



Curie temperature behaviour at relaxation and nanocrystallization of Finemet alloys

Sergey Kaloshkin^a, Margarita Churyukanova^{a,*}, Vladislav Zadorozhnyi^a, Igor Shchetinin^a, Rajat Kumar Roy^b

^a National University of Science and Technology «MISIS», Leninsky Prospekt, 4, Moscow 119049, Russia

^b National Metallurgical Laboratory, Jamshedpur 831007, India

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ABSTRACT

Dependence of Curie temperature (T_c) on time and temperature of annealing for Finemet-type amorphous alloys is studied by DSC. Structural relaxation of an amorphous phase at annealing is accompanied by increase of T_c . The σ -shaped time dependencies, however, are not characterized by the definite final value of T_c : long-term annealing of amorphous phase results in continuation of slow increase of T_c for every temperature. Apparent values of activation energy of relaxation were evaluated from the T_c time–temperature dependencies. It is found that the average value of activation energy increases with progress of the relaxation process. Correlation of the T_c data with structural alterations reflects redistribution of components in amorphous phase during annealing. Further increase of the annealing temperature results in precipitation of α -Fe(Si) nanograins in an amorphous matrix, that accompanied by gradual degradation of corresponding to T_c heat capacity peak. DSC measurements of T_c allow to detect the starting moment of amorphous phase crystallization.

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1. Introduction

Since last few decades, significant attention has been paid to the development of new soft magnetic materials based on amorphous-crystalline nanostructures, particularly Finemet-type alloys [1,2]. After partial crystallization, these alloys acquire unique magnetic properties with the combination of high permeability and high saturation magnetization. It also includes low core losses and good high frequency behaviour, allowing the reductions in size and components, e.g., switched mode power supplies.

Crystallization of ternary $\text{Fe}_{77.5}\text{Si}_{13.5}\text{B}_9$ alloy takes place over relatively narrow temperature range ($\Delta T = T_1 - T_2$, where T_1 is first crystallization onset and T_2 is second crystallization onset), which are not clearly distinguished (Fig. 1a). The addition of small amounts of Cu and Nb increases temperature range and shifts second crystallization peak to higher temperature (Fig. 1b and c). It leads to the improvement of thermal stability of alloys, resulting in superior control of nanocrystallization structure within a wide temperature range.

During crystallization Cu atoms facilitate nucleation and Nb atoms act as the growth inhibitors not only for nuclei but also for all types of diffusion controlled process occurred at the devitrification

of amorphous phases. It causes two well distinguished crystallization stages, i.e., the formation of α -Fe(Si) nanograins at the first stage and the formation of boride at the second one. There is a complicated change of final phase composition, resulting in the formation of Fe_3B phase instead of Fe_2B for parent ternary alloy [3,4]. Nevertheless, due to the presence of strong growth inhibiting element Nb, the partially crystallized $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ composition becomes very stable after the first crystallization stage, and that makes it possible to form reproducible amorphous-crystalline nanostructure with promising magnetic properties. However, extremely high soft magnetic properties of the alloys should be always close to zero magnetostriction of the material. On the other hand, the magnetostriction is dependent on the structure and composition of the constituting phases. Therefore, the reproducibility of the structure and properties of a priori nonequilibrium partially amorphous nanostructures always remain a problem for such unique alloys like Finemet. One of the methods of studying stability and transitions in an amorphous ferromagnetic phase by annealing consists in measuring Curie temperature, T_c , which depends on both a local composition and a fine structure of the phase [5–8].

2. Experimental

As-quenched ribbons of Finemet-type $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ composition of 20 μm thick and 12 mm width were used in our experiments. The Curie point alterations were studied using DSC 204 F1 Netzsch calorimeter under argon atmosphere

* Corresponding author. Tel.: +7 495 6384413; fax: +7 495 6384413.

E-mail address: mch@mis.ru (M. Churyukanova).

