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АННОТАЦИЯ

Изучалось влияние процесса структурной релаксации, происходящей при низкотемпературном отжиге металлических стекол, на точку Кюри и намагниченность. Установлено, что в случае сплава Fe-Ni-B точка Кюри является более чувствительным параметром, чем намагниченность. По влиянию релаксации на точку Кюри можно сделать вывод о некоторой переориентации атомов в ходе процесса, которая приводит к более низкому энергетическому состоянию металлических стекол.

KIVONAT

Fémüvegekben szerkezeti relaxációs folyamat játszódik le alacsony hőmérsékletü hőkezelés alatt, amelynek a Curie pontra és a mágnesezettségre gyakorolt hatását vizsgáltuk. Megállapitottuk, hogy a Curie pont érzékenyebb paraméter, mint a mágnesezettség a Fe-Ni-B ötvözet esetében. A relaxációnak a Curie pontra gyakorolt hatásából arra a következtetésre jutottunk, hogy bizonyos atomi átrendeződés játszódik le ezen folyamat során, amely a fémüvegek alacsonyabb energiáju állapotára vezet.

ABSTRACT

In metallic glasses a certain structural relaxation process takes place during low temperature heat treatment the influence of which on both the Curie temperature and the magnetization was investigated. It was found that the Curie point is a more sensitive parameter than the magnetization in the case of the Fe-Ni-B alloy. From the effect of the relaxation on the Curie point it was concluded that some kind of atomic rearrangement takes place during this process that leads to a lower energy state of the metallic glasses.

1. INTRODUCTION

The stability of metallic glasses is of interest both from theoretical and practical point of view since these materials are in a metastable state [1]. In this connection it is expedient to examine two quite separate problems: the first is being the stability of the amotphous state [2] determined by amorphous-crystalline transition, the other is the question of the constancy of physical properties of the glassy state [1]. The present work is devoted to the latter problem.

According to some experiments [3] the mechanical, magnetic and electrical properties of metallic glasses produced by rapid quenching are dependent on time and they sometimes change essentially with low temperature heat treatment. X-ray diffraction measurements show that after such heat treatment the material remains in the amorphous state [4]. This refers to the fact that metallic glasses are not produced in a glassy state of lowest energy, i.e. their amorphous structure is not "perfect".

During the low temperature heat treatment a certain structural relaxation process takes place and as consequence, the material gets into a lower energy state [5]. In our experiments on samples with low Curie temperatures, the relaxation process is followed by Curie point measurements which indicate any atomic rearrangement.

2. EXPERIMENTAL METHOD

The influence of low temperature heat treatment on the values of basic magnetic properties: on the Curie temperature and on the magnetization was investigated. To obtain the magnetization value and the Curie temperature a force magnetometer was used.

In the case of Curie point measurements samples with as high a demagnetization factor as possible were heated in a low external magnetic field ($B = 3 \cdot 10^{-3}$ T).

In each case the heating rate was about 0.23 K/s. As the breakdown at the Curie point was not always sharp enough, a modification of the kink point method was used. Therefore the temperature measured as the half of the maximum reading on the magnetometer was taken as a Curie point. The absolute values of Curie temperature were obtained with an accuracy of about ±2 K but the shift of the Curie point was determined with an accuracy of ±0.5K.

Magnetization was measured only for the sample II (Fe-Ni-B) at room temperature (293 K) and liquid nitrogen temperature (77 K) in a magnetic field of B = 0.75 T.

The samples produced by melt spinning method were selected according to whether they had the lowest possible Curie temperature in which case their crystallization temperature would be essentially higher.

3. RESULTS AND DISCUSSION

Two types of investigations were carried out. In the first type, before the investigation the samples were in as-quenched state, and in the other a preannealing was applied. The relaxation process was followed by both the Curie point and magnetization measurements in the case of first type of investigation as follows:

Separate samples were used for each temperature of heat treatment. The investigation began with the measurement of Curie point or magnetization; this was followed by heat treatment at a given temperature somewhat higher than the Curie temperature. The duration of the heat treatment was 60 or 300 s for the first time which was followed by measurement of the Curie point or magnetization and then the second heat treatment of the same sample at the same temperature was performed generally for 600 s. This was followed by measuring over again and so on. The maximum duration of the heat treatment was 10.8 ks. In such a way we could decrease the errors coming from the possible concentration inhomogeneities of the ribbon.

The first type of investigation was performed on samples of Table I.

Table I. *Curie points in as-quenched state and the annealing temperatures for the samples used in the first type of measurements*

Material	T_C (K) (as quenched)	T_a (K) for T_C meas.	T_a (K) for M meas.
I. $Fe_{87.5}B_{12.5}$	505	527,534,548, 563	-
II. $Fe_{17}Ni_{63.8}B_{19.2}$	339	423,435,457, 473,525	428,453
III. $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$	537	556,563,571	-
IV. $Fe_{30.9}Ni_{45.9}B_{17.6}Si_{5.6}$	451	504,544,573, 598	-

The second type of investigations were carried out on samples in Table II.

