JOURNAL OF MATERIALS SCIENCE 18 (1983) 1515–1521

Crystallization of Fe–P amorphous alloys as studied by the EDXD method

E. HILTUNEN
Department of Physical Sciences, University of Turku, Vesilinnantie 5, 20500 Turku 50, Finland

L. TAKÁCS
Central Research Institute for Physics, H-1525 Budapest 114, POB 49, Hungary

The crystallization of amorphous Fe–P alloys, made by electrodeposition, were studied using energy dispersive X-ray diffraction (EDXD), thermomagnetic, and Mössbauer measurements. EDXD proved to be especially useful, because its very short exposure time enabled us to perform isothermal crystallization measurements with practically continuous control by means of diffraction spectra. By measuring the intensity of the appropriate diffraction lines, the crystallization kinetics of each phase could be recorded simultaneously. At 610 K the crystallization of an $Fe_{81.2}P_{18.8}$ amorphous alloy was found to start within 5 min with the primary crystallization of α-iron. This step is followed by the eutectic crystallization of the stable phases α-iron and Fe_3P.

1. Introduction

The crystallization of amorphous alloys can be studied by several methods. It is not easy, however, to find an experimental technique which can be used to record the kinetics of crystallization simultaneously for each phase. Energy dispersive X-ray diffraction (EDXD) is well suited for this purpose because its very short exposure time enables us to make *in situ* crystallization measurements under practically continuous control by means of diffraction spectra. In this way not only the crystalline phases can be identified but their crystallized fraction can also be determined by measuring the intensity of the appropriate diffraction lines.

The EDXD method was used extensively to study the structure and relaxation of metallic glasses [1]. The main purpose of the present investigation was to apply EDXD for the investigation of the crystallization of an amorphous alloy. This kind of measurement has not been used previously for this purpose, so that the Fe–P system was chosen because a rather simple crystallization process directly into the stable phases α-iron and Fe_3P could be expected [2–4].

Before starting with the EDXD measurements, the general course of the crystallization was checked by thermomagnetic measurements. Similar studies on Fe–B metallic glasses proved to be very informative [5]. The crystalline phases were identified by the simultaneous use of X-ray diffraction and Mössbauer measurements.

2. Experimental procedure

The samples used for these investigations were circular plates, 12 mm in diameter and about 30 μm in thickness. They were prepared by electrodeposition from a bath similar to that used by Logan and Sun [6]. The temperature of the electrolyte was kept constant at 60° C. Three different current densities were chosen, namely, 200, 150 and 100 mA cm^{-2}. The composition of the samples, as determined from the intensity ratio of the Mössbauer sextuplets in the final crystalline state, was $Fe_{81.2}P_{18.8}$, $Fe_{80.0}P_{20.0}$ and $Fe_{77.1}P_{22.9}$ for the different current densities, respectively.

To get a general picture of the course of the crystallization process, thermomagnetic measure-

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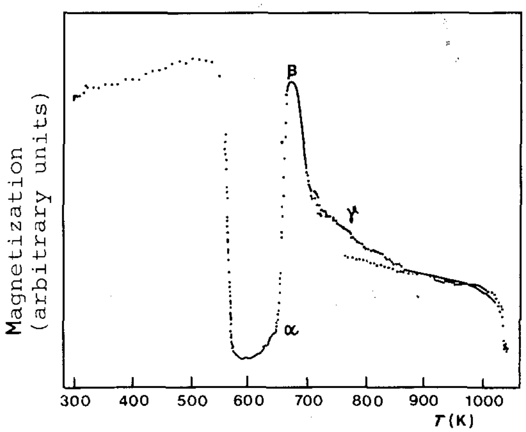


Figure 1 Typical thermomagnetic curve of an $Fe_{81.2}P_{18.8}$ amorphous alloy with a heating rate of $14\ K\ min^{-1}$.

ments were carried out in a magnetic balance using low magnetic fields of about 0.1 T. In low fields the magnetization is sensitive to the details of the domain structure, so it does not necessarily follow a Brillouin-like temperature dependence. A typical curve obtained at a heating rate of $14\ K\ min^{-1}$ is shown in Fig. 1. The decrease of the magnetization at about 570 K corresponds to the Curie temperature of the amorphous phase. At higher temperatures the increase of the magnetization corresponds to the appearance of crystalline phases whose Curie temperatures are higher than the actual temperature. The crystalline phases can be identified by the determination of their Curie temperature [5].

