The kinetics of amorphous–nanocrystalline transformation for a Finemet alloy

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Abstract

The kinetics of the nanocrystalline structure formation from its amorphous precursor was investigated for a Finemet alloy with the composition Fe\textsubscript{73.5}Nb\textsubscript{3}Cu\textsubscript{1}Si\textsubscript{13.5}B\textsubscript{9}. The time- and temperature-dependent transformation was followed in parallel by differential scanning calorimetry (DSC), thermoelectric power (TEP) and Vickers microhardness (HV) measurements on ribbon samples 10 mm wide. After annealing the samples in a tin bath at 500, 525, 550 and 575 °C for different annealing times between 5 s and 2 h, the TEP and HV data were measured at room temperature. Using the conventional Johnson–Mehl–Avrami method, for the apparent activation energy we deduced values from 3.58 to 3.93 eV from the TEP data and values from 3.84 to 4.08 eV from the HV data which agree well with the value we obtained from DSC measurements using the Kissinger method (4.1 ± 0.4 eV). Our DSC measurements on partially crystallized samples revealed a third intermediate exothermal peak beside the well-known two peaks. This was attributed to the segregation of a silicide compound out of the \(\alpha\)-Fe(Si) solid solution.

1. Introduction

Nanocrystalline materials can be obtained from any conventional metallic glass by controlled crystallization at relatively low temperatures (beneath the crystallization temperature) \cite{1}. Such nanostructures, however, are in a metastable state and, with sufficiently long annealing time or at high enough temperature, grain growth occurs up to the usual micrometre grain sizes. The peculiarity of the Finemet composition \cite{2} is that the desired magnetically soft nanostructure is relatively stable as a function of annealing time at a temperature around the first crystallization peak, between 790 and 880 K \cite{3, 4}, owing to the Cu and Nb additions to the Fe\textsubscript{77.5}Si\textsubscript{13.5}B\textsubscript{9} glass. The formation of nanostructure for the Finemet alloy has been found to occur by primary crystallization of Fe(Si) nanograins followed by the crystallization of the remaining amorphous matrix \cite{5, 6}. The two differential scanning calorimetry (DSC) peaks corresponding to the two stages of crystallization were found to be flatter and wider than those corresponding to the parent alloy (without Cu and Nb additions), suggesting a much slower kinetics of crystallization of this alloy, \textit{i.e.} a substantial decrease of the grain growth rate. Köster \textit{et al.} \cite{7} have shown that the radii of the primary crystals increase proportionally to the square root of annealing time and this can be used for calculating diffusivities. Allia \textit{et al.} \cite{8} claim that the Johnson–Mehl–Avrami (JMA) law can fit the experimental data over two narrow time–temperature intervals only, corresponding to the two steep decreases in the time dependence of the reduced electrical resistance \(r(t)\). Between these two decreases of \(r(t)\), a temperature-independent slowing-down occurs in a large annealing time interval where the resistance change cannot be described by the exponential-type JMA law.

While many studies exist on the crystallization of Finemet alloys \cite{2–8}, only a few data are available on the apparent activation energy. For the first stage of crystallization, 3.33 eV \cite{5} and 3.9–4.1 eV \cite{9} were reported for this quantity. The aim of this paper is to report some new experimental results on the kinetics of the formation of a nanocrystalline structure from its amorphous precursor, in order to optimize the soft magnetic properties of a Finemet alloy with the composition Fe\textsubscript{73.5}Nb\textsubscript{3}Cu\textsubscript{1}Si\textsubscript{13.5}B\textsubscript{9}.

2. Experimental details

The time- and temperature-dependent transformation was followed in parallel by DSC, room temperature thermopower and hardness measurements on
ribbon samples 10 mm wide. Short- and long-term heat treatments (between 5 s and 2 h) were carried out in a tin bath at 500, 525, 550 and 575 °C. The calorimetric studies were performed by a Perkin Elmer DSC-2 unit from room temperature up to 1000 K at different heating rates. The thermoelectric power was measured at room temperature with a home-made apparatus described in ref. 10. A Leitz-type Vickers microhardness tester was used for the determination of hardness under low loads (200 g) and an average of a minimum of ten readings was taken for each sample.

