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STRUCTURAL RELAXATION IN Ferromagnetic Metallic Glasses


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Abstract.—The dependence of the Curie temperatures on heat treatment measured by DSC and Mössbauer effect in different metallic glasses [(Fe, Ni)B, Fe40Ni40P14B6, FeNiCrP8] is correlated to the change in the iron hyperfine field distribution. The results suggest the occurrence of compositional short-range ordering in the structural relaxation.

One of the most significant features of the glassy state is its deviation from thermodynamic equilibrium. It is clearly manifested in its relaxation behaviour, i.e. the time dependence of different physical properties below the glass temperature. In the rapid cooling process involved in the fabrication of the metallic glasses the solidification indicates the loss of thermal equilibrium of the undercooled melt. The quenched-in excess energy and volume can be reduced by annealing. Besides by direct experiments [1,2] the details of the process can be studied by monitoring the time dependence of some structure sensitive property at different temperatures. The investigation of ferromagnetic Curie point /Tc/ ageing is used quite frequently for this purpose [3-8]. In this paper the Tc changes determined by Differential Scanning Calorimetry are correlated with the results of Mössbauer spectroscopy in order to characterize the changes in compositional and/or topological short range order on annealing.

In principle, the iron hyperfine field distribution, p(H) can provide information on the two dominant mechanisms of the structural relaxation, namely on the decrease in excess free volume and on compositional short-range ordering (CSRO). The decrease in free volume is manifested in a sharpening of the peaks of the pair distribution functions [1,2], in an increase of the density [9] by about 0.5% which results in better defined atomic positions. The smaller scatter of the atomic positions would cause a narrowing (and perhaps some shift) of p(H) but its shape would remain unchanged. Unfortunately, the expected change is smaller than 1% which cannot be observed because it is within the experimental accuracy.

Only indirect evidence is available for the existence of CSRO [7] which is a change in short range correlation among the different atoms due to the annealing. Depending on the number and kind of atoms involved in the rearrangement the CSRO would result in a distortion of the shape of p(H) because of the change in the number of iron atoms with different local neighbourhoods. In the present paper the first observation of this effect will be reported.

![FIG. 1. The effect of isothermal annealing on the Tc of amorphous Fe40Ni40P14B6. The meaning of the closed symbols is explained in the text.](http://dx.doi.org/10.1051/jphyscol:19808217)
but results in a lower Curie point. The closed symbols indicate the reversibility of the $T_C$ changes. The notation $T_1/T_2$ refers to a sample heat treated for approximately 1000 minutes at $T_1$ followed by an appropriate annealing at $T_2$. In the two examples, $T_2$ is 570 and 610 K, the fact that the $T_C$ changes correspond to the $T_2$ curves shows the reversible nature of the relaxation, in agreement with the result of Egami [7].

The annealing behaviour of amorphous (Fe$_{33}$Ni$_{67}$)$_{75}$B$_{25}$ and (Fe$_{25}$Ni$_{75}$)$_{80}$B$_{20}$ can be investigated in a wider temperature range due to the large difference between Curie point and crystallization temperature ($T_C \approx 400$ K, $T_{cr} \approx 700$ K). Besides the features similar to the previous case, one can observe an approximately linear increase of $T_C$ with the logarithm of heat treatment time at lower temperatures. This dependence may be characteristic for the slow relaxation towards the metastable local energy minimum corresponding to the given temperature. Fig. 2 summarizes the similarities and differences of $T_C$ ageing of these two Fe-Ni-B glasses with comparable $T_C$ but different metalloid content. It is apparent that the increase in $T_C$ is more pronounced in the glass containing 25 at% B. In all of the above cases the iron hyperfine field distribution remained the same, no change in $p(H)$ was observed for the different annealings. In part this is due to the mentioned insensitivity of $p(H)$ for the expected small change in the topological short-range order and to the insensitivity of the iron hyperfine fields to the Ni neighbours: the total change is about 15% for the complete substitution of Fe by Ni.

