Influence of hydrogen pressure on the kinetics of hydrogen-induced diffusive phase transformations in the $Nd_2Fe_{14}B$ alloy

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Abstract

The influence of hydrogen pressure on the kinetics of hydrogen-induced direct and reversed diffusive phase transformations in a $Nd_{15}Fe_{77}B_8$ alloy has been investigated. It was shown that increase (decrease) of hydrogen pressure provokes a marked acceleration of both the direct and reversed-phase transformations.
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1. Introduction

The principles of hydrogen-induced diffusive phase (HIDP) transformations form the scientific background for an understanding of the hydrogenation–disproportiona-tion–desorption–recombination (HDDR) treatment of magnetic compounds of the $Nd_2Fe_{14}B$ type. Application of the HDDR procedure to $Nd_2Fe_{14}B$ type compounds allows the hard magnetic properties to be optimised [1]. The reversible HDDR reaction can be schematised as follow:

$$Nd_2Fe_{14}B + 2.5H_2 \leftrightarrow 2(NdH_{2.5}) + 12\alpha\text{-}Fe + Fe_2B \qquad (1)$$
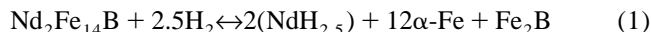
Analysis of the isothermal kinetic diagrams of the phase transformations is the key to the hydrogen treatments of these alloys and compounds [2].

In recent papers, the kinetics of hydrogen-induced diffusive phase transformations has been reported [3–5]. In these studies it was shown that temperature is the most important kinetic factor determining the phase transformation. The aim of the present paper is to investigate the influence of hydrogen pressure on the kinetics of direct and reverse hydrogen-induced diffusive phase transformation in $Nd_{15}Fe_{77}B_8$ alloy.

2. Experimental

Investigation of the direct and reversed-phase trans-formations was made by using a Sadikov's type magneto-meter [3]. $Nd_{15}Fe_{77}B_8$ (at.%) samples in the form of powder with a grain size < 50 μm were placed into the working chamber, which was evacuated to a pressure of ~1 Pa. Then, the samples were heated under vacuum to the desired temperature. After establishing isothermal con-ditions, the working chamber was filled with hydrogen under selected pressures ranging from 0.1 to 0.7 MPa. The direct HIDP transformation was monitored under iso-thermal annealing conditions by measuring the amount of newly formed ferromagnetic phases (α-Fe and Fe_2B) according to (1). After completion of the direct trans-formation, hydrogen was evacuated from the chamber. The development of the reverse transformations was then followed by monitoring the decreasing amount of the ferromagnetic phases. The resulting data were plotted as isothermal kinetic diagrams of the direct and reverse HIDP transformations occurring in the $Nd_2Fe_{14}B$ compound.

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3. Direct phase transformations