The Mössbauer measurements were made using a conventional spectrometer operating in the constant acceleration mode. The spectra were recorded in a multichannel analyser with 1000 channels resolution. The source was ^{57}Co in a rhodium matrix. The spectra were fitted by magnetically split six-fingers whose amplitude, width, isomer shift, hyperfine field and quadrupole splitting were determined by a least square computer program. To change the overlap between the lines, spectra were recorded at room and liquid nitrogen temperatures.

In the case of EDXD the continuous spectrum of X-rays was used and the diffraction pattern was measured at a fixed angle as a function of the energy of the photons. In this work, copper radiation and Bragg angle, $\theta = 15^\circ$, was used. The use of a fixed geometry has many technical advantages, as high-temperature measurements and *in situ* annealings can be made without moving the sample. Actually a modified Anton Paar high-temperature attachment was applied in our case. On the other hand, the exposure covers the whole spectrum simultaneously, so the method is rather insensitive to small changes in the voltage or the current. Also, the exposure time can be quite short (as short as 300 sec in some of the present investigations) and so the crystallization process can be monitored nearly continuously.

3. Results and discussion

At first, the general features of the crystallization process were studied by magnetization measurements. A typical thermomagnetic curve can be seen in Fig. 1. As already mentioned, the abrupt decrease of the magnetization at about 570 K indicates the ferromagnetic Curie temperature of the amorphous phase. At about 620 K, the magnetization starts to increase, indicating the start of crystallization. A very abrupt increase at 650 K shows the main step of the crystallization process. Above 680 K the magnetization decreases monotonously without any sign of further crystallization steps. However, there are differences between the heating curve and the cooling curve even up to about 850 K.

Thermomagnetic measurements were also used to anneal some samples up to definite stages of the crystallization process. The heating current of the furnace was switched off at the points denoted by α, β or γ in Fig. 1 and the samples were cooled down to room temperature. The phases present in these samples were analysed by X-ray diffraction and Mössbauer spectroscopy. It is important to note that the production of samples crystallized only to the α stage was rather difficult. Fig. 2a shows the thermomagnetic curve recorded during a successful heat treatment. It is clear that the crystallization stopped when point α was reached and the heating was switched off, because the magnetization increased abruptly when the sample cooled back to the Curie point of the remaining amorphous phase. However, the curve in Fig. 2b, for an alloy of slightly different composition indicates that the crystallization went on even after the heating current had been switched off and the whole of the glassy phase crystallized as indicated by the lack of any sign of the amorphous Curie temperature.

Typical Mössbauer spectra recorded in the different states are shown in Fig. 3. Spectrum (a) is that of the as-prepared amorphous material.

