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A thermal analysis of the crystallization of amorphous $Fe_{87}Zr_7B_6$[1]

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Abstract

The investigation of nanocrystalline materials is one of the very active areas in the material science and engineering. An important way of achieving nanocrystalline structure is to properly anneal a corresponding amorphous material. In this paper, a detailed thermal analytical study to the crystallization annealing of so far widely interested Fe–Zr–B material was reported, in order to supply valuable information of obtaining optimum microstructure and to be instructive to annealing processes.

Keywords: Amorphous $Fe_{87}Zr_7B_6$; Crystallization characteristics; DTA analysis; TGA analysis

1. Introduction

In recent years it was discovered that within suitable composition range of Fe–Zr–B material series one can achieve excellent high-frequency soft magnetic properties by developing a proper nanocrystalline structure, thus enable the material to be used in high-frequency magnetic cores and sensors. Makino et al. [1] reported an AC effective permeability μ_e of over 30 000, and Kim et al. [2] reported that with very small addition (1% atm.) of Ag, Cu to $Fe_{87}Zr_7B_6$ basic material and suitable annealing to the amorphous state to form nanocrystalline structure, μ_e can be further increased to over 100 000. These results attracted many more works, and Makino et al. [3] searched over a wide range in the Fe–Zr(Nb)–B pseudo-ternary phase diagram, or fixed the composition and tried different ways, temperatures, heating rates and time periods during annealing [4] to look for optimum conditions for the best result. Since the final structure will largely be affected by the annealing courses, a systematic thermal analysis will be effective for our understanding of the controlling mechanisms during crystallization. In this paper we report some of our results of samples with a typical composition of $Fe_{87}Zr_7B_6$ using various thermal analytical equipments such as DTA, DSC, TGA together with some X-ray diffraction data.

2. Experimental

Fe (99.9%), Zr (99.5%), and B (99.5%) were used to be melted using a radio frequency induction furnace with a protective atmosphere of pure Ar to form a homogeneous alloy ingot. The ingot was broken into pieces and put into a quartz tube with a small orifice at

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the lower end. The material was quickly melted again in R-F coil and pressed out from the orifice by an argon pressure. The molten jet impinged on the smooth rim of a rapidly rotating copper wheel with a tangential speed of 45 m/s. The cooling rate as high as 10^6 K/s made the molten jet suddenly solidified to form continuous ribbon with typical dimensions of 2 mm wide and 25 μm thick. The ribbon was first measured in a D/max-2c rotating target X-ray diffractometer. Then thermal analyzers of DTA-1700, DSC-7 and TGA-7 (produced by Perkin-Elmer) were used to measure the thermal curves with different heating rates of 5, 10, 20, and 40 K/min, respectively. During the TGA measurement a vertical magnetic field gradient was applied to the sample. Because the DSC-7 system has a very high heating and cooling rate which enables us to make abrupt stop during the heating course and rapidly cool the sample down to room temperature to monitor the evolution of crystallization process at each step.

3. Results and discussions

The X-ray diffraction spectrum shows that the as-quenched material was typically amorphous. Within a wide 2θ range (20–80°) only a dispersive peak was seen, without any trace of sharp peaks related to periodic lattice structure. We will mention later that we can have another even more sensitive way to prove the perfect amorphousness of the sample. From this fact we know that the crystallization consists of two steps of nucleation and growth of crystallites. Different ways and rates of heating will affect greatly the density of nuclei and thus the final size of crystallites and their distribution. From the theory of nucleation and grain growth it is not difficult to explain the experimental results of various researchers [1,2,7].

Fig. 1 shows a typical DTA curve of this material from room temperature to 800°C. Apparently, there are four exothermic peaks within the range. When we compared it with the X-ray diffraction data as well as