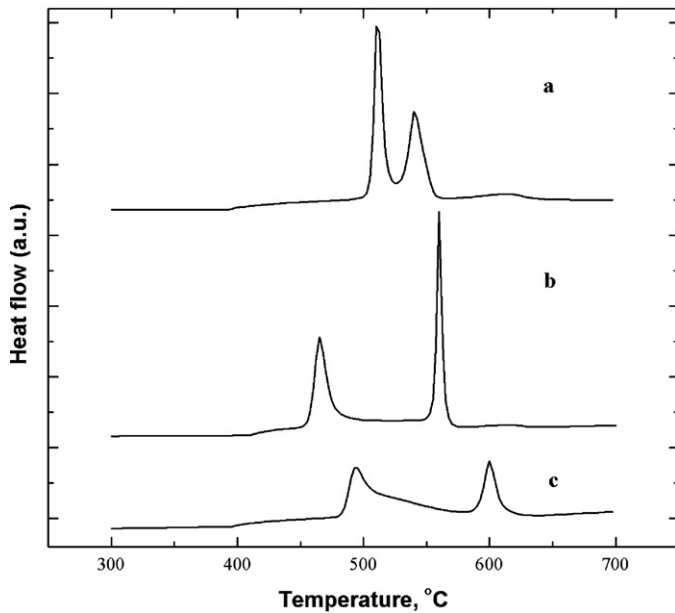


Fig. 1. The influence of alloying elements on temperature ranges of DSC crystallization peaks of amorphous alloys of Finemet-type family (a – $\text{Fe}_{77.5}\text{Si}_{13.5}\text{B}_9$, b – $\text{Fe}_{76.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1$, and c – $\text{Fe}_{75.5}\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_1$).

at a heating rate of 16 K/min as a peak of heat capacity. In order to increase sensitivity of DSC measurements a special attention was paid to the preparation of samples. The weight of a sample in aluminum container was about 100 mg, difference of the temperature on upper and bottom surface of the heated sample was no more than 0.2 K. X-ray diffraction (XRD) analysis was performed on Rigaku ULTIMA-4 diffractometer using CoK radiation. The results of T_c measurements received by DSC method were compared with the data obtained with the help of other experimental techniques: by direct measurements of magnetization as a function of temperature in vibrating sample magnetometer (VSM), by differential thermomagnetic analysis (DTMA) and measurements of electrical resistivity. The temperature dependencies of the magnetization were measured using the dynamical mode of magnetization reversal. DTMA was performed by modified thermo balance TGA of “TA Instruments”. The temperature dependence of electrical resistivity was measured by four probe method using system of Ulvac-Riko (TER-2000RH) at the heating rate of 10 °C/min. The applied current was 10 mA and the length of the sample was 33 mm. The samples for diffraction studies were prepared in a calorimeter under the same conditions as DSC measurements.

3. Results

To prove the fact that a small turn on DSC curve corresponds to magnetic transformation in the Curie point, the heating curves obtained by different isochronal methods for the same Finemet alloy of composition $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ were compared in Figs. 2 and 3.

The lowering of resistivity at two temperatures (500 °C and 675 °C) corresponds to two different stages of crystallization of an amorphous phase (Fig. 2a). A small hump at 310 °C might be related to Curie temperature of the alloy. It has a good agreement with the sudden drop of magnetization at same temperature, measured by VSM (Fig. 2b). However, the accuracy of T_c determination by both these methods is not satisfactory for studying kinetic parameters of the processes under study.

Fig. 3 shows DTA (a) and DTMA (b) signals, which were registered simultaneously from a sample of the same alloy as on Fig. 2 [9].

The structural transformations at different crystallization stages have been clearly distinguished by these methods. Although, the T_c point at 310 °C is shown as a smooth turn in DTA curve (Fig. 3a), the same point is proved by a sharp jump of sample weight under magnetic field (Fig. 3b). This point can be measured more precisely by DSC method (Fig. 4). The sharp peaks of heat capacity, mea-

