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Absorption of hydrogen by amorphous and crystalline 89Fe–11P powder: deformation of the powder under pressure and relaxation on heating

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Abstract

The process of hydrogen absorption by amorphous and crystalline powder of the 89Fe–11P alloy, obtained by electrolyzing an aqueous solution of the corresponding electrolytes, was studied by differential scanning calorimetry. It was shown that hydrogen absorption takes place exothermally in the temperature range 100–300 °C. The relevant kinetic and thermal parameters of the absorption process were determined: rate constants, enthalpies, activation energies and frequency factors. The process of powder deformation by pressing and its relaxation was investigated by measuring the electrical resistance during heating and cooling in the temperature range 20–610 °C. The X-ray diffractograms show that the powder obtained contains 10% crystal phase and that by heating to 500 °C complete crystallization takes place.

Keywords: Hydrogen absorption; Fe–P powder; Deformation; Relaxation

1. Introduction

In the last twenty years extensive work has been done on the preparation and investigation of alloys in glassy (amorphous) states. Modern powder metallurgy is particularly concerned with amorphous powders of metals and alloys.

Polycrystalline metal and alloy powders are prepared simply by grinding methods in combination with various other methods. However, amorphous alloy powders are prepared by far more complex methods, including spilling the melted alloy into a very cold environment [1–3]. Preparation by mechanochemical treatments is also significant. Electrochemical methods are of particular interest, because of the relative simplicity of the equipment with which one can obtain different alloys in an amorphous state by electrolysis. Polycrystalline and amorphous powders of metals and alloys are of increasing importance, owing to their great significance in modern technologies used in the manufacturing of precise components for various types of equipment by hot and cold sintering. It is also worth pointing out that powders of metals and alloys, particularly in the amorphous state, are more or less active absorbers of various gases.

In the present paper, the process of electrochemical preparation of amorphous iron–phosphorus alloys is investigated, along with their behaviour in hydrogen atmosphere at different temperatures. The change in the electrical resistance of the samples pressed in hydrogen atmosphere is observed as the temperature is increased.

2. Experimental

An amorphous Fe–P powder was obtained by electrolyzing an aqueous solution containing, in 1 dm^3 of solution, 5 g $NaH_2PO_3 \cdot 5H_2O$, 0.5 g $C_2H_2O_4 \cdot 4H_2O$, 12 g glycine and 200 g $FeSO_4 \cdot 7H_2O$ at a current density j of 7 A dm^{-2}, with a Cu cathode and a Pt anode, in a flowing atmosphere of purified nitrogen, whose continuous flow was used for stirring the electrolytes in the electrolyzer. Chemical analysis of the cathode power obtained showed 89 wt.% Fe and 11 wt.% P. Microscopy analysis showed that 97% of the particles have dimensions in the range 0.5–4.5 μm. The process of hydrogen absorption was investigated by differential scanning calorimetry (DSC) using a Du Pont thermal analyzer (model 1090). Samples weighing several milligrams were heated in the DSC cell from room temperature to 500 °C in a flowing hydrogen atmosphere. The kinetics of hydrogen absorption was investigated by the method of nonisothermal DSC [6].

For the measurements of the electrical resistance, amorphous and crystalline powders were pressed at 100 MPa into 3 cm long samples with a cross section of 0.36 mm^2. The measurements were carried out by the four-point method in hydrogen atmosphere. The amorphous and crystalline state

of the alloy was investigated before and after the thermal treatment by X-ray analysis by a Philips PW-1051 diffractometer using a graphite monochromator and Cu Kα radiation.

3. Results

Inspection of the structure of the electrochemically obtained powder alloy 89Fe–11P was done by comparing its X-ray diffractogram (Fig. 1(a)) with the one for α-Fe crystal powder (Fig. 1(c)).

