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ABSTRACT

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

АННОТАЦИЯ

Методами рентгеновской дифракции с энергодисперсным датчиком (EDXD) термомагнитных измерений и Мессбауэровской спектроскопии была исследована кристаллизация аморфных сплавов Fe-P, полученных электролитическим путем. Наиболее полезным оказался EDXD метод, потому что краткое время экспозиции дало возможность практически непрерывно следить за состоянием образца во время изотермической термообработки. При измерении интенсивности соответствующей линии дифракции одновременно можно исследовать кинетику кристаллизации отдельных фаз. Обнаружено, что после обработки одного из аморфных сплавов $Fe_{81.2}P_{18.8}$ при температуре 610K кристаллизация началась в течение 5 минут с выделением α-Fe. Спустя, примерно, 50 минут процесс продолжается с эвтектической кристаллизацией стабильных фаз α-Fe и Fe_3P.

KIVONAT

Elektrolitikusan leválasztott Fe-P amorf ötvözetek kristályosodását vizsgáltuk energia diszperziv röntgen diffrakció (EDXD), termomágneses mérések és Mössbauer spektroszkópia segitségével. Különösen az EDXD módszer bizonyult hasznosnak, mivel nagyon rövid expoziciós ideje lehetővé tette, hogy a minta állapotát gyakorlatilag folyamatosan tudjuk követni egy izoterm hőkezelés folyamán. Mérve a megfelelő diffrakciós vonalak intenzitását egyidejüleg vizsgálható az egyes fázisok kristályosodási kinetikája. Egy $Fe_{81.2}P_{18.8}$ amorf ötvözetet 610K-en hőkezelve azt találtuk, hogy a kristályosodás 5 percen belül, α-Fe kiválásával kezdődik. Körülbelül 50 perccel később a folyamat a stabil fázisok, α-Fe és Fe_3P eutektikus kristályosodásával folytatódik.

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 a practically continuous control by 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. For this kind of measurements had not had any trandi-tions, the Fe-P system has been chosen because a rather simple crystallization process directly into the stable phases α-Fe and Fe_3P could be expected [2,3,4].

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

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 ^{o}C. Three different current densities were chosen, namely 200 mA/cm^2, 150 mA/cm^2 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 about the course of the crystallization process, thermomagnetic measurements were carried out in a magnetic balance using low magnetic fields of about 100 Oe. 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 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 magnetiza-

tion 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.

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 Rh 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 at liquid nitrogen temperature.

In the case of EDXD the continuous spectrum of X-rays is used and the diffraction pattern is measured at a fixed angle as a function of the energy of the photons. In this work copper radiation and $\Theta=15^{o}$ Bragg's angle 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 300s 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. The abrupt decrease of the magnetization at about 570K indicates the ferromagnetic Curie temperature of the amorphous phase. At about 620K, the magnetization starts to increase indicating the start of the crystallization. A very abrupt increase at 650K shows the main step of the crystallization process. Above 680K the magnatization 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 850K.

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 to the stage α was rather difficult. Fig. 2/a 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. 2/b 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. (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].) Spectrum b corresponds to the stage α. This is the spectrum of just the sample produced during the thermomagnetic measurement shown in Fig. 2/a. Although the spectrum resembles that of the amorphous sample very much, some sign of the presence of crystalline α-Fe can be identified at the outer part of the spectrum. (The amount of the solved phosphorus may be much higher than the equilibrium solubility. Because of this, the lines corresponding to the α-Fe 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 1050K for about 1 hour ("final" state) were practically identical (Fig. 3/c, d). Each of them could be fitted to seven Zeeman-split sextuplets, one corresponding to α-Fe, the other six to Fe_3P. The parameters of these latter sextuplets agreed well with the results of Lisher [8]. 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 1050K the Fe_3P compound is stoichiometric and the concentration of phosphorus solved in the α-Fe 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. Figure 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 stages α, β, γ and to the final crystalline state. The presence of the α-Fe phase at stage α is more clear here than in the Mössbauer spectrum, because the line broadening caused by the solved phosphorus is less important in the diffraction measurement than in the Mössbauer study and so the lines corresponding to the α-Fe phase are better resolved. The spectra taken at the stages β, γ and in the final state are essentially similar. Each of them consists of the lines of α-Fe 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 curve in Fig. 1 above 680K can be a consequence of

changes of the domain structure without any change of the phase composition.)