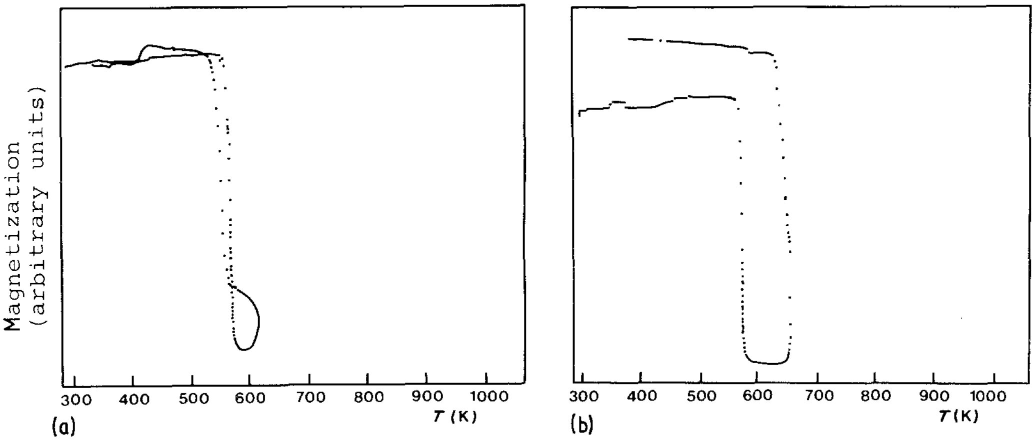


Figure 2 Thermomagnetic curves taken during annealings to the start of the crystallization (α stage): (a) $Fe_{81.2}P_{18.8}$, and (b) $Fe_{80.0}P_{20.0}$.

(The second and fifth lines were partially suppressed by tilting the sample relative to the γ-ray direction and applying a small external magnetic field parallel to the sample plane [7, 8].) Spectrum (b) corresponds to the α stage. This is the spectrum of the same sample produced during the thermomagnetic measurement shown in Fig. 2a. Although the spectrum resembles that of the amorphous sample very much, some sign of the presence of crystalline α-iron can be identified in the outer part of the spectrum. (The amount of the dissolved phosphorus may be much higher than the equilibrium solubility. Because of this, the lines corresponding to the α-iron phase are broadened and their identification is made more difficult.)

The Mössbauer spectra of the samples crystallized up to the β and γ stages and heat treated at 1050 K for about 1 h ("final" stage) were practically identical (spectra (c) and (d) in Fig. 3). Each of them could be fitted to seven Zeeman-split sextuplets, one corresponding to α-iron, the other six to Fe_3P. The parameters of these latter sextuplets agreed well with the results of Lisher *et al.* [9]. Besides the two stable phases, no sign of the spectral components of any other phase could be seen in the spectra.

Assuming that after the heat treatment at 1050 K the Fe_3P compound is stoichiometric and the concentration of phosphorus dissolved in the α-iron phase is negligible, the concentration of the samples can be estimated from the relative amount of the two crystalline phases, i.e. from the intensity ratio of the spectral components. These are the data used as the nominal compositions throughout this paper. Although the absolute values can have systematic errors of about 1 at%, the differences between the samples are well represented by these data.

To identify the phases present at the different stages of the crystallization process, the EDXD spectra of the samples studied by Mössbauer spectroscopy were also measured. Fig. 4 shows the EDXD spectra of the $Fe_{81.2}P_{18.8}$ sample taken in the amorphous state as well as having crystallized to the α, β and γ stages and to the final crystalline state. The presence of the α-iron phase at the α stage is clearer here than in the Mössbauer spectrum, because the line broadening caused by the dissolved phosphorus is smaller in the diffraction measurement than in the Mössbauer study and so the lines corresponding to the α-iron phase are better resolved. The spectra taken at the β and γ stages and in the final state are essentially similar. Each of them consists of the lines of α-iron and Fe_3P, but no lines indicating the presence of any other – stable or metastable – phases could be found. (The difference between the heating and the cooling curves in Fig. 1 above 680 K may be a consequence of changes of the domain structure without any change of the phase composition.)

Fig. 5 shows the EDXD spectrum of the $Fe_{80.0}P_{20.0}$ sample after the heat treatment shown in Fig. 2b. Again, only the lines of α-iron and Fe_3P can be seen without any other crystalline phase or amorphous background. This result gives further evidence that crystallization proceeds very quickly after the first nuclei are formed, even if the heating is stopped.

