Preparation and magneto-nanocrystallization of amorphous alloy Fe$_{60}$Co$_{26}$Hf$_{7}$B$_{6}$Cu$_{1}$

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Abstract. Amorphous alloy ribbons Fe$_{60}$Co$_{26}$Hf$_{7}$B$_{6}$Cu$_{1}$ (3mm in width and 30μm in thickness) were prepared using the single-roller melt-spinning technique. Amorphous specimens were treated by pulsed magnetic field with lower frequency. The microstructure and crystallization of amorphous specimens were investigated by Mössbauer spectroscopy, XRD and TEM etc. The results show that the magnetic pulsing can induce the crystallization of amorphous alloy at low temperature. With the increasing of pulsing frequency, the precipitated fraction and corresponding hyperfine magnetic field of the base metal phase α-Fe(Co) is increased.

1. Introduction

Nanocrystalline alloys obtained by primary crystallization of Fe-based amorphous alloys have been extensively investigated in the last 15 years. FINEMET- Fe-Co-M-B-Cu (M =Zr, Nb, Hf) alloys are examples of such materials, which have been developed from Fe–Zr–B glass-forming alloys. Cu is added as a nucleating agent and Nb/Zr/Hf restrict the size of the nanocrystalline bcc phase. Partial substitution of Co by Fe in Fe-Co-M-B-Cu (M =Zr, Nb, Hf) was proposed to extend the soft magnetic behavior of nanocrystalline alloys up to higher temperatures. This new nanocrystalline alloy is one of the excellent candidates for soft magnetic materials used at high temperature applications with the range of 773–873K. In the present work, nanocrystallization behavior and evolution of microstructure on low-frequency magnetic pulsing treatment of amorphous Fe$_{60}$Co$_{26}$Hf$_{7}$B$_{6}$Cu$_{1}$have been investigated by using transmission electron microscopy (TEM), X-ray diffraction (XRD) and Mössbauer spectroscopy (MS).
2. Experimental

Mixed Fe、Co、Hf、B and Cu ingredients (purity above 99.99wt%), and then melted in a quartz tube with nozzle. The alloys were prepared in a vacuum induction melting furnace (Hechigen). Rapidly solidified ribbons were produced using a single roll melt spinner with the surface linear velocity of a copper wheel at a speed of 39m/s (the equipment named Edmund Bühler in Institute of Metal Reserch Chinese Academy of Sciences), in an argon atmosphere at the temperature of 1300°C. Rapidly solidified ribbons of 3mm width and 30μm thickness were thus obtained. The samples were characterized by X-ray diffraction (XRD), Differential thermal analysis (DTA) and Mössbauer spectroscopy (MS). The samples were treated on the low-frequency magnetic/current pulsing equipment, the treatment conditions were given in table 1.

| sample | Field intensity/Oe | frequency/Hz | Acting time/s |
|--------|--------------------|--------------|---------------|
| A0     | 0                  | 0            | 0             |
| A1     | 222                | 10           | 240           |
| A2     | 222                | 20           | 240           |
| A3     | 222                | 30           | 240           |
| A4     | 222                | 40           | 240           |

3. Results and discussion

Figure 1 shows the XRD patterns of Fe_{60}Co_{26}Hf_{7}B_{6}Cu_{1} alloy ribbons, and from the free and wheel-contacted surfaces of the alloy ribbon presented a broad peak. The as-quenched (A0) alloy was confirmed integral amorphous. Figure 2 (a) shows TEM images and corresponding selected area diffraction (SAD) patterns of as-quenched (A0) alloy sample. The featureless contrast in microstructure and diffused rings in SAD pattern confirms the presence of amorphous phase in the as-quenched sample. Combined the two results, the as-quenched (A0) alloy was further confirmed integral amorphous.
Figure 1. The XRD patterns of Fe_{60}Co_{26}Hf_{7}B_{6}Cu_{1} alloy ribbons.

Figure 2. TEM morphology and SAD pattern of specimen Fe_{60}Co_{26}Hf_{7}B_{6}Cu_{1}.

Figure 3 shows the Mössbauer spectrum of as-quenched (A0) alloy and the samples after the low-frequency magnetic pulsing treatment (because the trait of Mössbauer spectrum of amorphous have no big difference, just the spectrum of A0, A2 and A4 are given), the fitting results are shown in Table 2.
Figure 3. Mössbauer spectra of amorphous alloy specimens before and after treatment. 
(a) as-quenched A0; (b) after treatment A2; (c) after treatment A4

The Mössbauer spectra of samples (A0) are shown in Figure 3. It is immediately obvious from this figure that the spectrum is a non-symmetrically broadened sextet, typical of an amorphous material. After the treatment, the spectra have no big change. However, when the frequency change from 10Hz to 40Hz, the relative intensity ratio (A2,5/A3,4 of peak 2 (or 5) and peak 3 (or 4)) is from 2.73 to 1.74 respectively which given in Table 2. By the formula:

\[
b = \frac{A_{2,5}}{A_{3,4}} = \frac{4\sin^2 \theta}{1 + \cos^2 \theta}
\]  

where \( \theta \) is the angle between the \( \gamma \)-ray propagation direction and the direction of the magnetic hyperfine field. On these grounds, the decrease in \( b \) indicates that a rotation of the average magnetic moment directions from the in-plane ( \( \theta = 90^\circ \) ) to the out-of-plane orientation has taken place. The transmission Mössbauer \( \gamma \)-ray experiment is the vertical incidence of the sample surface, so \( \theta \) from 0 \( ^\circ \) → 90 \( ^\circ \), corresponding to the \( b \) from 0 → 4, the corresponding hyperfine magnetic field direction of the transition from the vertical surface parallel to the surface. For ferromagnetic polycrystal of disorder magnetic moments, \( b=A2,5/A3,4=2.0 \). While for the alloy ribbon prepared using a single roll melt spinner that the magnetic moment is parallel to the swing direction, the value of \( b \) is bigger than 2.0 (Table 2). The increase of the frequency, consisting in a decrease of the relative intensity ratio of the second (fifth) to the third (fourth) lines. In other words, the microstructure manipulation had taken
place. In Table 2, with field strength of 222Oe, the acting time of 240s, the frequency of 20–30Hz, initial crystallization appeared—the volume fraction of precipitated phase (α-Fe(Co)) is 0.5%. When the frequency increased by 40Hz, the volume fraction of precipitated phase (α-Fe(Co)) got to 3.5%. So the volume fraction of crystallization phase increased with the increase of the frequency of magnetic field.