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

Because the crystallization of α-Fe and Fe_3P was the easiest to separate in the case of the $Fe_{81.2}P_{18.8}$ sample, this alloy was chosen for further crystallization studies using EDXD. To verify that the formation of the α-Fe phase starts before that of Fe_3P, isochronal EDXD measurements were carried out. The samples were annealed for 10 minutes at each temperature and the measurements were carried out at room temperature after the annealings. The presence of α-Fe could first be identified after annealing at 620K. 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 670K 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 measurements 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-Fe can be seen in Fig. 6/b as an asymmetry of the first and the second amorphous line. The presence of Fe_3P is clear in Figs. 6/d and e. Representing the times when one or the other phase was first identified as a function of the annealing temperature, a TTT diagram can be obtained (Fig. 7).

A series of EDXD spectra (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-Fe 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-Fe. After a short period, the increase of the amount of α-Fe and Fe_3P become nearly parallel indicating an eutectic crystallization (Fig. 8).

Assuming that the α-Fe phase does not contain phosphorus impurities and Fe_3P is stoichiometric and using the nominal concentration $Fe_{81.2}P_{18.8}$, 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 (EDXD) measurements proved to be useful in studying the crystallization process of Fe-P amorphous alloys.

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

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

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

5. ACKNOWLEDGEMENTS

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Figure captions

Fig. 1. Typical thermomagnetic curve taken on an $Fe_{81.2}P_{18.8}$ amorphous alloy with a heating rate of 14K/min

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

Fig. 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

Fig. 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.

Fig. 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. 2/b

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

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

Fig. 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 610K

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

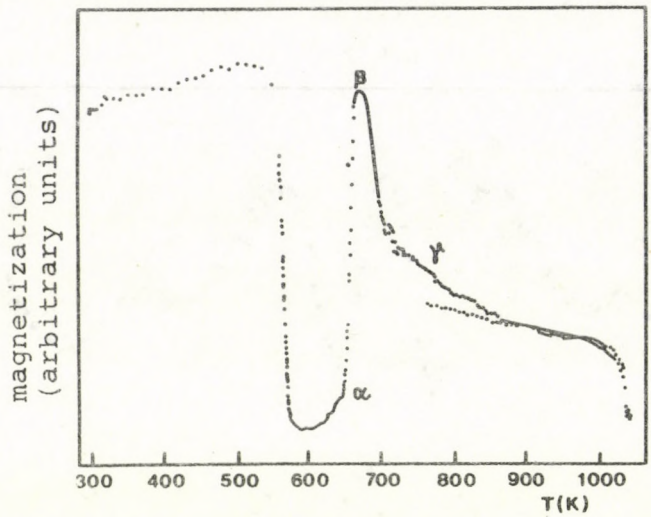
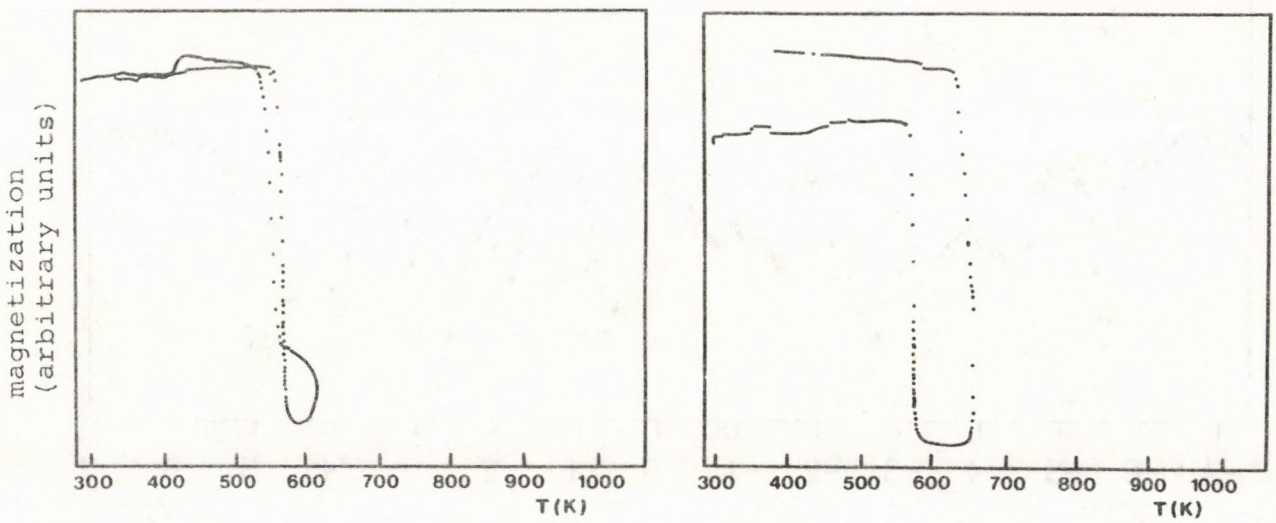

magnetization
(arbitrary units)
300
400
500
600
700
800
900
1000
T(K)
β
γ
α

Fig. 1.