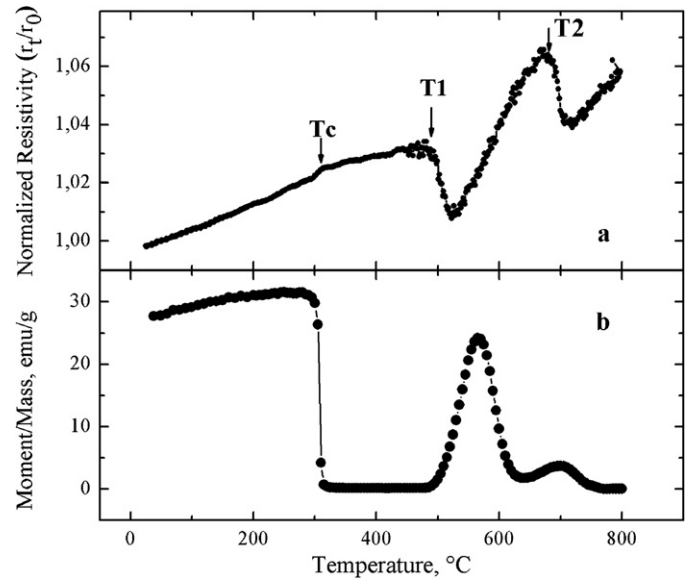


Fig. 2. Temperature dependencies of electrical resistivity (a) and magnetization (b) for $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ amorphous alloy.

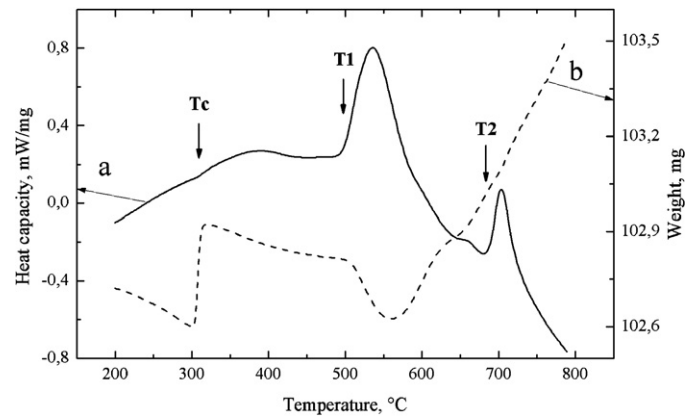


Fig. 3. DTA (a) and DTMA (b) curves of $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ amorphous alloy.

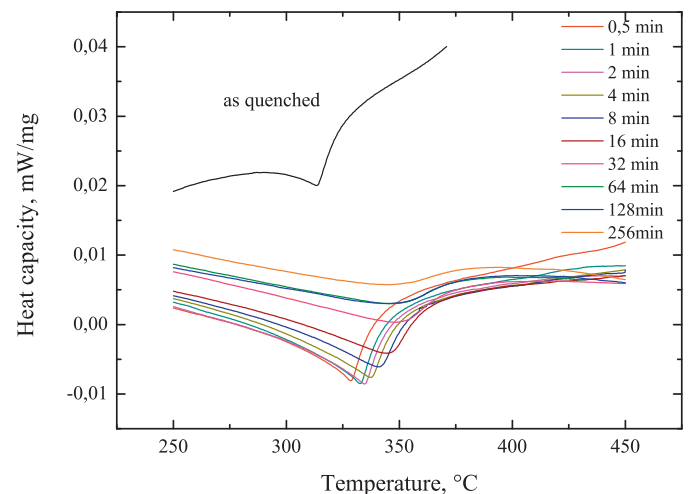


Fig. 4. DSC curves for $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ amorphous alloy obtained by repeating heating after annealing at 470 °C during various time periods.

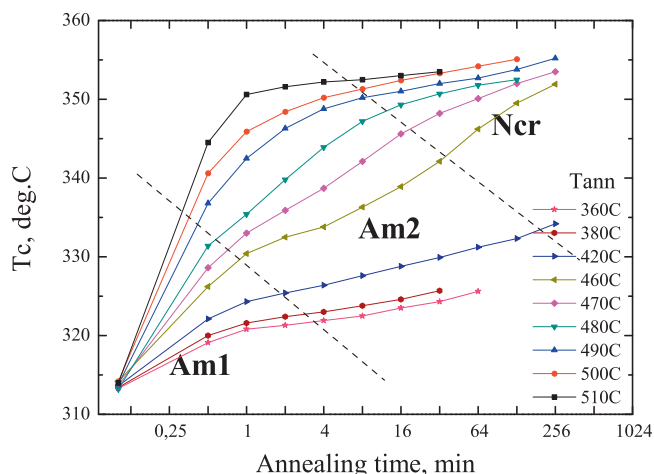


Fig. 5. Time dependencies of TC for $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloy for different annealing temperatures.

sured with high resolution explains the T_c points of as-quenched and isothermally annealed Finemet ribbons.

