

# Oscillations of structural parameters and magnetic properties of metallic glasses

V. I. Lad'yanov, D. S. Rybin, I. A. Novokhatskiĭ, I. I. Usatyuk, and I. Yu. Shumilov

*Physicotechnical University, Ural Mountain Branch of the Russian Academy of Sciences, 426001 Izhevsk, Russia<sup>1)</sup>*

(Submitted 23 December 1994)

Zh. Éksp. Teor. Fiz. **61**, No. 4, 270–273 (25 February 1995)

The behavior of structural parameters and other properties of amorphous alloys of the Fe–Cr–P–C system prepared with various durations of the isothermal hold of the initial molten metal is nonmonotonic and oscillatory. The changes in the structural parameters of the metallic glass are correlated with the kinetics of structure-sensitive properties of the original nonequilibrium molten metal during its isothermal hold. A possible explanation of the oscillations is based on a microscopic chemical heterogeneity and a change in the composition short-range order in the nonequilibrium melt after the crystal–liquid phase transition. © 1995 American Institute of Physics.

In a material deprived of its equilibrium state, the relaxation to thermodynamic equilibrium may be nonmonotonic and oscillatory.<sup>1</sup> In a liquid just after the melting of the solid phase and a subsequent heating to a fixed temperature, an equilibrium is reached over a time which may be a matter of minutes or even hours.<sup>2</sup> One observes a complex oscillatory evolution of structural parameters and of structure-sensitive properties of the melt. On the other hand, the state of the liquid phase and the history of its preparation significantly influence the structure and properties of cast metal alloys,<sup>3</sup> including metallic glasses,<sup>4–6</sup> in which the inheritance of structural features of the original melt is seen most vividly. Because of the finite cooling rate under actual technological conditions, the structural state of amorphous alloys does not completely reproduce the structure of the original melt. However, the basic structural features of the melt are fixed in metal glasses in the case of high cooling rates of the liquid. One might therefore expect a correlation in the changes in the structure and properties of the liquid and amorphous phases. There is particular interest in studying how relaxation processes in melts affect the amorphous state when the duration of the isothermal hold before quenching is comparable to the time required to reach a steady state in the liquid. To the best of our knowledge, there has been no previous study in this direction.

We studied amorphous alloys of the Fe<sub>70</sub>Cr<sub>10</sub>P<sub>13</sub>C<sub>7</sub> system, produced by spinning a melt on the inner surface of a quenching disk. As the variable parameter we selected the duration ( $\tau$ ) of the isothermal hold of the original melt before the pouring, after the melt was heated to a point 100°C above the liquidus line of the equilibrium state diagram. All other experimental parameters were held constant. The time  $\tau$  was varied up to 1 h. Equal amounts of melt were spun after a corresponding hold for one smelting. The thickness of

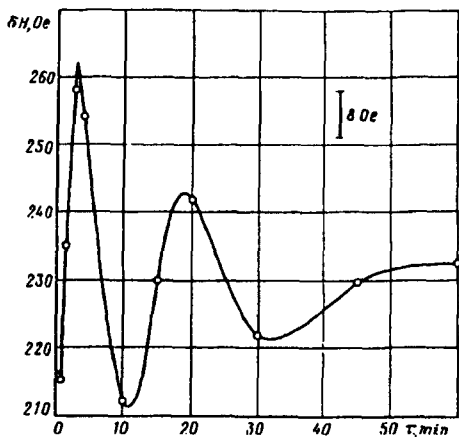


FIG. 1. Linewidth of the uniform ferromagnetic resonance in the metal alloy  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  versus the duration of the isothermal hold of the original melt.

the tapes was  $15 \mu\text{m}$ . We measured the parameters of the limiting magnetic-hysteresis loop and of the integrated x-ray structure, and we observed the ferromagnetic resonance at  $f=9.44 \text{ GHz}$ , for all samples.

Figures 1–3 show experimental results. We see that the changes in the properties studied and the structural parameters of the amorphous tapes are nonmonotonic and oscillatory, as a function of the duration of the hold in the liquid state.