Because the crystallization of α-iron and Fe_3P was the easiest to separate in the case of the

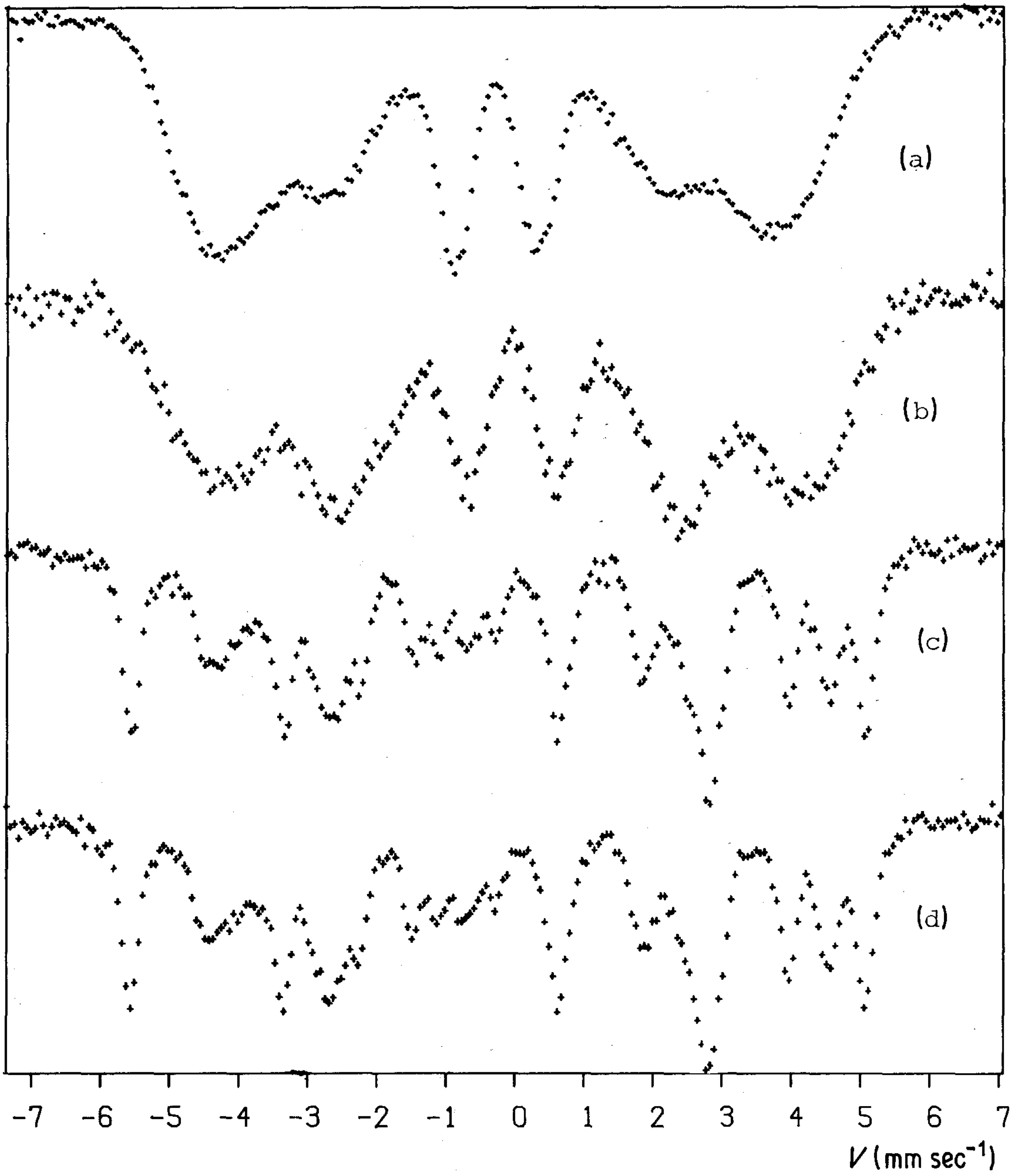
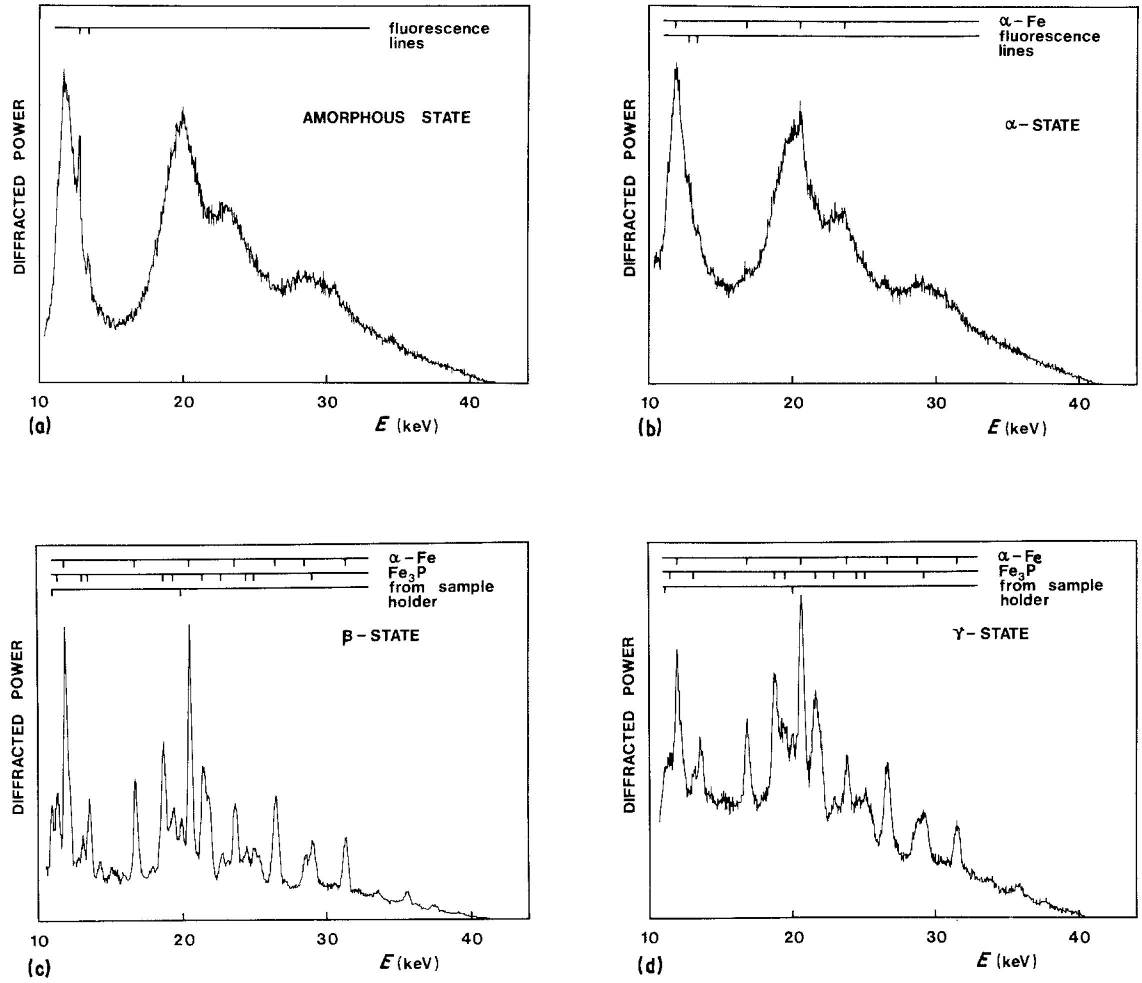