magnetization
(arbitrary units)
300
400
500
600
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800
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T(K)
300
400
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600
700
800
900
1000
T(K)

a

b

Fig. 2.

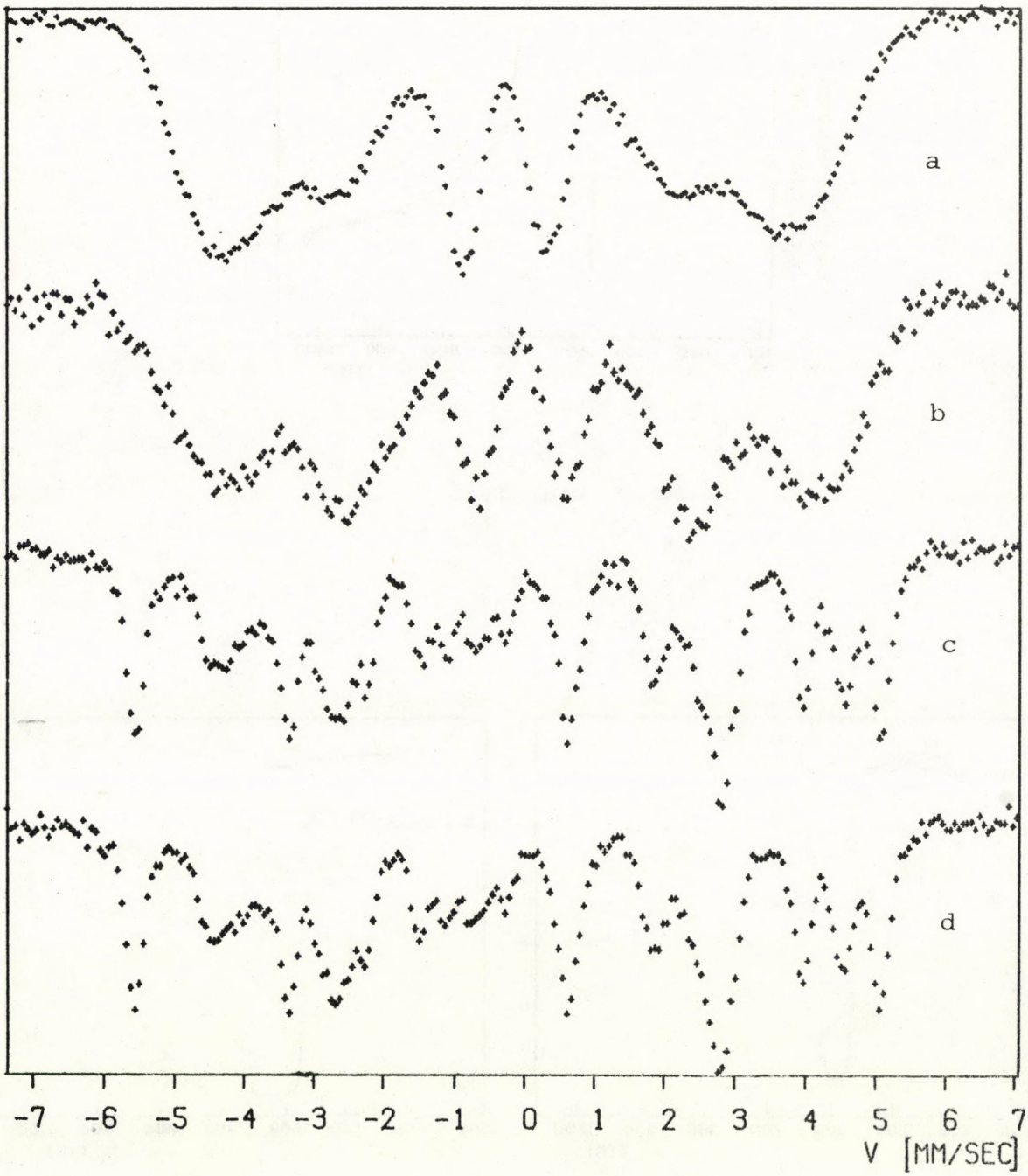

Fig. 3.

