

# Analysis of the heterogeneous structure of the surface of amorphous alloys by means of the Mössbauer effect

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A new procedure of nondestructive layer-by-layer analysis (the Mössbauer differential conversion-electron spectroscopy) is used to study the complex multilayer structure of the surface of a crystallizable amorphous alloy  $\text{Fe}_{84}\text{B}_{16}$ .

One of the interesting problems of the physics of amorphous metals is the analysis of the gradual transition from a well-developed amorphous state to the crystal state. As the temperature is raised to  $T < T_{\text{cr}}$  (the crystallization temperature), the amorphous metal may undergo spatially inhomogeneous phase transitions. This phenomenon is particularly clearly manifested near the surface, where the crystallization and the change in the magnetic structure in a bounded volume begin much earlier than in the entire volume of the sample.

Mössbauer spectroscopy raised new possibilities for studying structural transformations in amorphous metals. It was established<sup>2,3</sup> that spatially inhomogeneous structural transformations can be studied by combining the standard Mössbauer technique, which yields information about the average properties (over the volume) of the sample, with the technique of detecting the conversion electrons which carry the information about the limited surface layer of depth<sup>1</sup>  $\sim 100$  nm.

The efficiency of the conversion-electron Mössbauer-spectroscopy method can be substantially increased by measuring the energy distribution of the outgoing electrons and by establishing a link between the energy at which the electrons escape from the layer ( $E$ ) and the depth of the layer ( $x$ ) in which they are produced.<sup>4</sup> To construct such a two-dimensional escape function  $f(E, x)$  for electrons which are detected in a proportional detector with a 20% resolution, we have used for the first time a technique based on the measurement of the energy distribution of electrons in tapered stainless-steel films of different thicknesses, enriched with an  $\text{Fe}^{57}$  isotope.<sup>5</sup> To obtain the best possible function for the escape of electrons from the film made from the

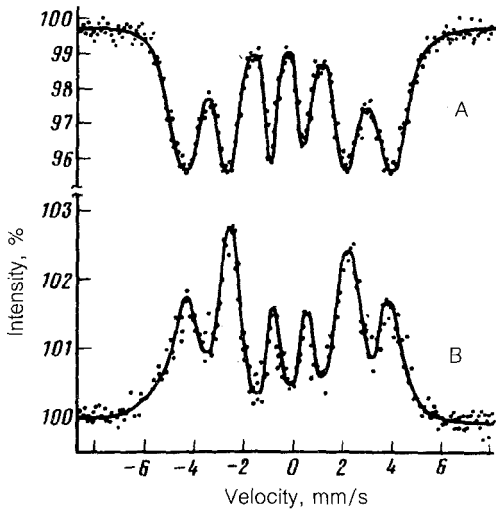


FIG. 1. Mössbauer spectra of the original  $\text{Fe}_{84}\text{B}_{16}$  sample. A—Absorption spectrum giving information about the structure of the sample throughout its volume; B—conversion-electron spectrum giving information about the structure of the surface region of depth  $\sim 100$  nm.

material under study, we have studied the amorphous alloy  $\text{Fe}_{84}\text{B}_{16}$  with a small content of light boron.

Under these experimental conditions, it is possible to single out an energy group of electrons whose escape function is localized in a  $\sim 30$ -nm layer, in contrast with the  $\sim 100$ -nm layers which are conventionally studied (in the case of integrated detection of conversion electrons).

Figure 1 shows the Mössbauer spectra for absorption (A) and for conversion electrons from a depth of 100 nm (B) for the original sample, i.e., the sample of amorphous  $\text{Fe}_{84}\text{B}_{16}$  alloy which was not subjected to heat treatment. We see a magnetic hyperfine structure whose spectral lines are broadened considerably ( $\Gamma \sim 0.6\text{--}0.8$  mm/s), because the iron atoms of the alloy are in a nonequivalent nearest surroundings. The spectrum of the surface layer [Fig. 1(B)] shows an increase in the intensities of the second and fifth lines, indicating that we are dealing with a magnetic texture,<sup>2</sup> in which the magnetic moments of the iron atoms in the surface layer of the alloy are oriented in the plane of the amorphous tape.

Figure 2 shows the spectra of  $\text{Fe}_{84}\text{B}_{16}$  samples which were subjected to a linear heating to a temperature of  $350^\circ\text{C}$  at the rate of  $40\text{ K/min}$  (2A–2C) and the spectra of samples which were subjected to additional heating of  $350^\circ\text{C}$  for 10 min [Fig. 2(A)'–2(C)'].

The information obtained by conventional means differs from that obtained on the basis of conversion electrons. The Mössbauer absorption spectra [Figs. 2(A) and 2(A')] of the samples are essentially the same. These spectra differ in the width and intensity of the lines only slightly from the spectrum of the original sample [Fig. 1(A)] (primarily a decrease in the magnetic texture is seen).