3. Results and discussion

The thermoelectric power (TEP) $S$ is very sensitive to the stage of crystallization in Fe-based alloys since the various phases appearing during this process have very different thermopowers: $\alpha$-Fe grains have a positive contribution to the TEP while the amorphous matrix gives a negative contribution which depends slightly on the boron content [10]. The boride compounds (both Fe$_3$B and Fe$_2$B) have large negative TEP values at room temperature [10]. In Fig. 1, the results of TEP measurements are shown as a function of the annealing time $t$ for the different annealing temperatures. The evolution of TEP reflects the various crystallization stages. At all annealing temperatures $T_a$, an incubation time $\tau$ can be observed which decreases with increasing $T_a$. In this stage ($t < \tau$), X-ray diffraction indicates no traces of $\alpha$-Fe grains; thus only structural relaxation occurs but not excluding precrystallization clustering.

Taking the starting time for TEP change as the incubation time of the transformation, we obtained:

$$\tau = 17 \text{ s, } 64 \text{ s, } 300 \text{ s and } 1000 \text{ s for } T_a = 575^\circ C, 550^\circ C, 525^\circ C \text{ and } 500^\circ C \text{ respectively. If we assume that the crystallized fraction is proportional to the change of TEP, we can carry out the JMA analysis of the measured data. Although probably not strictly correct, we may suppose that the development of a nanosized crystalline phase can be described in terms of a single (apparent) activation energy. The time difference corresponding to any fixed amount of transformation is then given by}$$

$$\ln(t - \tau) = A + Q/R T_a$$

where the activation energy $Q$ can be found from a plot of $\ln(t - \tau)$ against $1/T_a$. The present results give $Q = 3.58 \text{ eV}$ and $3.93 \text{ eV}$ for $\Delta S = 0.3 \mu \text{V K}^{-1}$ and $0.5 \mu \text{V K}^{-1}$ respectively.

Similar JMA analysis can be carried out on the basis of the mechanical hardness data. Figure 2 shows the result of microhardness measurements as a function of annealing time for different annealing temperatures. Precipitation of nanograins leads to a much stronger increase in microhardness than the primary crystallization of $\alpha$-Fe particles in the hypoeutectic Fe–B alloys [11].

Although the scatter of the hardness data ($\pm 50 \text{ HV}$) is much larger than that of the TEP data ($\pm 0.05 \mu \text{V K}^{-1}$), different incubation times can be determined by the two methods, especially at lower annealing temperatures. From the starting time of the HV change, we obtained incubation times $\tau = 10 \text{ s, } 60 \text{ s, } 110 \text{ s and } 350 \text{ s for annealing temperatures } T_a = 575^\circ C, 550^\circ C, 525^\circ C \text{ and } 500^\circ C \text{ respectively. Again we assume that the hardness change is proportional to the crystallized
fraction. By plotting $\ln(t-\tau)$ vs. $1/T_a$ where the times corresponding to $HV=1300$ and 1500 kg mm$^{-2}$ were taken, we can derive the apparent activation energies from the slope of the fitted straight lines, in accordance with eqn. (1). This analysis gives $Q=3.84$ eV and 4.08 eV respectively for the two arbitrarily selected hardness values. These $Q$ data are slightly higher than those obtained from the TEP data, probably because of the different apparent incubation times appearing in these experiments. The error of these determinations is rather high, about $\pm 0.5$ eV, so a comparison with a "classical" method is necessary.

Using the DSC thermographs, the value of activation energy was calculated according to the Kissinger method from the heating rate ($r$) dependence of the position $T_m$ of the first DSC peak (Fig. 3) with the help of the relation

$$\ln(r/T_m^2) = B - Q/RT_m$$

From the slope of the fitted straight line, an activation energy of $Q=4.1 \pm 0.4$ eV is obtained. The relatively high uncertainty is inherent to the limited range of heating rates that can be applied.