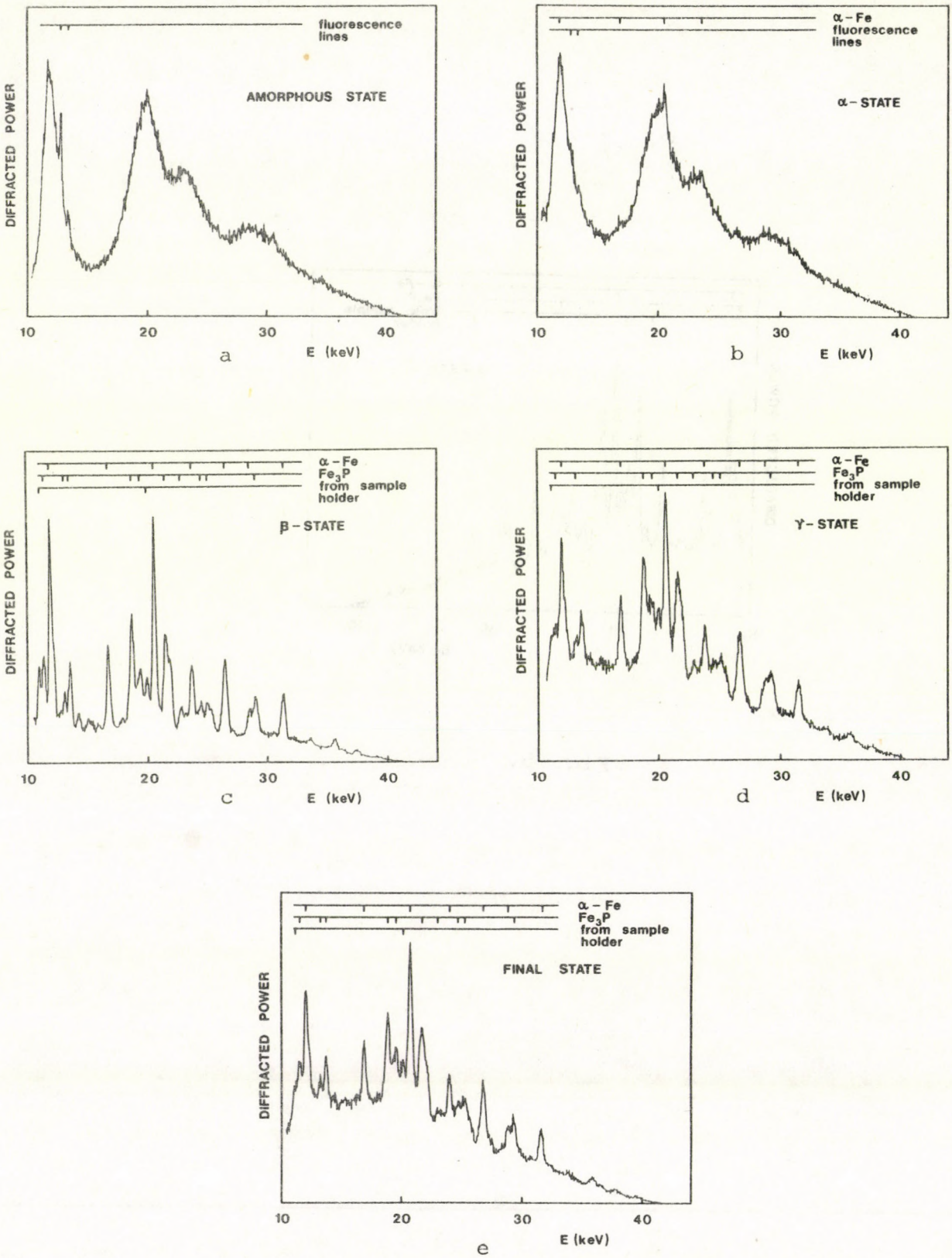
fluorescence lines
AMORPHOUS STATE
DIFFRACTED POWER
10
20
30
40
E (keV)
a
α – Fe fluorescence lines
α – STATE
b
α – Fe
Fe3P
from sample holder
β – STATE
c
γ – STATE
d
FINAL STATE
e

Fig. 4.