Figure 3 Mössbauer spectra of the $Fe_{81.2}P_{18.8}$ alloy measured at room temperature. The spectra (a), (b), (c) and (d) correspond to the amorphous state and to the α, β and final stages of the crystallization process, respectively.

$Fe_{81.2}P_{18.8}$ sample, this alloy was chosen for further crystallization studies using EDXD. To verify that the formation of the α-iron phase starts before that of Fe_3P, isochronal EDXD measurements were carried out. The samples were annealed for 10 min at each temperature and the measurements were carried out at room temperature after the annealings. The presence of α-iron could first be identified after annealing at 620 K. The steps of the temperature scan were rather rough in these measurements. Therefore, the crystallization of the Fe_3P phase was definitely noticed only after annealing at 670 K, which seems to be too high as the crystallization temperature. Again, only the stable crystalline phases were formed.

The most effective way to use EDXD measure-



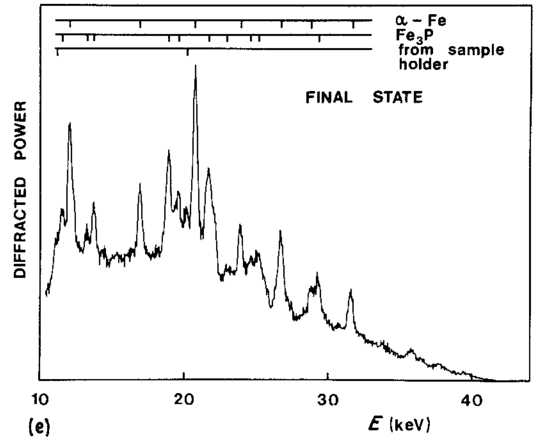


Figure 4 EDXD spectra of the $Fe_{81.2}P_{18.8}$ alloy measured at room temperature. The spectra (a), (b), (c), (d) and (e) correspond to the amorphous state and to the α, β, γ and final stages of the crystallization process, respectively.

ments to study crystallization is the *in situ* isothermal study. In this case the high temperature is kept constant even during the measurement and the spectra are taken after definite annealing times. Some typical spectra are shown in Fig. 6. The appearance of α-iron can be seen in Fig. 6b as an asymmetry of the first and the second amorphous line. The presence of Fe_3P is clear in Figs. 6d and e. Representing the times when one or other phase was first identified as a function of the annealing temperature, a time-temperature-transformation (TTT) diagram can be obtained (Fig. 7).

A series of EDXD spectra (see Fig. 6) can also be used to study the crystallization kinetics of each phase separately. The amount of a phase can be described by the area of its characteristic diffraction lines. The line intensities are normalized to the intensities measured in the equilibrium crystalline state (after a long annealing time at a sufficiently high temperature). These line-areas are plotted as a function of the annealing time in Fig. 8. To get these results, the areas of two diffraction lines belonging to α-iron and two lines characteristic of Fe_3P were followed. Both Figs. 7 and 8 show that the crystallization of the $Fe_{81.2}P_{18.8}$ alloy starts as a primary crystallization of α-iron. After a short period, the curves showing increase of the amount of α-iron and Fe_3P become nearly parallel, indicating eutectic crystallization (see Fig. 8).

Assuming that the α-iron phase does not contain phosphorus impurities and Fe_3P is stoichiometric and using the nominal concentration

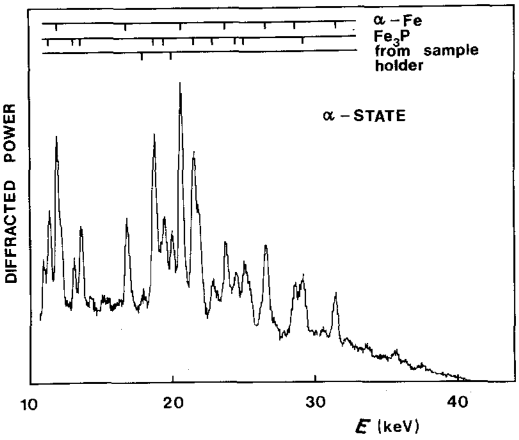


Figure 5 EDXD spectrum of the $Fe_{80.0}P_{20.0}$ sample heat treated to the α stage of the crystallization process as indicated in Fig. 2b.