The alloy powder diffractogram indicates amorphization of iron in the presence of phosphorus. The α-Fe peaks are deformed, have lower intensity, are widened and shifted towards lower 2θ values with respect to the peaks of the crystalline α-Fe. This indicates partial incorporation of phosphorus into the iron crystal lattice, which causes its deformation, owing to the somewhat larger atomic diameter of phosphorus. The crystallinity of the powder obtained is estimated at roughly 10% by comparing the intensities of these peaks. Heating of the alloy for 2 h at about 500 °C under vacuum in a sealed quartz tube results in crystallization, as shown by diffractograms a and b in Fig. 1.

3.1. Hydrogen absorption

The DSC thermograms in Fig. 2, obtained with the alloy under investigation in hydrogen flow in the temperature range 20–500 °C, show a series of exothermal processes of the sample thermal stabilization and hydrogen absorption, expressed by appearance of the corresponding, more or less well-formed maxima labeled 1–4. During the first heating in the temperature range 100–300 °C (Fig. 2(a)), a double exothermal maximum appears (1 and 2), which indicates the complexity of this process. The maximum labeled 1 we ascribe to the reduction of the oxide film formed on the surface of the alloy grain during drying after the synthesis, which proceeds to further hydrogen absorption, labeled 2. At higher temperatures, in the range 350–500 °C, two exothermal maxima appear, labeled 3 and 4, which correspond to the two steps of the crystallization process. Repeated hydriding of the same sample (Fig. 2(b)), by heating up to 500 °C and cooling down to 120 °C, produces a thermogram with one absorption maximum during heating, which corresponds to peak 2 on the thermogram in Fig. 2(a), and one absorption maximum during cooling, labeled 2'. This indicates that the repeated heating increases the absorption capacity by activation of the absorber during hydriding. This is proved by a similar effect observed in a third hydriding of the same sample (Fig. 3) by increasing the absorption enthalpy. It is worth emphasising that the thermograms in Fig. 2(b) and Fig. 3 really represent hydrogen absorption by the crystalline sample, since during only the first hydriding is the absorber in an amorphous state.
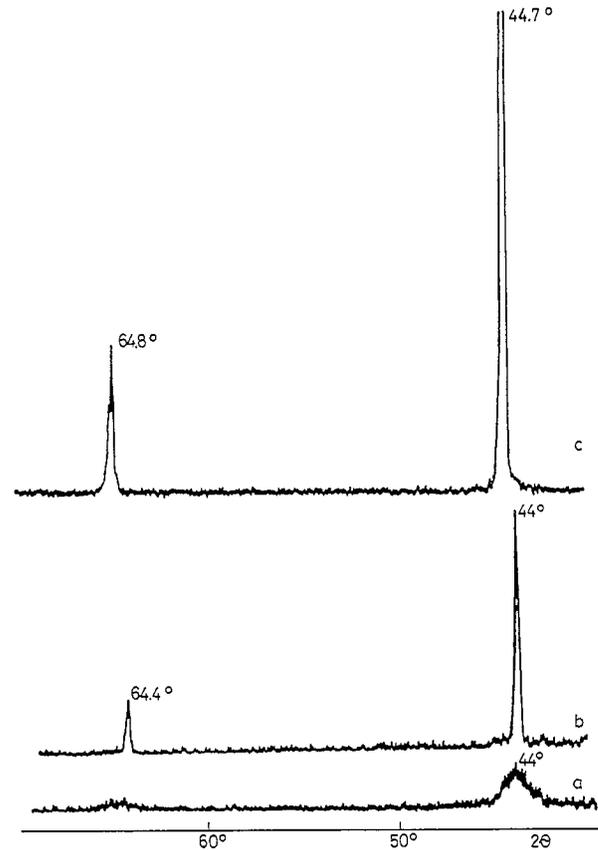

Fig. 1. X-ray diffractograms: (a) the original powder; (b) after heating the powder at about 500 °C under vacuum for 1 h; (c) crystalline α-phase of iron.
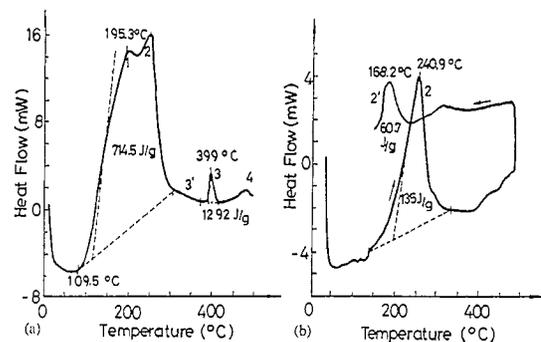

Fig. 2. DSC thermograms in hydrogen flow: (a) first heating; (b) second heating/cooling cycle. Heating rate 30 °C min⁻¹.