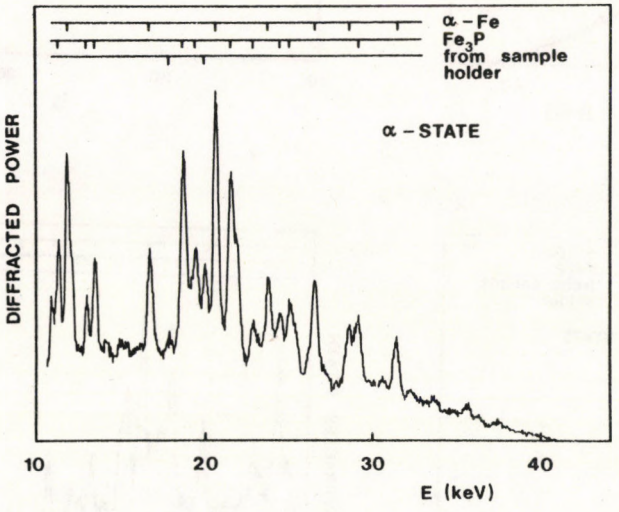
α - Fe
Fe_3P
from sample holder
α - STATE
DIFFRACTED POWER
10
20
30
40
E (keV)

Fig. 5.

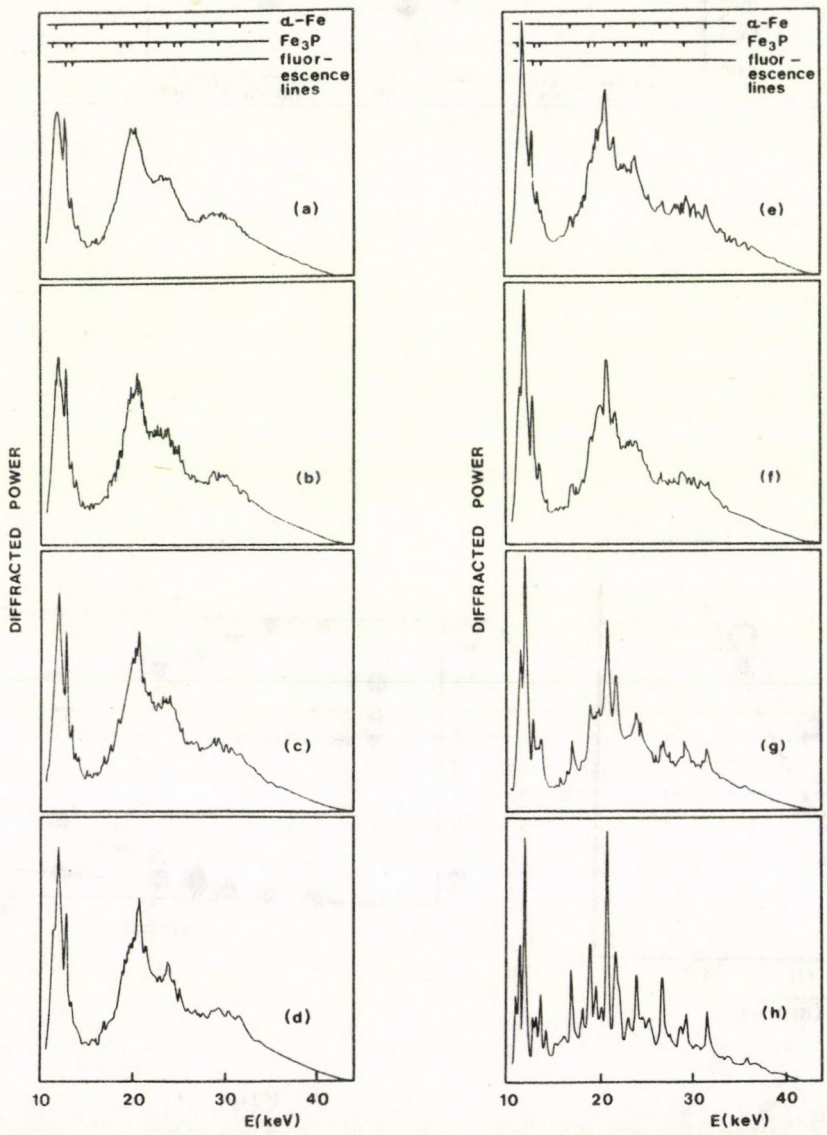
α-Fe
Fe3P
fluor-escence lines
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
DIFFRACTED POWER
10
20
30
40
E(keV)

Fig. 6.