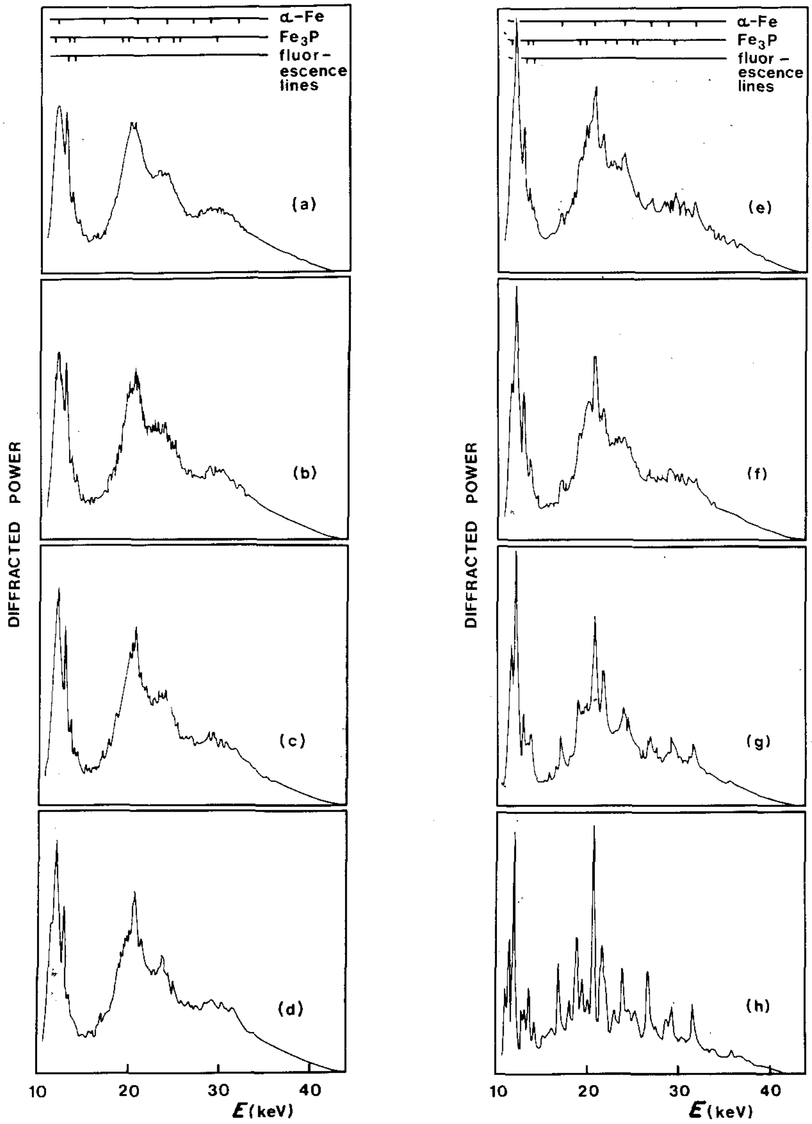


Figure 6 EDXD spectra taken during the isothermal crystallization of an $Fe_{81.2}P_{18.8}$ sample at 610 K. The annealing times were 0, 5, 35, 55, 75, 100 and 240 min for curves from (a) to (g), respectively. Curve (h) was taken after annealing for 15 min at 870 K.

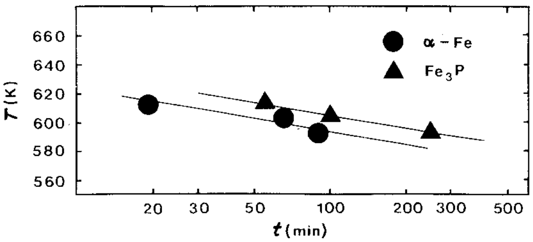


Figure 7 The start of the crystallization of α-iron and Fe_3P as a function of the annealing time and temperature for an $Fe_{81.2}P_{18.8}$ amorphous alloy.

$Fe_{81.2}P_{18.8}$, the relative amount of the phases can be calculated by some simple algebra. The results are shown in Fig. 9.

4. Conclusions

The combination of thermomagnetic, Mössbauer, and energy dispersive X-ray diffraction measurements proved to be useful in studying the crystallization process of Fe–P amorphous alloys.