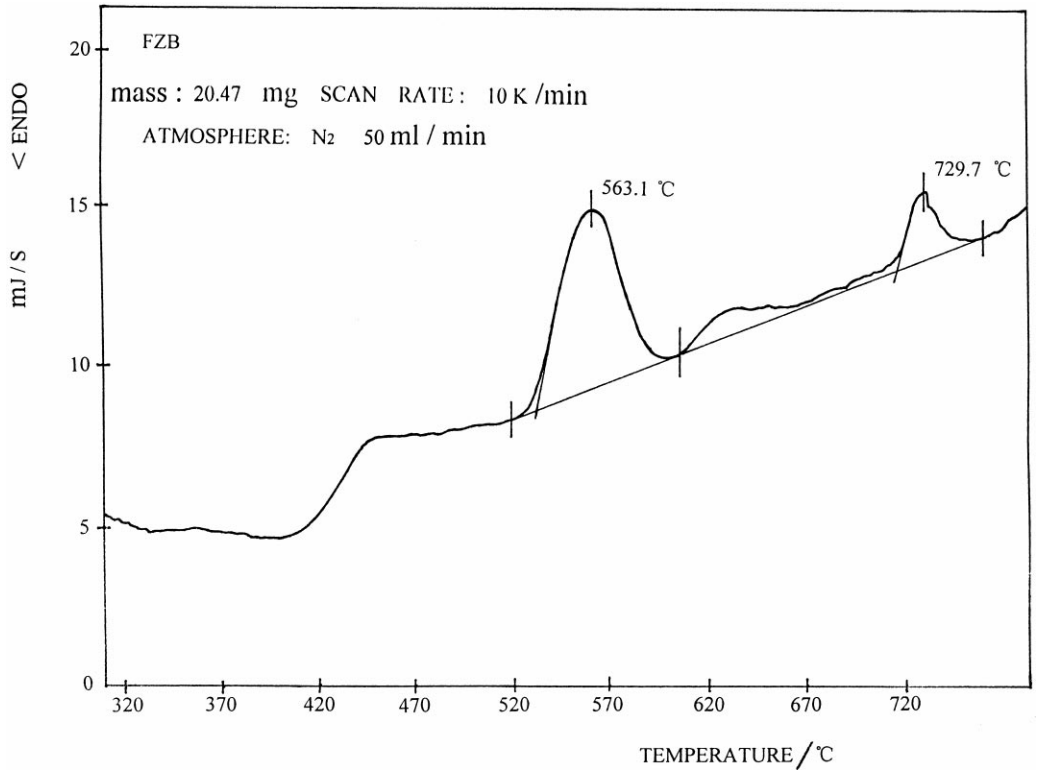

Fig. 1. A typical DTA curve of $Fe_{87}Zr_7B_6$ amorphous ribbon.

DTA curves with different heating rates, we found that only two peaks at 563°C and 729°C are related to the crystallization. The two lower peaks are a reflection of an exothermic plateau caused by the oxidation of Zr at the surface with the residual O_2 in the protection N_2 and (or) the O_2 trapped in the sample pan. According to Weast [5], α-Zr will readily be oxidized in a wide temperature range with a formation heat of 1048 kJ/mol, slightly surface oxidation can account for such a widespread exothermic behavior. Comparing with the DTA curve of the same composition and same heating rate in Fig. 1 of Ref. [2], we can see an excellent agreement for the first crystallization peak. But Ref. [2] did not give the whole picture of the crystallization. The second peak at 729°C reflects that after the large amount of α-Fe precipitated at the first stage, the final crystallization and phase separation of intermetallic compounds Fe_2Zr and Fe_2B take place. The products formed in this stage and their morphology will also be an important factor to the ultimate magnetic characteristics of the material.

Based on the first and second crystallization peak temperatures T_{p_i} relative to the DTA curves with different heating rates Φ, using well-known Kissinger method in crystallization dynamics, we plotted $\ln(T_{p^2}/\Phi)$ versus $1/T_p$. (Table 1, Fig. 2.) We can find good linear relations in both cases with linear regression correlation coefficients of 0.998 and 0.987, respectively. From the corresponding slopes we can calculate the activation energies E_a of these two crystallization processes to be 245.5 and 400.6 kJ/mol which will be useful in analyzing the activation behaviors from microscopic consideration. Comparing with the known data of similar amorphous materials as $Fe_{77}B_{23}$. (E_a=237.6 kJ/mol) [6], the activation energy is quite close, but the much higher T_p implies better thermal stability when the material is used at amorphous state.

Table 1
The first and second crystallization peak temperatures T_{p_i} with different heating rates Φ

	Heating rate Φ (K/min)			
	5	10	20	40
T_{p_1} (K)	822.6	836.1	856.4	873.4
T_{p_2} (K)	988.3	1002.7	1021.5	1029.2

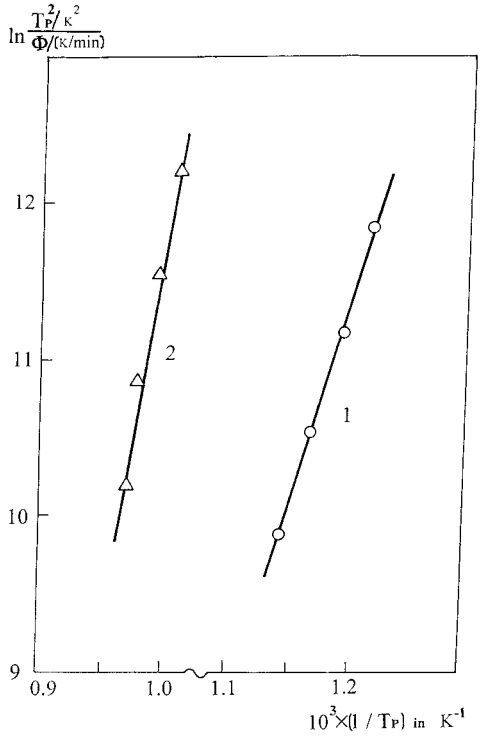

Fig. 2. Kissinger plots of first and second crystallization.