In Fig. 1 we report parts of the isothermal kinetic diagrams of the hydrogen-induced direct phase transformation at different isothermal conditions and under different hydrogen pressures. During an isothermal exposure at 670 °C for 360 min and at 0.1 MPa hydrogen pressure, the transformation is only 62%, as seen in Fig. 1. With increasing the hydrogen pressure to 0.3 MPa, the rate of the transformation was markedly accelerated and the transformation was fully achieved within 320 min. The same behaviour was observed after successive increases of pressure. For applied pressure of 0.5 and 0.7 MPa, the transformation was completed within 200 and 180 min, respectively. Upon an increase of hydrogen pressure of 0.4
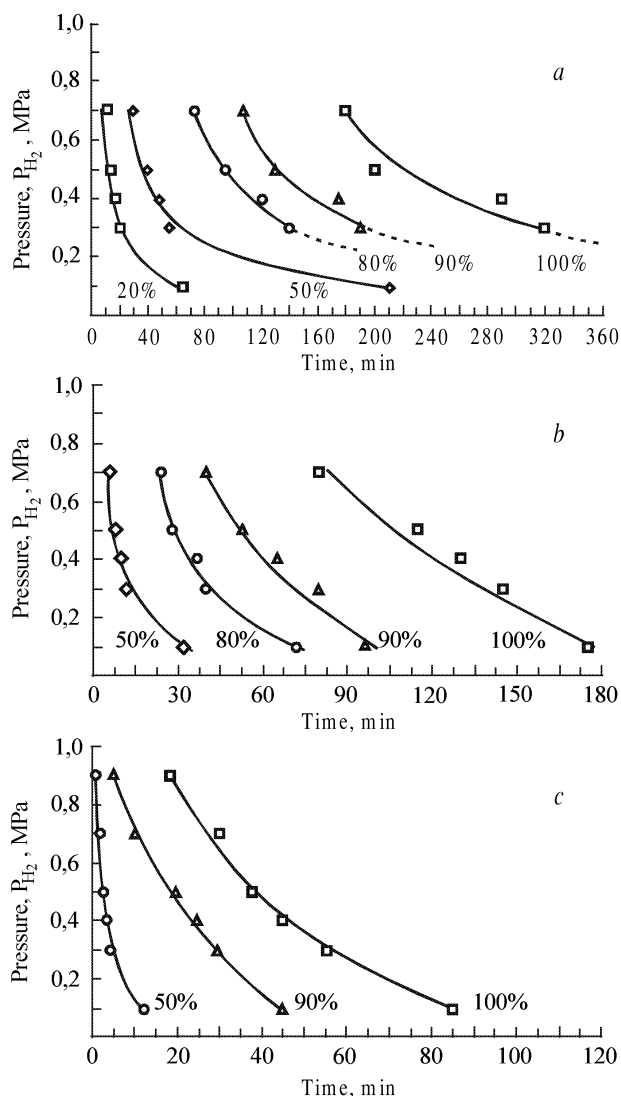
MPa only, from 0.3 to 0.7 MPa, the transformation accelerates and its characteristic time was shortened by a factor of 2. Similar effects were also observed for isothermal exposure at 710 and 750 °C. As seen in Fig. 1b, at 710 °C and under a hydrogen pressure of 0.1 MPa, the transformation was completed in 175 min, while under 0.7 MPa hydrogen pressure, it was completed in 80 min only. Moreover, as can be deduced from Fig. 1c, at 750 °C and under 0.1 MPa, the transformation was complete within 85 min, while only 30 min was needed when the hydrogen pressure was increased to 0.7 MPa. After a final increase of hydrogen pressure to 0.9 MPa, the transformation was markedly accelerated and was fully achieved within 18 min.

Within the temperature range of 670–750 °C, an increase of the hydrogen pressure causes a net acceleration of the phase transformation of almost 2.5 times.

How does the hydrogen pressure influence so directly the kinetics of the direct hydrogen-induced phase transformation? A HIDP transformation operates via a mechanism of nucleation and growth and is controlled by the long-range diffusion transport of solid elements, in the present case Nd, Fe and B [3]. In addition an increase of interstitial atom concentration should lead to an increase of the large atoms self-diffusion coefficient as proposed in Ref. [6]. Thus, when the concentration of interstitial atoms increases, there is a corresponding increase in the concentration of vacancies in the compound [7]. The impact of a superabundant concentration of vacancies in metals generated by the presence of interstitial hydrogen has been analysed both experimentally and theoretically, e.g. in Ref. [8] and could serve as a model for the driving force of the direct hydrogen-induced phase transformation in the present case.

Hence, the increase of the vacancy concentration under the influence of the interstitial hydrogen atoms, yielding acceleration of the interstitial atoms diffusion, reveals a rather common physical phenomenon. It appears to apply to various types of materials, and can be assumed to operate in the present case. Upon the increase of hydrogen pressure, the amount of dissolved hydrogen increases correspondingly, therefore leading to an increase of the diffusion coefficient of the elements and finally of the phase transformation rate. In other words, it results in a corresponding acceleration of the transport of atoms favouring the nucleation of new phases (NdH$_2$, α-Fe, Fe$_2$B). The net impact of the hydrogen pressure on the kinetics of transformation clearly appear relevant to the thermodynamic considerations [1]. In fact, increasing the hydrogen concentration leads to a decrease of the Gibbs energy for the formation of binary rare-earth hydrides.

Thus, the interaction of both kinetic and thermodynamic factors results in a significant increment of the driving force of the transformation. When hydrogen pressure changes from 0.1 to 0.9 MPa, the characteristic time of the direct transformation is reduced by about 2.5.

Fig. 1. Parts of the isothermal kinetic diagrams of the disproportionation stage (a direct HIDP transformation) in Nd$_2$Fe$_{14}$B at different hydrogen pressures and temperatures of isothermal exposure: (a) 670 °C; (b) 710 °C; (c) 750 °C.