In that case, the work was begun with the measured of the Curie point, this was followed by a preannealing at 598 K for 1.8 ks. After the preannealing the actual investigation was started in the manner similar to the first type of investigation.

The typical curves for both types of investigation are given in Figs 1-4.

In Fig. 1 the increase of magnetization due to the relaxation is shown for the sample II. It seems that the increase in magnetization is relatively high at room temperature but it is

Table II. *Curie point in as-quenched state and after preannealing at 598 K for 1.8 ks and the annealing temperatures as well for the samples used in the second type measurements.*

	C_{Fe}/C_{Ni}	T_C (K) (as-quench.)	T_c (K) (preanneal.)	T_a (K)
III. $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$	0.64	530	543	556,563, 598
IV. $Fe_{30.9}Ni_{45.9}B_{17.6}Si_{5.6}$	0.67	452	479	504,543, 573
V. $Fe_{36.9}Ni_{36.5}B_{21}Si_{5.6}$	1.01	501	531	543,563, 583,623
VI. $Fe_{39.3}Ni_{39.1}B_{13.8}Si_{8.1}$	1.01	566	583	593,613, 623
VII. $Fe_{38.4}Ni_{37.5}B_{16.6}Si_{7.5}$	1.02	535	562	-
VIII. $Fe_{37.8}Ni_{37.2}B_{18.5}Si_{6.5}$	1.02	524	551	-
IX. $Fe_{40}Ni_{40}B_{16}Si_4$ ж)	1.00	464	484	-
X. $Fe_{34.3}Ni_{42.5}B_{17.5}Si_{5.7}$	0.81	507	539	-

ж) nominal composition

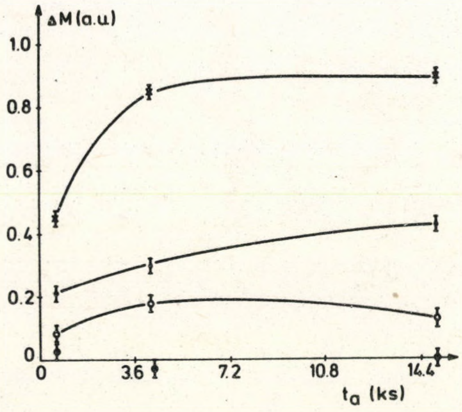

Fig. 1. *Increase in magnetization of $Fe_{17}Ni_{63.8}B_{19.2}$ metallic glass plotted against the annealing time. Measuring and annealing temperatures: x T_m=293 K, T_a=453 K; ● T_m=293 K, T_a=428 K; o T_m=77 K, T_a=453 K; ⊗ T_m=77 K, T_a=428 K.*

very low or zero at liquid nitrogen temperature. This shows that in the present case the whole change in magnetization is caused by the change in Curie temperature. Nevertheless at other compositions one can expect significant change in magnetization due to the relaxation processes similarly to in some crystalline materials, where the atomic ordering may have influence on the magnetization, while in other materials there is no effect at all. For the same sample the kinetics of relaxation is shown by plotting the increase in Curie point agains the annealing time (a) and temperature (b) in Fig. 2. The isothermal curves (a) show that during the time of experimental the equilib-

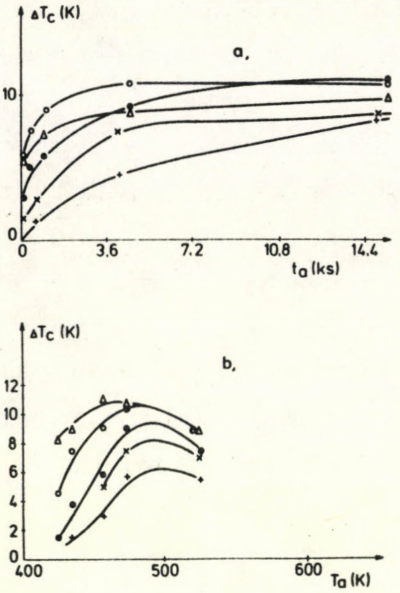

Fig. 2. Increase in Curie temperature of $Fe_{17}Ni_{63.8}B_{19.2}$ metallic glass as a function of annealing time /a/ and annealing temperature /b/. Annealing temperatures for curves a: + 423 K, x 435 K, ● 457 K, o 473 K, Δ 525 K. Annealing times for cuves b: +0.06 ks, x 0.3 ks, ● 0.6 ks, o 4.6 ks, Δ 10.8 ks.

rium is approached only at higher temperatures.