Fig. 3 shows the TGA curve of the sample with vertical gradient magnetic field applied. From the high initial value at the ordinate we can see that at room temperature the sample started with strong ferromagnetism. Because the average distance between nearest neighbor Fe atoms is quite different from that of bcc α-Fe, the exchange interaction between neighboring 3d electrons becomes much weaker, causing the much lower Curie temperature. We can see very steep drop of magnetic force above room temperature which makes it possible to be a potential candidate to be used as a special sensor. The high thermal stability of the amorphous state helps in this respect. The ferromagnetism of the sample disappears completely below 100°C. The existence of gradient magnetic field will have no detectable additional force on the sample. If we suddenly withdraw the field, the sensitive electronic balance does not show abrupt change in reading which is a strong evidence of the sample being homogeneous, perfectly amorphous, because for this material with extremely high percentage of Fe,

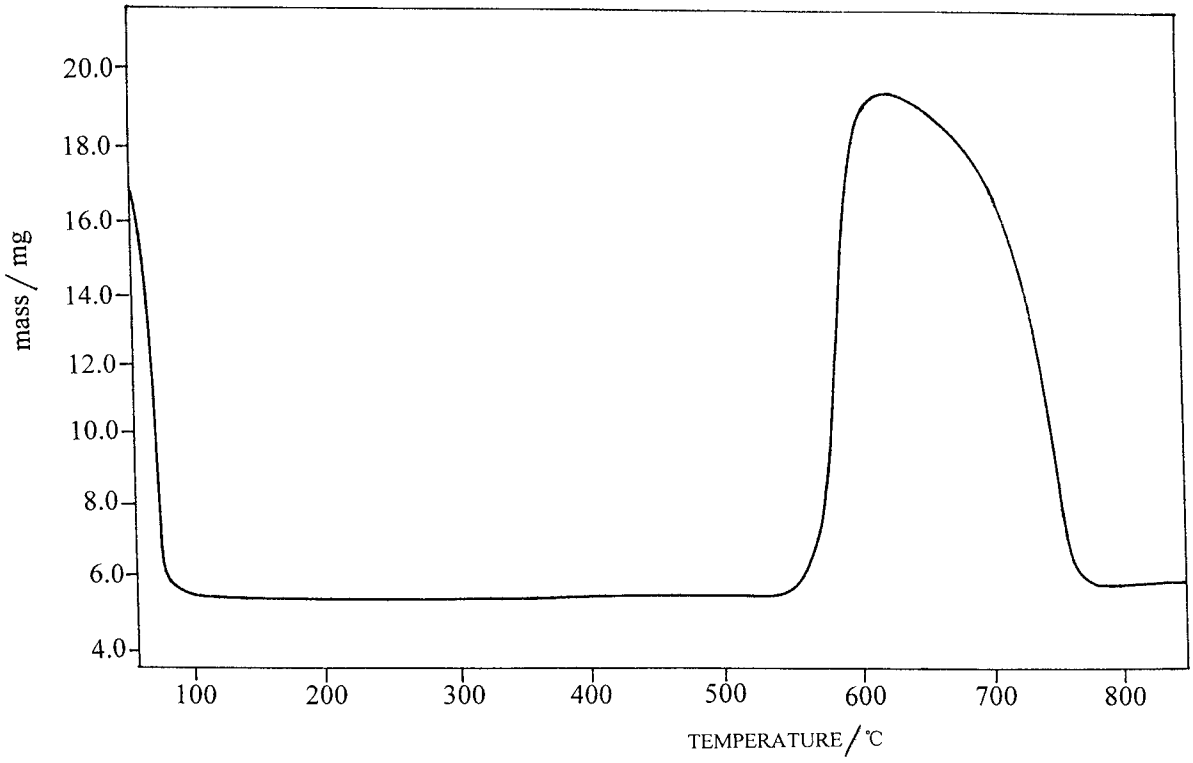

Fig. 3. TGA curve of $Fe_{87}Zr_7B_6$ with vertical gradient magnetic field applied.

ferromagnetic α-Fe crystallites are the most possible crystalline residual in amorphous matrix. This suggests another sensitive way of proving the perfect amorphousness of the sample. When the temperature reaches the first crystallization temperature, a large amount of α-Fe generated, the TGA curve started to raise steeply, and finally dropped to the bottom again when reached T_c of α-Fe.

4. Conclusion

Based on our study we conclude that in the recent current of nanocrystalline Fe–Zr–B studies, systematic thermal analysis is an effective way. The crystallization of this material consists of two stages. The first stage is the formation of α-Fe and the second stage is the phase separation of Fe_2B and Fe_2Zr leading to the complete crystallization.

To control the proper annealing conditions based on the dynamic crystallization theory we can optimize the grain size and the granular boundary to achieve desired properties, much works need be done in this respect. This series of material under amorphous state has fairly good thermal stability and unique thermal magnetic property which shows the potential to be further developed as a thermal-magnetic sensor.

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