The as-quenched amorphous ribbons were heated in a calorimeter up to a definite temperature and annealed during various time periods. It follows the cooling of sample and again heating up to the same or a new temperature for one more annealing. T_c was measured during every heating. DSC curve for the first heating (as-quenched sample) is higher than those that follow. The reason is different relaxation and oxidation processes, which usually take place with a heat release when an amorphous alloy is first heated. It seems surprising that modern DSC devices may provide more convenient and fast method for T_c determination than even measurements of magnetic characteristics. It takes place owing to a very precise temperature control provided by standard DSC method. T_c variation can reach 50 K during a structural relaxation, while the accuracy of T_c measuring is not worse than ± 0.5 K and its reproducibility is better than ± 0.2 K. Taking into account a high sensitivity and a wide range of variety of heating rates DSC controlling T_c becomes a powerful method of studying relaxation and crystallization of amorphous phases (see also [10,11]).

In all cases under study T_c occurred higher after annealing than in initial state [7,12]. Fig. 5 shows “the map of the Curie temperature”: how T_c changes with various annealing time at different temperatures. Systematic measurements of T_c may give necessary data for kinetic study of relaxation.

One can see a nonmonotonic growth of T_c , which is especially well seen on the curve corresponding to annealing at 460°C . However, X-ray diffraction does not detect any crystalline precipitations by annealing in low and middle time–temperature areas in Fig. 5. It means that at least two relaxation processes with different mechanisms take place in an amorphous state. High time–temperature annealing results in α -Fe nanocrystals appearance, that is confirmed by XRD (Fig. 6).

An increase in time and temperature of annealing leads to an increase in the amount and size of growing nanocrystals. Hence three zones can be roughly singled out on T_c map (Fig. 5): two zones of relaxation of amorphous phase (Am1 and Am2), and zone of the initial stage of nanocrystallization (Ncr). These zones are separated from each other by dotted lines. Simultaneously with nanocrystals precipitation in zone Ncr we observed degradation of DSC peak on DSC curve (Fig. 7).

It has been reported that annealing of an amorphous alloy up to starting a crystallization process may result in splitting the T_c calorimetric peak [13,14]. Growing crystals change the composition of a surrounding amorphous phase. This leads to inhomogeneity of

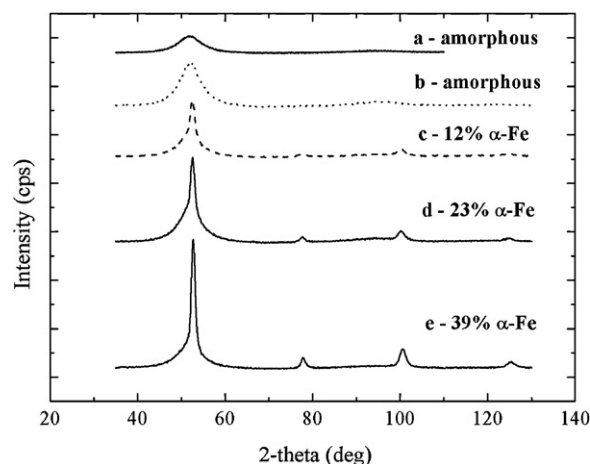


Fig. 6. X-ray diffraction of $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ alloy after annealing at 460°C (a – as quenched, b – 16 min, c – 2 h, d – 4 h; e – 4 h at 480°C).

composition in an amorphous structure, which in its turn results in formation of distribution of local areas in an amorphous phase with different T_c points. A decrease in the height of T_c peak correlates with a decrease in the amount of an amorphous phase by crystallization, as well as with lowering magnetostriction of the remaining amorphous phase [14].

Kinetics of the relaxation process was studied on the basis of the time–temperature dependencies of T_c . The apparent value of activation energy E of relaxation can be defined from the time–temperature dependencies using the following equation [14]:

$$\ln \left(\frac{dT_c}{d\tau} \right)_{\tau=\text{const}} = \frac{-E}{RT_{\text{ann}}} + \text{const} \quad (1)$$

The data in Fig. 5 for the initial points of relaxation process give two sections of dependence, which can be represented by two straight lines (Fig. 8).

