, 2.6 for Fe$_{83.3}$Si$_4$B$_{12}$Cu$_{0.7}$ annealed at 646 K, and 2.7 for Fe$_{83.3}$Si$_4$B$_3$P$_4$Cu$_{0.7}$ annealed at 635 K. The values of $n$ are range from 2.5 to 3, which indicates that the crystallization mechanism followed inhomogeneous nucleation and diffusion-controlled three-dimensional growth.\(^{25}\)

It is obvious that the plots of $\ln[\ln(1/(1 - \chi))]$ versus $\ln(t - \tau)$ are not simple straight lines, indicating that the Avrami exponent $n$ is not a constant during the whole crystallization process of an amorphous alloy. Therefore, the so-called local Avrami exponent was introduced by Calka\(^{26}\) which is defined as the first derivative of the Avrami exponent with respect to the crystallized volume fraction. The local Avrami exponent can be deduced by the equation:

$$n(\chi) = \frac{\partial \ln \left( \frac{1}{1 - \chi} \right)}{\partial \ln(t - \tau)} \quad (5)$$

Figure 10 shows the local Avrami exponents as a function of crystallized volume fraction for the as-quenched Fe$_{84}$Si$_4$B$_{12}$, Fe$_{83.3}$Si$_4$B$_{12}$Cu$_{0.7}$, and Fe$_{83.3}$Si$_4$B$_3$P$_4$Cu$_{0.7}$ alloys isothermally annealed at different temperatures. The local Avrami exponent is not considered for a crystallized volume fraction lower than 5\% or higher than 95\% because of large error. For the Fe$_{84}$Si$_4$B$_{12}$ alloy annealed at 660 K, the value of $n(\chi)$ decreases with the crystallized volume fraction between 5\% and 50\%, and stabilizes after the crystallized volume fraction exceeds 50\%. This behavior indicates that the crystallization process is governed by three-dimensional growth with decreasing nucleation rate at the initial stage of crystallization, and that the nucleation rate remains relatively constant when the crystallized volume fraction exceeds 50\%. This may result from the pre-existing crystalline phase in the amorphous matrix. For Fe$_{83.3}$Si$_4$B$_{12}$Cu$_{0.7}$ annealed at 646 K, the value of $n(\chi)$ lies between 2.5 and 3 when the crystallized volume fraction is between 5\% and 30\%. The $n$ steadily decreases to around 2.0 for fraction beyond 30\%, indicating that the subsequent crystallization process is controlled by a one-dimensional diffusion process (nucleation and growth).\(^{25}\) For the Fe$_{83.3}$Si$_4$B$_3$P$_4$Cu$_{0.7}$ alloy annealed at 635 K, during the main stage of crystallization, i.e., $5\% < \chi < 85\%$, the value of $n(\chi)$ is almost the same,
implying that the main crystallization process is governed by three-dimensional growth with a constant rate of nucleation. It may be associated with the presence of crystal-like nano-clusters in the hetero-amorphous alloy. When the crystallized volume fraction exceeds 85%, the growth of existing nuclei.