At low heating rates new stages of crystallization appear which overlap with each other as can be seen in Fig. 4. These new stages are probably connected with the appearance and disappearance of metastable products such as Fe$_{23}$B$_6$, Fe$_3$B, $\alpha$-Fe(Si) solid solution etc. A DSC apparatus working above our upper temperature limit (1000 K) is needed to elucidate all the crystallization stages and to determine precisely the enthalpy changes during crystallization.

Nevertheless, plots obtained with the actual DSC apparatus working only up to 1000 K can still help us to elucidate the relative contribution of the individual low temperature processes by using annealed samples with different degrees of partial crystallization. In Fig. 5, DSC plots are shown that were obtained on partially crystallized samples annealed at 550°C.

Annealing at 550°C, corresponding to the first DSC peak, activates only the precipitation of $\alpha$-Fe(Si) solid solution as was proved by X-ray diffraction experiments [12]: a magnetically soft Finemet material was found to be free of Fe$_3$Si segregations after annealing at 550°C for 2 h.

As Fig. 5 shows, an intermediate peak is revealed after annealing for 2 h which is covered by the first peak of the as-quenched sample. Its presence is indicated by the shoulder of the first peak. After annealing at a higher temperature (at 575°C for 2 h), the intermediate peak disappears and the X-ray pattern indicates the presence of Fe$_3$Si precipitates [12]. As a consequence, we attribute the third, intermediate, peak to the decomposition of the Fe(Si) solid solution. A very small enthalpy change is associated with this process, about half of that corresponding to the decomposition at 980 K of the remaining amorphous matrix which is $\Delta E_2 = 12 \pm 2$ J g$^{-1}$. The enthalpy change corresponding to the first stage of crystallization is $\Delta E_1 = 125 \pm 5$ J g$^{-1}$ which is more than 10 times larger than that corresponding to the "second" stage of crystallization. It must be emphasized that...
In Fig. 6, the total enthalpy change $\Delta E$ measured between 750 and 1000 K is represented as a function of annealing time for partially crystallized samples at 550°C.

Comparing the annealing time dependence of $\Delta E$ with those of TEP and microhardness, it turns out that even during the so-called incubation time heat is released, connected probably with the precrystallization clustering. The total enthalpy change $\Delta E$ shows a steeper decrease after about 60 s which corresponds to the incubation time of both TEP and HV at this annealing temperature (550°C).

4. Summarizing remarks

Thermopower and microhardness measurements on partially crystallized samples annealed at temperatures between 500 and 575°C as a function of time allowed us to follow the crystallization kinetics in an Fe$_{73.5}$Nb$_3$Cu$_1$Si$_{13.5}$B$_9$ alloy. The onset of Fe(Si) precipitation induces a sudden change in both TEP and HV. In the amorphous state, the changes of these parameters during annealing are much smaller. As the annealing time and temperature dependences of these physical parameters are regular, the apparent activation energy $Q$ for the crystallization of $\alpha$-Fe nanograins may be deduced by the conventional JMA method. From the TEP and HV data apparent activation energies of 3.58–3.93 eV and 3.84–4.08 eV respectively were deduced which agree within the experimental error ($\pm 0.5$ eV). $Q$ was also determined by using DSC experiments performed at various heating rates. The application of the Kissinger method gives $Q = 4.1 \pm 0.4$ eV. The good agreement between these two kinds of data is probably because all the physical parameters investigated here are related to the onset of the formation of $\alpha$-Fe nanoparticles.

Our DSC measurements revealed the existence of a third, intermediate, exothermic peak besides the well-known two peaks corresponding to the primary $\alpha$-Fe precipitation and the transformation of the remaining amorphous matrix. This third peak was attributed to a segregation of the Fe$_3$Si compound out of the $\alpha$-Fe(Si) solid solution. To investigate the crystallization of the second stage, a DSC unit working at temperatures higher than 1000 K is necessary.

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References