For the low temperature section the value of apparent activation energy makes up 28 kJ/mol, while the high temperature section corresponds to 90 kJ/mol. This means that an increase in annealing temperature higher than 460°C results in a change of the main mechanism of the relaxation process. And we see a good correlation of this fact with data in Fig. 5, where also at least two mechanisms

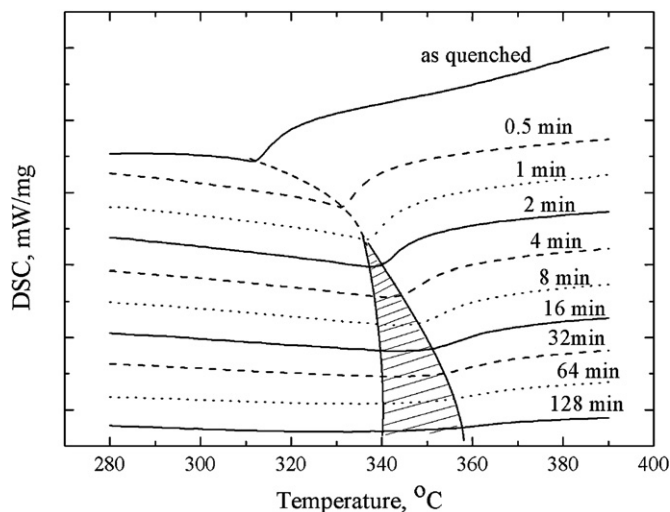


Fig. 7. DSC curves for $\text{Fe}_{73.5}\text{Nb}_3\text{Cu}_1\text{Si}_{13.5}\text{B}_9$ amorphous alloy depending on duration of annealing at 480°C .

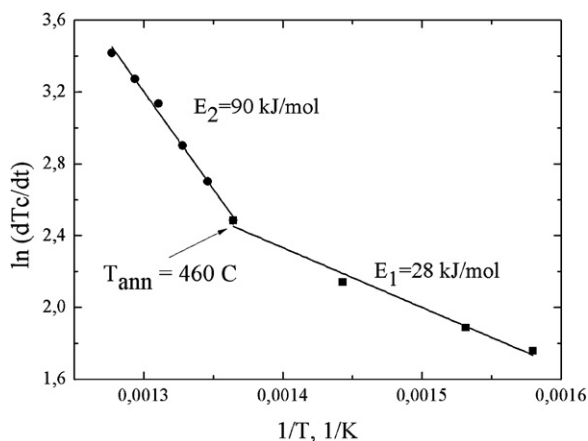


Fig. 8. The evaluation of activation energy from time–temperature dependences of T_c by Eq. (1).

of relaxation can be guessed from the shape of time–temperature dependencies of T_c .

An increase in temperature makes the processes with higher activation energies be involved into structural relaxation. So, a long-term low-temperature annealing is not equivalent to a short-term annealing at high temperature – more significant structural alterations occur in an amorphous phase at a higher temperature. For selection of annealing regimes of amorphous materials in order to achieve a specified level of properties (especially magnetic) it is important not only to control a degree of structural relaxation, but also a way, by which this degree has been achieved.

Curie temperature strongly depends on short-range order composition in an amorphous structure. One can assume that T_c increases with the number of neighbouring atoms Fe–Fe in an amorphous structure and reduction of a distance between them [10]. Topological ordering of an amorphous structure during annealing brings about the reduction of average distances between atoms of iron and subsequently results in some increase of T_c . Further annealing stimulates the development of chemical ordering. Therefore, it brings about an increase in the number of Fe–Fe atomic pairs that also causes an increase of T_c .

4. Conclusions

Measurements of the Curie temperature of ferromagnetic amorphous alloys are a very powerful method of compositional and structural state control of an amorphous phase. The DSC is especially suitable for such investigations as it provides a very fast and precise method of measuring T_c as a heat capacity peak. This method enables us to study kinetics of relaxation as well as to distinguish the processes of relaxation and crystallization. At least two processes of relaxation of an amorphous phase with apparent activation energies 28 kJ/mol and 90 kJ/mol, respectively, were identified by study of T_c evolution during annealing. These processes were interpreted as topological and chemical ordering. The Curie temperature for Finemet-type alloys is also sensitive to the decomposition of an amorphous phase and the redistribution of components between an amorphous phase and growing nanocrystals.

Acknowledgements

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