According to Chen et al. [6] in general the change in $T_C$ increases with decreasing metalloid content and increasing number of the alloy constituents. This trend agrees quite well with our expectation based on the similarity of the local neighbourhoods in the glass and in the relevant TM$_7$B$_{5}$ intermetallic compound [10]. In this model the chemical local surrounding is identical in the "stoichiometric" TM$_{75}$B$_{25}$ glass and in the TM$_3$B$_{25}$ compound: in other words all the TM-atoms occupy the TM-sublattice sites, which have mainly metalloid atoms as nearest neighbours (Here, TM assumes the possibility of more than one kind of transition metal atoms). While, chemically, the TM$_{75}$B$_{25}$ glass is a nearly ordered phase, disorder is introduced when the B-content is lowered. For example, in the off-stoichiometric TM$_{80}$B$_{20}$ glass part of the TM-atoms occupy metalloid sites, which results in an increased number of close contacts between the TM-atoms. This will enhance the possibility of CSRO among the TM-atoms of different kinds.

In the case when there is only one type of TM atom present, e.g. Fe$_{80}$B$_{20}$, we expect only a small $\Delta T_C$ as it is observed [8].

The results of Fig. 2, namely that $\Delta T_C$ is larger for the glass with 25 at.% B than for 20 at% B apparently contradict the above-discussed trend. However, the $p(H)$ distributions in Fig. 3 clearly show that this is not the case. The $p(H)$ of (Fe$_{33}$Ni$_{67}$)$_{75}$B$_{25}$ is broader than that of (Fe$_{25}$Ni$_{75}$)$_{80}$B$_{20}$ which indicates that the distribution of Fe atoms is better "ordered" in the latter case (most of the Fe atoms occupy a particular off-stoichiometric

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**FIG. 2.** Comparison of (Fe,Ni)B glasses as a function of annealing temperature and time.

**FIG. 3.** Iron hyperfine field distributions for (Fe, Ni)B glasses measured at 5 K.
site, while in the stoichiometric case we have approximately equal numbers of Fe atoms with 2B and 3B neighbours) \[11\]. Since this \((\text{Fe}_{25}\text{Ni}_{75})_{80}\text{B}_{20}\) glass is quite "ordered" already in the as-received state no important compositional short-range ordering is expected during the structural relaxation. Thus the anomalous \(\Delta T_C\) behaviour of \((\text{Fe},\text{Ni})\text{B}\) glasses gives an indirect evidence for the occurrence of CSRO.

More direct support for the presence of CSRO was obtained from the study of the \(\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_{6}\) (MG 2826 A) alloy. In this case the Curie temperature \(T_C\) (as-rec.) = 270 K is strongly reduced by the presence of the Cr atoms \[3,12\] which also have a strong influence on the Fe hyperfine fields. A long time (2 months) annealing at low temperature (520 K) results in a significant increase of \(T_C\) \((\Delta T_C = 45 K)\) and a definite change of the Mössbauer spectra (Fig. 4). These changes correspond to an increase in the intensities of the low- and high-field components and the maximum-probability field increases (Fig. 5). Neglecting the possible small contribution of the small homogeneous decrease of the interatomic distances upon annealing - which is \(\Delta 0.12\%\) for this alloy \[4\] - the distortion in the shape of p(H) can be attributed to a change in the CSRO. The number of Fe atoms with a smaller and larger number of Cr neighbours has increased due to this annealing. The kinetics of Curie-temperature ageing (Fig. 6) indicates that at least two processes are present (the slope changes at \(\Delta T_C \approx 25 K)\). According to Chen \[3\] the low temperature structural relaxation involves both topological and chemical short-range ordering. Although these processes overlap, the \(T_C\) kinetics of Fig. 6 strongly suggests that above \(\Delta T_C \approx 25 K\) the CSRO is considerably enhanced.

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REFERENCES

FIG. 6. Increase of Curie temperature relative to as-received material $\Delta T_c$ as a function of annealing time $t_a$ at different temperatures $T_a$ for MG 2826 A.