An oscillatory behavior of the width of the ferromagnetic resonance line,  $\delta H$ , indicates a time variation of the extent of microscopic structural inhomogeneity of the amorphous tapes.<sup>7</sup> Specifically, an increase in  $\delta H$  corresponds to an increase in the extent of microscopic inhomogeneity of the system. It can be seen from Fig. 2 that the half-width of the first maximum of the structure factor,  $\delta S$ , is out of phase with  $\delta H$ . In general, a relatively high degree of order of an amorphous alloy corresponds to a relatively small value of  $\delta S$ . In a first approximation, this behavior of  $\delta H$  and  $\delta S$  can be described on the basis of the cluster model for the structure of metallic glasses,<sup>8</sup> as a change in the relative

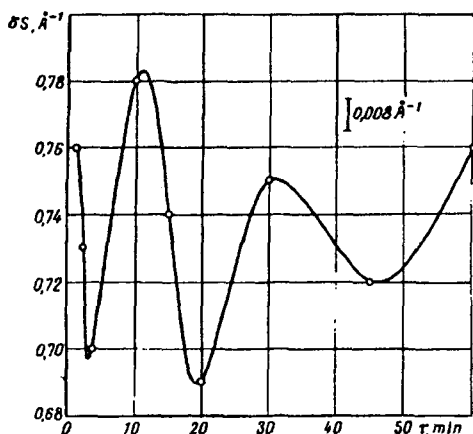


FIG. 2. Half-width of the structure factor of the metallic glass  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  versus the duration of the isothermal hold of the original melt.

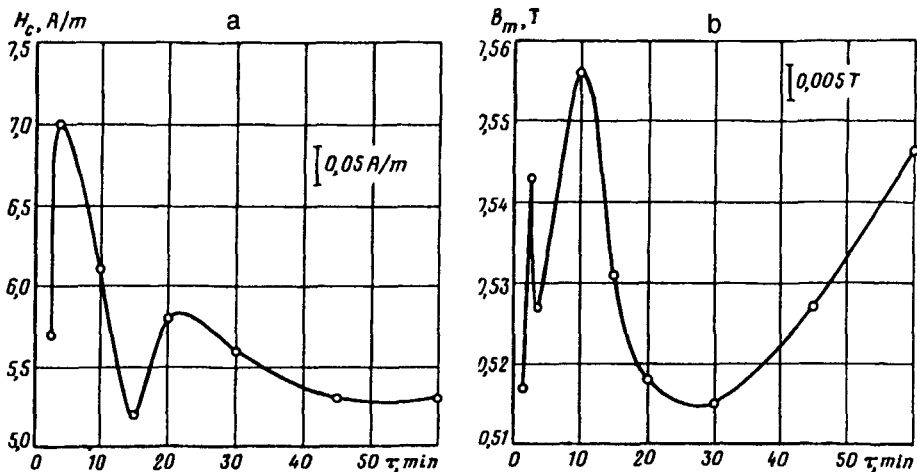


FIG. 3. Parameters of the limiting magnetization-reversal cycle [the coercive force (a) and the technical-saturation induction (b) in a field of 10 kA/m] of the metallic glass  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  versus the duration of the isothermal hold of the original melt.

amounts of structural components in the original melt over time ( $\tau$ ). With increasing  $\tau$ , the ratio of concentrations which is the equilibrium ratio for the given temperature is reached in the system, as is demonstrated by the decrease in the oscillation amplitude.

A nonmonotonic and oscillatory behavior is also observed in hysteresis properties: the coercive force and the technical-saturation induction. The latter is of the same nature as the change in the saturation magnetization found from the magnitude of the resonant ferromagnetic-resonance field.

This behavior of these properties correlates with the known evolution of structure-sensitive properties of nonequilibrium melts during their structural relaxation. A study of the behavior of viscosity isotherms  $\nu = f(\tau)|_{T=\text{const}}$  of a melt of the specified nominal composition was carried out in Ref. 9. It turned out that the kinetics of the structural parameters and the properties which we observed for the metallic glass correlates with the nature of the changes in  $\nu$  of the metallic melt. The amplitude of the oscillations in  $\nu$  (Ref. 9) falls off over time, but one does not observe a complete stabilization of the properties or the attainment of a steady state, even after the melt is held for an hour.<sup>9</sup> It can be seen from Figs. 1–3 that corresponding results were found for the metallic glass.

The experimental results reported here indicate structural changes in the metallic melt and an inheritance of these structural changes by the metallic glass upon fast quenching. The changes  $\delta S$  and  $\delta H$  are evidence of a change in the topological short-range order in the melt and the amorphous tape. An oscillation in the absolute value of the saturation magnetization indicates a change in the composition short-range order in both states of aggregation.