4. Reversed-phase transformations

Fig. 2 shows the parts of the kinetic diagrams related to hydrogen-induced reversed-phase transformation of $Nd_2Fe_{14}B$ during isothermal exposures at different temperatures. Fig. 2a indicates that at 670 °C the reverse transformation initiated under an initial hydrogen pressure of 0.1 MPa was not complete after 360 min. Increasing the initial hydrogen pressure to 0.5 and then to 0.7 MPa leads to the completion of the reverse transformation, in 185 and 163 min, respectively. In Fig. 2b and c, the same tendency is observed at 710 and 730 °C when steeply increasing the hydrogen pressure. With the rise of hydrogen pressure to 0.7 MPa, completion of the reverse transformation is obtained in 50 min at 710 °C and in 10.5 min at 750 °C.

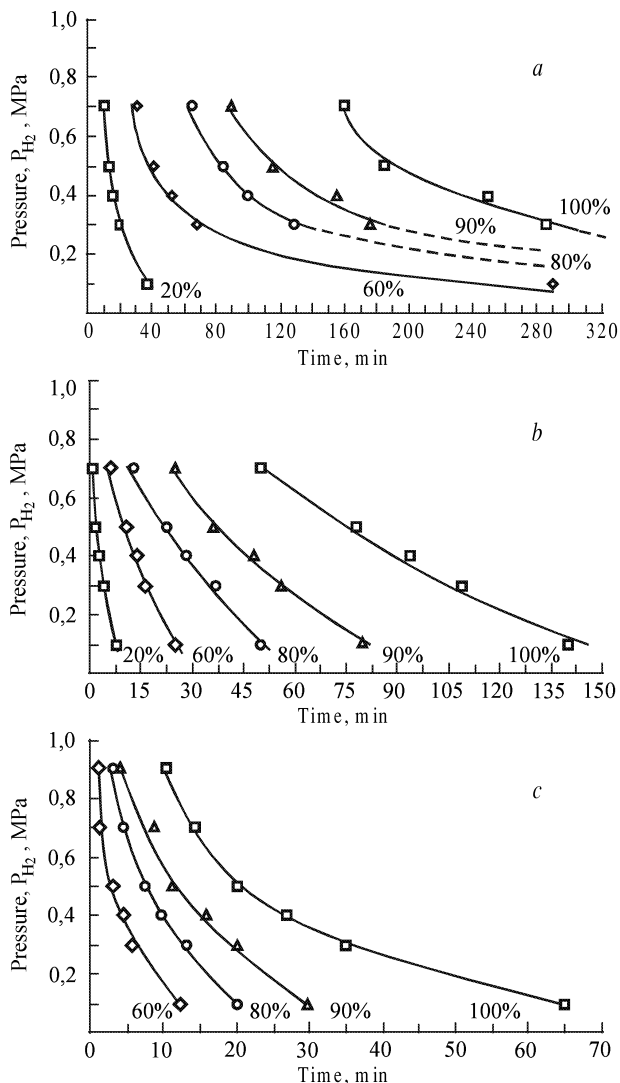It should be noted that an increase of the hydrogen pressure (e.g. 0.1 to 0.7 MPa) during the direct transformation induces a displacement of lines in the isothermal kinetic diagrams of the reversed-phase transformation towards faster times.

To summarise the impact of the initial hydrogen pressure on the kinetics of the reverse phase transformation, the following applies:

- progressively larger hydrogen pressure results in an increase of hydrogen solubility in a metal
- a diffusion flow of atoms leads to the formation of an excess concentration of vacancies as proposed in Ref. [9]
- in the case of a reverse transformation, when hydrogen is evacuated a diffusion flow of atoms is stimulated, and this might lead to a temporarily increased concentration of vacancies.

The larger the initial hydrogen pressure and thus the hydrogen content in the alloys, the larger is the diffusion flow of hydrogen and the concentration excess of vacancies. Thus, the acceleration of both the diffusion of the heavy atoms and of the reverse transformations are assumed to derive from such a behaviour. In addition, larger hydrogen pressures during a direct transformation could increase the proportion of nucleation centres of the resulting phases (such as $NdH_{2,5}$, α-Fe, Fe_2B). Consequently, this should yield a reduction of the mean atomic distance of diffusion during the reverse transformation. Confirmation of these assumptions requires further and more detailed studies.

5. Conclusion

Hydrogen is not only a necessary thermodynamic agent which makes possible the development of HIDP transformations, its pressure is a very strong kinetic factor, which as well as the temperature, controls the kinetics of the transformations and subsequent microstructural features in the material.

Fig. 2. Parts of the isothermal kinetic diagrams of the recombination stage (a reversed HIDP transformation) in $Nd_2Fe_{14}B$ at different hydrogen pressures and temperatures of isothermal exposure: (a) 670 °C; (b) 710 °C; (c) 750 °C.

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