The possibility of measuring the crystallization kinetics of each phase simultaneously should be especially emphasized.

The stability of the Fe–P amorphous alloys is rather low: at 600 K the crystallization starts within an hour. In the range of temperatures and annealing times studied here only the stable phases α-iron and Fe_3P are formed.

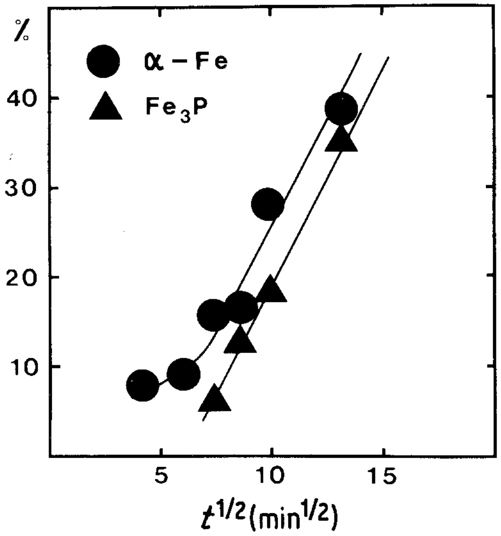


Figure 8 The amount of the crystalline phases normalized to their values in the final crystalline state as a function of the annealing time during an isothermal annealing at 610 K.

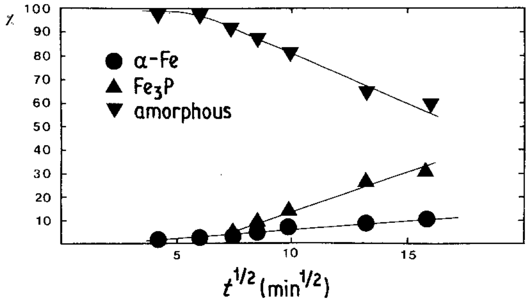


Figure 9 Change of the phase-composition of the $Fe_{81.2}P_{18.8}$ sample during an isothermal annealing at 610 K (in at%).

The crystallization starts with the primary crystallization of α-iron (with some dissolved phosphorus) and continues with the eutectic crystallization of α-iron and Fe_3P.

Acknowledgements

The authors are grateful to M. Palásti for preparing the samples, to M. Hossó for performing the thermomagnetic measurements and to M. Tamminen for helping in the EDXD measurements. The discussions with E. Laine and C. Hargitai are also acknowledged.

References

1. T. EGAMI, in "Glassy Metals I" in series "Topics in Applied Physics" Vol. 46, edited by H.-J. Günterodt and H. Beck (Springer-Verlag, Berlin, 1981) p. 25.
2. M. TAKAHASHI and M. KOSHIMURA, *Jpn. J. Appl. Phys.* **16** (1977) 2269.
3. D. MUSSER, C. L. CHIEN and H. S. CHEN, *J. Appl. Phys.* **50** (1979) 7660.
4. M. NAKA and T. MASUMOTO, *Sci. Rep. RITU (Sendai Jpn.)* **A27** (1979) 118.
5. T. TARNÓCZI, I. NAGY, C. HARGITAI and M. HOSSÓ, *IEEE Trans. Magn.* **Mag-14** (1978) 1025.
6. J. LOGAN and E. SUN, *J. Non-Cryst. Solids* **20** (1976) 285.
7. I. VINCZE and L. TAKÁCS, in Proceedings of the International Conference on Mössbauer Spectroscopy, Vol. 1, Bucharest, Rumania, September 1977, edited by D. Barb and D. Tarina (Central Institute of Physics, Bucharest, 1977) p. 419.
8. I. VINCZE, *Solid State Commun.* **25** (1978) 689.
9. E. J. LISHER, C. WILKINSON, T. ERICSSON, L. HÄGGSTRÖM, L. LUNDGREN and R. WÄPPLING, *J. Phys. C: Solid State Phys.* **7** (1974) 1344.

Received 7 October
and accepted 12 November 1982