### 3.2 Thermal stability and microstructure evolution

Figure 11 shows XRD profiles for all the alloys annealed at 748 K for 10 min. In the case of the Fe$_3$Si$_4$B$_{12}$ alloy, the Fe$_2$B, Fe$_2$B and α-Fe phases were formed. For Fe$_{83.3}$Si$_4$B$_{12}$Cu$_{0.7}$ alloy, both Fe$_2$B and α-Fe were identified. For the Fe$_{83.3}$Si$_4$B$_4$P$_3$Cu$_{0.7}$ alloy, only α-Fe was detected. TEM observations confirmed that the presence of α-Fe in these alloys (shown in Fig. 12). In the SAED pattern of the Fe$_3$Si$_4$B$_{12}$ alloy, there are some crystalline phases except α-Fe phase randomly dispersed. These crystallites might correspond to Fe-B compounds taking into account the XRD results. The precipitation of metastable phase of Fe$_2$B, the stable phases of Fe$_2$B and α-Fe shows that more than one interaction occurred during the crystallization of the Fe$_3$Si$_4$B$_{12}$ alloy, which is confirmed by DSC measurement, showing that the first exothermic peak has decreased in peak height and increased in peak width (shown in Fig. 3). Commonly, amorphous FeSiB subjected to annealing transforms to firstly α-Fe phase, metastable Fe$_3$B and stable Fe$_2$B phase, then, Fe$_2$B phase decomposes into the final Fe$_2$B and α-Fe. Furthermore, the formation of Fe$_2$B with high magnetocrystalline anisotropy could deteriorate the soft magnetic properties. Optimized annealing temperature should be considered to avoid the precipitation of Fe$_2$B and Fe$_3$B in the FeSiB(PCu) alloys. When the annealing temperature increases to 843 K above the second peak temperature, the Fe$_2$B and Fe$_2$B were also formed in the Fe$_{83.3}$Si$_4$B$_4$P$_3$Cu$_{0.7}$ alloy (shown in Fig. 13). For the Fe$_3$Si$_4$B$_{12}$ and Fe$_{83.3}$Si$_4$B$_{12}$Cu$_{0.7}$ alloys, only Fe$_2$B and α-Fe were formed. This suggests that the precipitated phases in these alloys are similar during the crystallization process.

As mentioned above, the different microstructure in the as-quenched state could result in various grain sizes during subsequent annealing process by taking into account the difference of apparent activation energy for the selected alloys, which is confirmed by the TEM observations. The grain size of α-Fe in the annealed Fe$_3$Si$_4$B$_{12}$ alloy is in the range of 20~200 nm (shown in Fig. 12(a)) which may result from the pre-existing crystals with higher growth rate than the crystals formed later. For the annealed FeSiB alloy with addition of 0.7 at%Cu, the grain size decreases to 20~90 nm
(shown in Fig. 12(b)). On the other hand, the annealed Fe$_{83.3}$Si$_x$B$_{12-y}$P$_4$Cu$_{0.7}$ alloy is composed of a uniform nano-crystalline structure with grain size of about 20 nm (shown in Fig. 12(c)), which results from the high densely dispersed nano-clusters or absence of coarse crystallites phase in the as-quenched state, and the highest apparent activation energy. The complexity of atomic size and the various interactions among the constituent elements may contribute to the high thermal stability against crystallization, which is consistent with the results of the thermal analysis. The atomic mobility decreases in the alloys with more alloying elements. It is also difficult to form more stable phases after long-range diffusion. As a result, Fe$_{83.3}$Si$_x$B$_{12-y}$P$_4$Cu$_{0.7}$ exhibits excellent soft magnetic properties, resulting from the uniform nanocrystalline structure and only $\alpha$-Fe phase precipitation.

4. Conclusions

The thermal properties and microstructure evolution of the annealed Fe$_{84-x}$Si$_x$B$_{12-y}$P$_y$Cu$_z$ ($x$: 0 and 0.7, $y$: 0 and 4) alloys are investigated.

1) The addition of 4 at%P and 0.7 at%Cu to FeSiB alloys shifts $T_{x1}$ and $T_{p1}$ to lower temperatures and increases the apparent activation energy. The structure of the hetero-amorphous Fe$_{83.3}$Si$_x$B$_{12-y}$P$_y$Cu$_{0.7}$ is more stable in the as-quenched state.

2) The crystallization process is mainly dominated by three-dimensional growth with various nucleation rates for the various Fe$_{84-x}$Si$_x$B$_{12-y}$P$_y$Cu$_z$ ($x$: 0 and 0.7, $y$: 0 and 4) alloys.

3) The crystallization phases are similar for all the alloys studied. The grain size decreases from 200 nm to about 90 nm with addition of 0.7 at%Cu, and dramatically decreases to about 20 nm with simultaneous addition of 4 at%P and 0.7 at%Cu to FeSiB alloy.

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REFERENCES