In Figs 3 and 4 the isochronal curves of the not preannealed (a) and preannealed (b) Fe-Ni-B-Si samples of different composition are compared. From these figures one can establish that there is an essential difference in the relaxation behaviour between the as quenched and preannealed samples. This different behaviour can not be explained by assuming that the effect of preannealing is nothing but release of internal stresses. One has to suppose that in amorphous materials

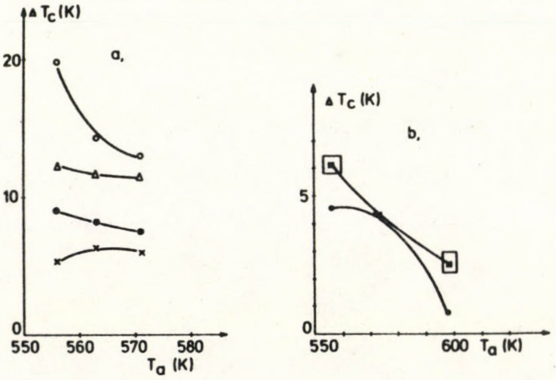

Fig. 3. Increase in Curie temperature of $Fe_{31.5}Ni_{49.2}B_{12.3}Si_7$ amorphous alloy as a function of annealing temperature for as-quenched /a/ and for preannealed at 598 K for 1.8 ks /b/ samples. Annealing times:
a/ x 0.3 ks, ● 0.9 ks, Δ 4.5 ks, o 15.3 ks.
b/ o 1.8 ks, x 5.4 ks, ● 10.8 ks.

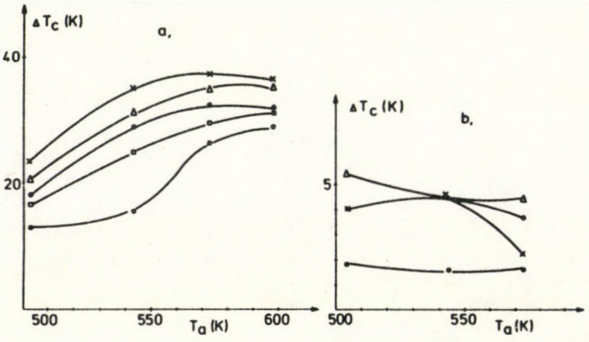

Fig. 4. Increase in Curie temperature of $Fe_{30.9}Ni_{45.9}B_{17.6}Si_{5.6}$ metallic glass as a function of annealing temperature for as-quenched /a/ and for preannealed at 598 K for 1.8 ks /b/ samples. Annealing times:
a/ o 1.8 ks, □ 5.4 ks, ● 10.8 ks, Δ 21.6 ks, x 46.8 ks.
b/ o 1.8 ks, x 5.4 ks, ● 10.8 ks, Δ 21.6 ks.

there is no stress release without any change in short range order. It is interesting to note that at about 570 K (Fig. 3) and 540 K (Fig. 4) there are some anomalies in ΔT_C (T_a) curves for the preannealed samples. Considering that these temperatures are near the preannealing temperature we can suppose that this anomaly has the same origin as the so called "cross-over" [5], namely the existence of at least two processes with different time constants.

In Fig. 3 there are two points marked by □ which were obtained after the subsequent annealing of one sample at these two temperatures. The coincidence of these points with the original ones demonstrate the reversible change of the Curie point after the sample reaches its equilibrium state which was found earlier by others [6].

In Fig. 5 the concentration variation of increase in T_C due to the preannealing of the samples with nearly equiatomic Fe-Ni concentration is shown as a function of B content (curve a) and of the total metalloid content (curve b). The metalloid content of the sample with highest B or B+Si concentration was estimated from the dependence of Curie point in amorphous state on composition of samples of nearly equiatomic Fe-Ni concentration (see Table II). It may be seen that both curves have a maximum at about 20 and 27 at.%, respectively. Further works are needed to clarify whether only B atoms play a role in this effect or the Si atoms also take part in it. Some preliminary FMR experiments show that in samples having large ΔT_C a phase separation takes place during the relaxation annealing without any crystallization. The results of FMR measurements will be published later.

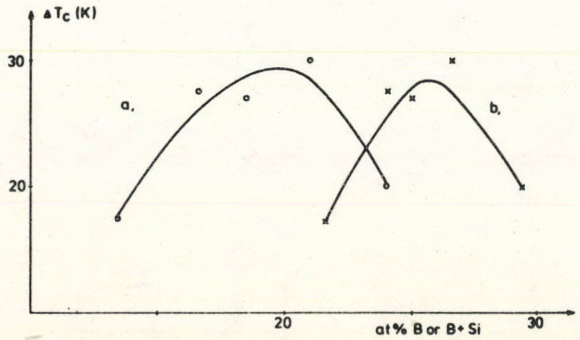

Fig. 5. Increase in T_C *due to the preannealing at 598 K for 1.8 ks as a function of B content /a/ and B+Si content /b/.*

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