| samples    | Phase structure       | A2.5/A3.4 | Hhf(KOe) | H*hf(KOe) |
|------------|-----------------------|-----------|----------|-----------|
| A0 (as-quenched) | amorphous             | 2.73      | 269.47   | —         |
|            |                       |           | 308.38   |           |
|            |                       |           | 267.48   |           |
|            |                       |           | 229.50   |           |
| A1 (222Oe, 240s, 10Hz) | amorphous             | 2.66      | 232.04   | —         |
|            |                       |           | 292.43   |           |
|            |                       |           | 250.44   |           |
|            |                       |           | 300.85   |           |
|            |                       |           | 220.91   |           |
| A2 (222Oe, 240s, 20Hz) | amorphous             | 2.69      | 294.38   | —         |
|            |                       |           | 249.02   |           |
|            |                       |           | 303.27   |           |
|            |                       |           | 170.08   |           |
| A3 (222Oe, 240s, 30Hz) | Residual amorphous+0.5% | 2.35      | 150.38   | 262.03    |
|            | α-Fe(Co)              |           | 210.94   |           |
| A4 (222Oe, 240s, 40Hz) | Residual amorphous+3.5% | 1.74      | 261.74   | 319.44    |
|            | α-Fe(Co)              |           | 263.48   |           |
|            |                       |           | 284.35   |           |

The results show that the crystallization of the Fe_{60}Co_{26}Hf_{7}B_{6}Cu_{1} amorphous alloy can be promoted by the low-frequency pulse magnetic field at the room temperature, a temperature rise of less than 20°C. The DTA curve shows that crystallization only can occur at the temperature of Tp1=515°C. From the TEM results in Figure 2 (b), grain size of the crystallization phase is about 10 nm. In short, the amorphous alloy treated by pulsating magnetic field could be nanocrystallized at lower temperature.

Magnetic moments of Fe atoms tend to orient towards the direction of external magnetic field ($\vec{H}_p$) due to the magnetic interaction ($E_H = -\mu_0 M_s H_p \cos \phi$, where $\mu_0$ is vacuum permeability, $M_s$ is spontaneous magnetization, $\phi$ is the angle between the atomic magnetic moment direction and
the direction of pulsing magnetic field $\vec{H}_p$ between the atomic magnetic field and hyperfine magnetic field. The magnetic moments constantly changed in orientation and vibrated in the process of magnetic pulsing. It subsequently led to the change of the distance between each atom. Namely the phenomenon was associated with the macroscopic magnetostriction ($E_\perp = \frac{1}{2} \lambda_s \sigma \sin^2 \theta$, where $\lambda_s$ is saturation magnetostriction, is the angle between magnetization direction and the direction of stress). The atom would across potential barrier of energy and change from metastable amorphous state to stable crystalline state in proper condition. The periodical vibrations of atoms due to the pulsating magnetic-field action increase the initial energy of atoms, 

$$E = E_\| + E_\sigma = -\mu_0 M_\perp H_\perp \cos \phi + \frac{1}{2} \lambda_s \sigma \sin^2 \theta$$

as a result, the potential barrier $u$ of nucleation of amorphous alloy was relatively reduced hence the nucleation rate of matrix metal phase was increased. That is the low-frequency magnetic-field, which promote the crystallization. The increase of frequency of pulsing led to the increase of the vibratory frequency, so that the diffusion factor $D(D = D_0 \exp[-u/KT]$, where $D_0$ is a constant, $D_0 = a^2 \nu / 6$) increased. The nucleation rate determined by the following equation:

$$I = I_0 \exp[-\Delta G/KT] \exp[-u/KT]$$

This suggests that increase in pulse frequency will increase the diffusion coefficient of atoms to fill the gap of amorphous structure of non-ferrous atom, so the degree of precipitation is increased. The metal matrix phase $\alpha$-Fe(Co) crystallization precipitation increased, at the same time, the crystalline precipitate of the corresponding value of hyperfine magnetic field increased (from 262.0 kOe to 319.4 kOe) due to weakened metal iron and other non-iron hybrid electronic orbital effect.

Amorphous microstructure, crystallization precipitation situation to deal with the magnetic pulse parameters (frequency, field strength and the role of time) for the change remains to be further study.

4. Conclusions

(1) Fe$_{60}$Co$_{26}$Hf$_7$B$_6$Cu$_1$ alloy ribbons prepared by single-roller melt-spinning were confirmed integral amorphous.

(2) Low-frequency magnetic pulsing can lead to the structural transformation of Fe60Co26Hf7B6Cu1 alloy ribbons and the precipitation of crystallization phase-$\alpha$-Fe(Co).

(3) With the increase of pulsing frequency, the volume fraction of precipitated phase $\alpha$-Fe(Co) is increased from 0.5% to 3.5% and the hyperfine magnetic field is increased from 262.0 kOe to 319.4 kOe.

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