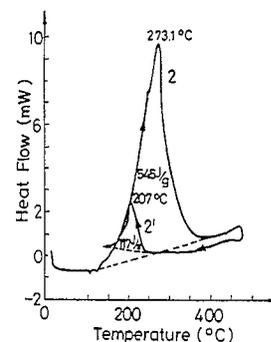

Fig. 3. DSC thermograms of the third heating and cooling cycle in a hydrogen flow. Heating rate 30 °C min⁻¹.

The enthalpies of the absorption processes are determined by integrating the area under DSC thermograms. The kinetics of hydrogen absorption is analyzed by nonisothermal differential scanning calorimetry specifically adapted for the analysis of hydrogen absorption and similar processes [4,5]. The method of nonisothermal differential scanning calorimetry analysis of DSC thermograms is based on the work done by Borchardt and Farrington [6]. These authors developed nonisothermal differential thermal analysis (DTA) and differential enthalpy analysis (DEA) for the investigation of the kinetics of processes in homogeneous liquid systems.

For DTA thermogram analysis the rate constant follows the equation

$$k = (KAV/n_0)^{x-1}[C_p(d\Delta T/dt) + K\Delta T]/$$
$$[K(A-a) - C_p\Delta T]^x$$

where C_p is the molar heat capacity of the reactants in the given medium; ΔT is the ordinate of the thermogram; K is the heat conductance of the system; A denotes the total area under the maximum, whereas a is the area under the maximum for time t of the process duration up to the temperature T; n_0 is the number of reactant moles at the beginning; V is the reaction volume of the system; and x denotes the order of the reaction. It was shown that the parameters $C_p(d\Delta T/dt)$ and $C_p\Delta T$ are one order of magnitude smaller than the parameters to which they are added or from which they are subtracted, so that they can be neglected without causing great error. In this way, for a first-order reaction ($x=1$), the equation takes the following form:

$$k = \Delta T/(A-a)$$

For the differential enthalpy analysis (DEA), i.e., differential scanning calorimetry, the following equation was derived:

$$k = [(AV/n_0)^{x-1}(dH/dt)]/(A-a)^x$$

For $x=1$, this equation becomes

$$k = (dH/dt)/(A-a)$$

or

$$k = \Delta mW/(A-a)$$

where ΔmW is the ordinate in the DSC thermogram expressed in milliwatts. The rate constant k is determined by measuring both the total area A and the partial area a up to temperature T and time t at the corresponding ΔmW value, read off the ordinate. Plotting $\log k$ versus $1/T$, if the process corresponds to a first-order reaction, gives a straight line whose slope, $\Delta \log k/\Delta(1/T)$, yields the activation energy E, while the reaction frequency factor Z can be determined from the relation $k = Z\exp(-E/RT)$.

The $\log k = f(1/T)$ diagram for the second and third heating (Fig. 2(b) and Fig. 3) is presented in Fig. 4 and shows two ranges of the mentioned linear dependence. This indicates a complex mechanism of absorption, which proceeds in two stages, noted on the DSC diagrams. These stages are now
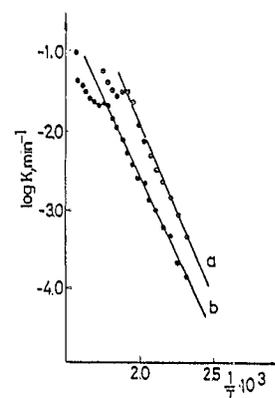

Fig. 4. Energy activation plots, $\log k = f(1/T)$, for thermograms in heating: (a) plot for thermogram of Fig. 2(b); (b) plot for thermogram of Fig. 3.