For hold durations greater than 30 min, one observes a stabilization of the coercive

force. This stabilization implies the attainment of an equilibrium distribution of sources of fluctuations in the magnetic anisotropy, which are effective centers for the pinning of domain walls. Structural defects are such sources. Note also the tendency for the coercive force to fall off with increasing  $\tau$ . This effect is usually observed during isothermal annealing of amorphous alloys of metal-metalloid systems in the temperature range below the beginning of crystallization. A decrease in the coercive force during annealing is usually linked with a decrease in the concentration and strength of structural defects and a relaxation of internal stress. One might suggest that relaxation of a metallic melt leads to a decrease in the defectiveness of the metallic glass and is in a sense equivalent to an annealing in the solid state. On the other hand, the other structural parameters and properties have not yet stabilized even after a hold for an hour.

The reasons for the oscillatory relaxation to thermodynamic equilibrium in nonequilibrium metallic melts remain open questions. One possible explanation of the physical causes of the oscillatory behavior of the structural parameters and properties of the metal alloy  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  might be a change in the nature of the chemical short-range order upon the transition from the crystalline phase to the liquid phase. The type of short-range order in the alloy  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  is known to change substantially in a transition from one state of aggregation to another. In the Fe-Cr system, at a chromium concentration above 13 at. %, a covalent bond involving  $d$ -electrons forms.<sup>10</sup> The formation of microscopic Me-C groups in a crystalline solid, on the other hand, is not favorable from the energy standpoint. This problem is not a factor in a liquid, and  $\text{Cr}_x\text{C}_{1-x}$  complexes begin to form upon melting, since the difference between the electronegativities of the elements in Cr-C(P) compounds is larger than that in Fe-C(P) compounds. The  $\text{Cr}_x\text{C}_{1-x}$  complexes are weakly bound to other atoms in the melt, and they lead to a minimum of the free energy.<sup>10</sup> The formation of Cr-C bonds is thus equivalent to a change in the number of chromium atoms which are interacting with iron with increasing  $\tau$ . The results are a modification of the iron  $d$ -band and a change in the magnitude of the magnetic moment per Fe atom. Since the concentration dependence of the magnetic susceptibility of a metallic melt of the Fe-Cr system is oscillatory at a constant temperature,<sup>11</sup> it can be assumed that the oscillatory evolution of structure-sensitive properties of molten  $\text{Fe}_{70}\text{Cr}_{10}\text{P}_{13}\text{C}_7$  and of a metallic glass formed from it is due to the nonmonotonic concentration dependence of structure-sensitive properties reported in Ref. 11.

In summary, it has been shown for the first time that the behavior of structural parameters and properties of amorphous alloys of the Fe-Cr-P-C system prepared with various durations of the isothermal hold of the original melt is oscillatory, because of relaxation processes in the liquid phase.

<sup>1)</sup>e-mail: uufti@fti.udmurtia.su

<sup>1</sup>D. M. Zayachuk, JETP Lett. **54**, 394 (1991).

<sup>2</sup>B. A. Baum, I. N. Igoshin *et al.*, Rasplavy **2**(5), 102 (1988).

<sup>3</sup>B. A. Baum, Rasplavy **2**(5), 18 (1988).

<sup>4</sup>K. Shiiki, T. Watanabe, and M. Kudo, J. Appl. Phys. **50**, 5419 (1979).

<sup>5</sup>Z. Altounian and J. O. Ström-Olsen, J. Non-Cryst. Solids **61/62**, 469 (1984).

<sup>6</sup>S. H. Lim and W. K. Pi, J. Appl. Phys. **73**, 865 (1993).

<sup>7</sup>E. A. Turov, in *Ferromagnetic Resonance* [in Russian], ed. by S.V. Vonsovskii (GIFML, Moscow), p. 215.

<sup>8</sup>I. A. Novokhatskii, V. I. Lad'yanov *et al.*, *Izv. Akad. Nauk SSSR, Met.* **6**, 25 (1986).

<sup>9</sup>V. I. Lad'yanov, S. V. Logunov, and S. V. Pakhomov, *Raspilavy* (in press).

<sup>10</sup>V. A. Trapeznikov and I. N. Shabanova, *Electron Probe Microscopy of Ultrathin Surface Layers of Condensed Systems* [in Russian] (Nauka, Moscow, 1988).

<sup>11</sup>V. E. Sidorov, V. S. Gushchin, and B. A. Baum, *Izv. Vyssh., Chern. Met.* **8**, 152 (1985).

Translated by D. Parsons