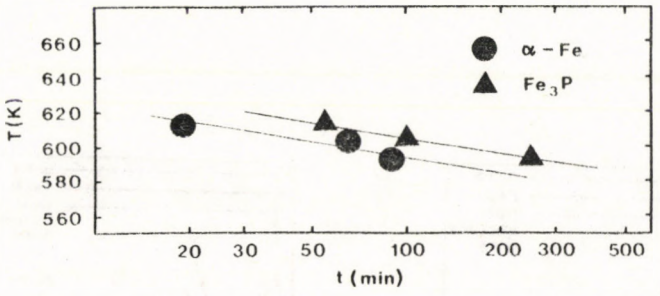

Fig. 7.

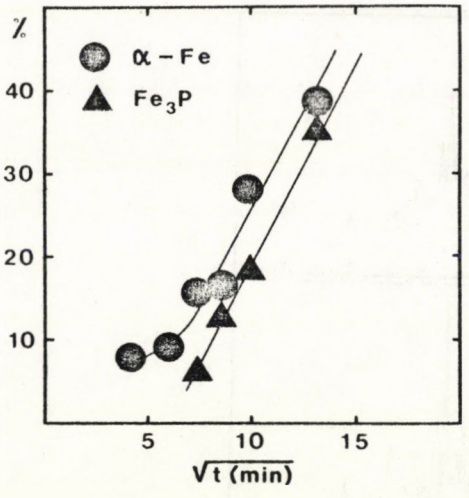

Fig. 8.

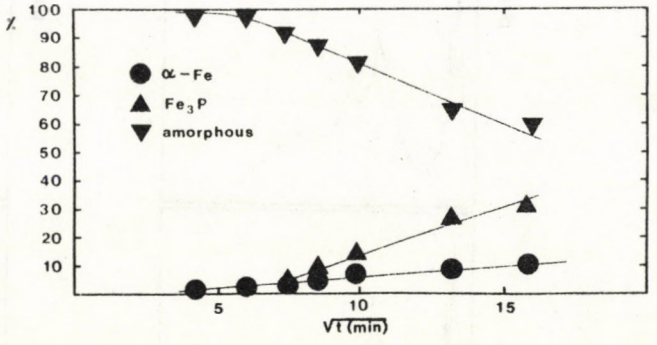

Fig. 9.

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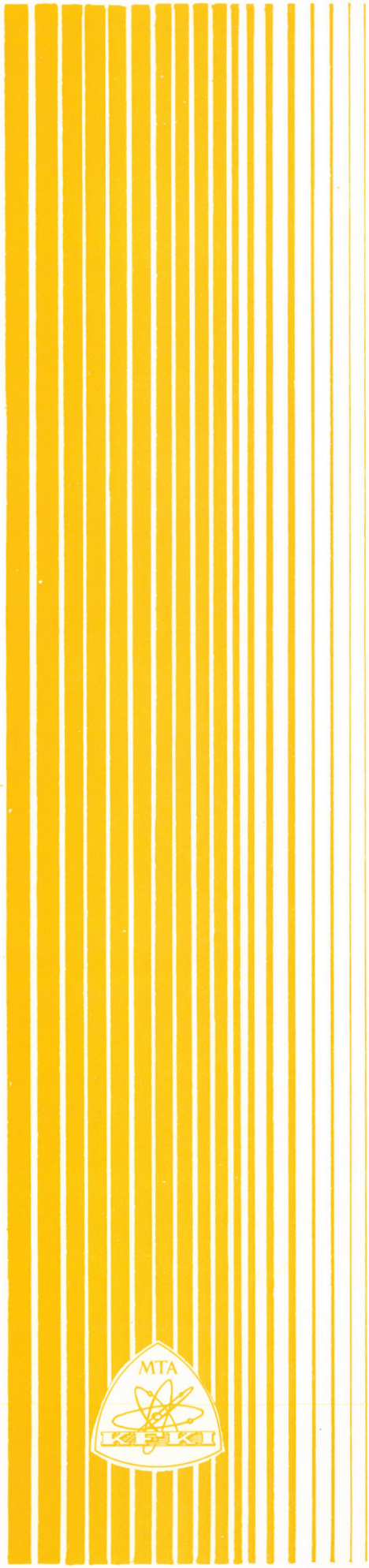

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