Table 1
Kinetic parameters of hydrogen absorption for amorphous and crystalline 89Fe–11P

Thermal treatment	Temp. of maximum (°C)	Enthalpy (J g^{-1})	E (kJ mol^{-1})	Z (min^{-1})
First heating	–	714.5	–	–
Second heating	240.9	135.0	87.0	2.38×10^5
			50.0	
Second cooling	168.2	60.7	–	–
Third heating	273.1	545.0	76.6	1.6×10^7
			61.3	
Third cooling	207.1	117.0	–	–

clearly distinguishable. The linear dependence of $\log k$ versus $1/T$ indicates that the absorption process proceeds as a first-order reaction. From the slope of the straight lines, $\Delta \log k = \Delta(1/T)$, the activation energy E and frequency factor Z are determined for the temperature at the top of the thermogram of hydrogen absorption. All relevant parameters of the absorption process are given in Table 1.

The exothermal maxima formed during cooling appear at lower temperatures than during heating, owing to a difference in the rates of temperature change.

3.2. Measurement of electrical resistance of pressed samples

Fig. 5(a) shows the electrical resistance change of the pressed powder during heating from 20 to 610 °C and cooling down to 20 °C, in hydrogen atmosphere. Two processes of heating and one process of cooling are presented. During the first heating, the resistance decreases, with a minimum in the temperature range 300–450 °C, and then increases while the temperature is raised to 610 °C. The resistance decrease in this case is ascribed to a stabilization of the deformed structure (10% crystallinity) and to a change in the amorphous phase disorder, which is in connection with the change in the electronic structure. During the observed minimum resis-
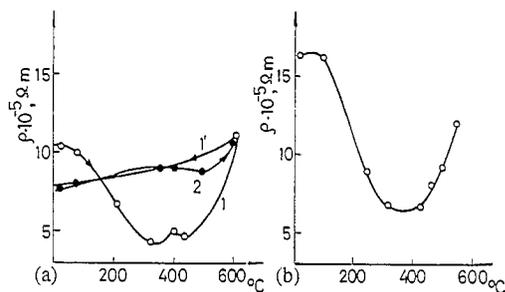
Fig. 5. Change in electrical resistance with temperature: (a) for two cycles of heating and cooling; (b) for the third heating of the sample crushed and pressed again, in hydrogen flow.

tance, the relaxation of the pressed sample is almost completed; the crystallization process takes place already at 440 °C (Fig. 2(a)) and the resistance increases while the temperature is raised to 610 °C. At this temperature the heating and crystallization is ended, and cooling to the initial temperature begins, followed by a slight, almost linear, decrease in the resistance, curve 1′.

In repeated heating of the same sample, the resistance increases slowly, with a small minimum at about 400 °C, and continues increasing slightly up to 610 °C to reach a minimum value at the point of completed crystallization of the sample (Fig. 5(a)). After these processes, the sample is crushed and pressed again with the same pressure. For the newly pressed sample, the electrical resistance is measured in the same manner from 20 to 610 °C, as shown in Fig. 5(b). It is seen that now the initial resistance is higher than in the case of the primarily pressed sample, since heating led to a complete crystallization and caused a higher degree of deformation, while the other features are the same. The resistance decreases because of the stabilization process up to 380 °C, and then increases rapidly up to 610 °C when the crystallization is finished and the resistance reaches normal values, being equal in both Fig. 5(a) and Fig. 5(b). It is shown that a pressure

of 1000 MPa gives rise to more deformation (defects) in the sample with more crystallinity.

4. Conclusions

It is shown by the method of differential scanning calorimetry that the amorphous and crystalline powder of the 89Fe–11P alloy is an active hydrogen absorber in the temperature range 20–300 °C. The absorption process takes place exothermally. All relevant kinetic and thermal parameters of this process were determined. It was also shown that amorphous and crystalline powders pressed at 1000 MPa undergo a reordering and deformation. Heating produces relaxation of the deformed structure, as proved by the electrical resistance measurements of the pressed samples in the course of their thermal treatment.

Acknowledgements

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