On the other hand, the conversion spectra of surface layers undergo substantial changes [Fig. 2(B) and 2(B') and Fig. 2(C) and 2(C')]. In contrast with the spec-

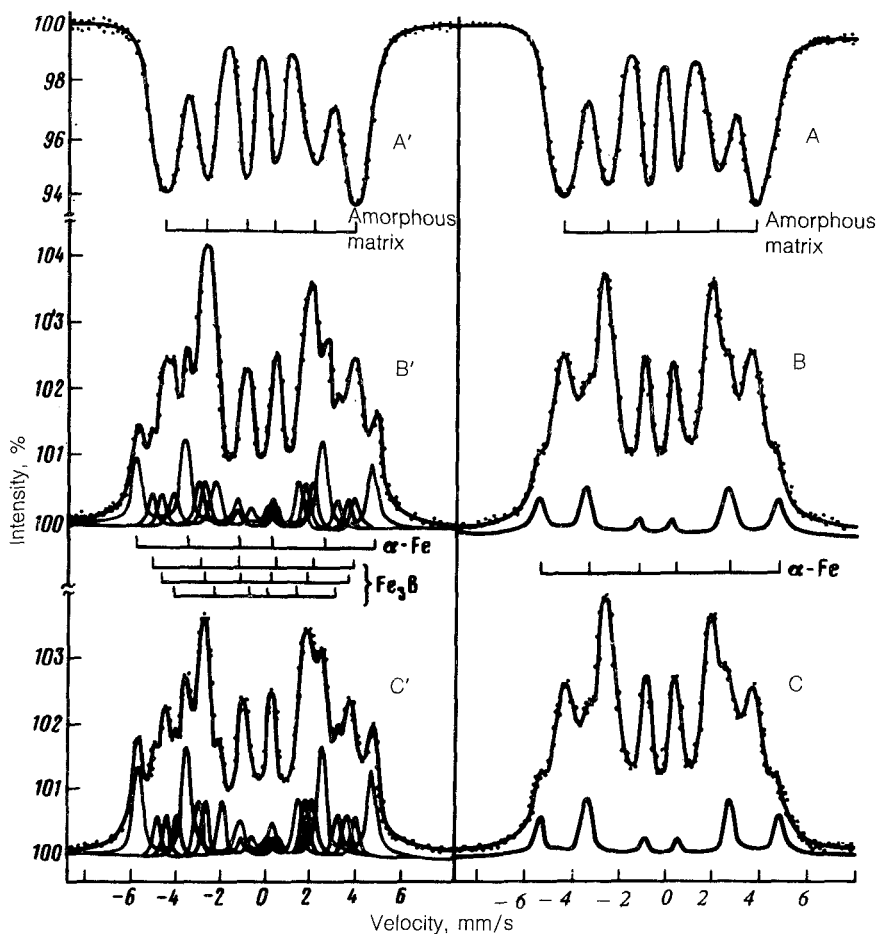


FIG. 2. Mössbauer spectra of heat-treated  $\text{Fe}_{84}\text{B}_{16}$  samples. A–C—Linear heating up to  $T = 350^\circ\text{C}$ ; A'–C'—linear heating and holding the samples at  $T = 350^\circ\text{C}$  for 10 min; A, A'—absorption spectra; B, B'—conversion spectra taken from a depth of  $\sim 100$  nm; B, B'—conversion spectra from a depth of  $\sim 30$  nm.

trum of the original sample [Fig. 1(B)], these spectra exhibit additional lines, which are clearly seen in Figs. 2(B') and 2(C'). A mathematical analysis of the spectra on a computer has made it possible to identify in them, in addition to the principal component—the spectrum of the amorphous matrix with broad lines—the partial spectra of the crystal phases of  $\alpha\text{-Fe}$  and three modifications of  $\text{Fe}_3\text{B}$  with narrow spectral lines ( $\Gamma \sim 0.28$  mm/s).

A comparison of the 2(B) and 2(B') spectra shows that the lines of the  $\alpha\text{-Fe}$  phase appear first and the changes in the spectrum corresponding to the isolation of the  $\text{Fe}_3\text{B}$  crystal phases appear only after holding the sample at  $T = 350^\circ\text{C}$  for 10 min. Such kinetics of phase isolation is not random, since  $\text{Fe}_3\text{B}$  cannot be obtained without a boron enrichment of the region in which the crystallization occurs, so that this process is limited at least by the diffusion of boron.

A comparison of the conversion spectra obtained from 100- and 30-nm depths of the sample [Figs. 2(B), 2(C), 2(B'), and 2(C')] shows that the relative intensity of the partial spectrum corresponding to the  $\alpha$ -Fe phase is higher in a 30-nm layer than in a 100-nm layer and that in the case of linear heating this intensity amounts to 11% and 8%, respectively, and 16% and 13%, respectively, after a 10-min annealing. On the other hand, the crystallization of the Fe<sub>3</sub>B phases occupies a deeper region: the relative intensities of their partial spectra amount to  $\sim$ 18% in both the 30- and 100-nm layers [Figs. 2(B') and 2(C')].

The partial spectra of the crystal phases measured at the depths of 30 and 100 nm have the same limiting magnetic texture, while the partial spectrum of the amorphous matrix reveals a certain reduction of the magnetic texture similar to that observed in the Mössbauer absorption spectrum [Figs. 2(A) and 2(A')].

Three important conclusions can be drawn from the analysis of the spectra: 1) The crystal phases are formed near the surface at a temperature as low as 350 °C, which is 40° lower than the crystallization temperature; 2) the crystallization of  $\alpha$ -Fe is confined to a surface layer of  $\sim$ 30 nm; and 3) the magnetic structure changes at a depth of  $>$  100 nm. Further studies must be carried out, however, in order to determine the principal cause of the change in the magnetic structure of the sample; specifically, to determine whether the removal of the hardening-induced stress, the magnetoelastic effects, or the partial diffusion is the key factor.

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