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Fundamentals of the HDDR treatment of $Nd_2Fe_{14}B$ type alloys

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Abstract

There are generalized experimental data on the kinetics of direct and reverse hydrogen-induced diffusive phase transformations in $Nd_2Fe_{14}B$ type alloys, which is the basis of the HDDR technology. Their most general mechanisms, types of isothermal kinetic diagrams characteristic of both direct and reverse HIDP transformations, and mechanism of temperature influence on the kinetics are discussed. A conclusion is drawn that temperature (in parallel with hydrogen) is not only a necessary thermodynamic factor, but the most important kinetic factor characterizing general features of HIDP transformations.

Keywords: Rare earth alloys and compounds; Kinetics; Phase transition; Magnetisation measurement

1. Introduction

Hydrogen treatment of materials is based on the specific peculiarities of hydrogen and hydrogen-induced phase transformations. For example, HDDR process is based on hydrogen induced direct and reverse-phase transformations in a hard magnetic of the $Nd_2Fe_{14}B$ type. A characteristic feature of these alloys is the fact that upon hydrogenation they lose their thermodynamical stability and at elevated temperatures undergo a phase transformation, namely, decomposition into a hydride of a rare-earth component (NdH_x), an α-phase of Fe, and the iron boride Fe_2B. Hydrogen evacuation causes a reverse-phase transformation with the formation of an initial $Nd_2Fe_{14}B$ phase. This hydrogen treatment results in a significant structure refinement and an increase in the coercive force of the $Nd_2Fe_{14}B$ type alloys. From the viewpoint of chemistry, hydrogen-induced reformation of the $Nd_2Fe_{14}B$ type alloys are described by the following solid state reactions [1]:

$$Nd_2Fe_{14}B + (2 \pm x)H_2 \leftrightarrow 2NdH_{2\pm x} + 12Fe + Fe_2B \pm \Delta H, \quad (1)$$

where ΔH is the reaction enthalpy.

An exothermal reaction in the forward direction is called ‘disproportionation’, and this emphasizes that a chemical formula of the initial compound is disturbed. An endothermal reaction in the return direction taking place upon degassing is called ‘recombination’ which means a recovery of the compound assumption formula.

Thus, the first aim of this paper is to summarize the knowledge of the kinetics of hydrogen-induced diffusive phase transformations in the $Nd_2Fe_{14}B$ type alloys, and the second one is to discuss some general features of these transformations from the viewpoint of physical metallurgy and solid-state physics.

2. The direct hydrogen-induced phase transformations

The kinetics of direct hydrogen-induced diffusive phase (HIDP) transformations in $Nd_2Fe_{14}B$ type alloys was systematically studied in works [2–4] by Sadikov’s magnetometrical method [5].

Hydrogen-induced hydrogenolysis (disproportionation) of an intermetallic of the $Nd_2Fe_{14}B$ type from the viewpoint of physics and metal science is nothing more than a phase transformation in a solid which results in changes of the alloy structure and phase composition [6]. Such a phase transformation can be given in the following structural scheme:

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$$Nd_2Fe_{14}B(MP) + H_2 \rightarrow [HT] \rightarrow Nd_2Fe_{14}BH_{5\pm y}(MHP) + H_2 \rightarrow [\text{HIDP trans.}] \rightarrow \alpha\text{-}FeH_{z\sim 0.0001}(MP) + NdH_{2\pm x}(HP) + Fe_2BH_{z*}\ (BP), \quad (2)$$

where MP is a matrix phase, MHP is a matrix hydride phase, HP is a hydride phase, BP is a boride phase, HT is a hydride (diffusive−cooperative) transformation, HIDP trans. is a hydrogen-induced phase transformation.

Thus, an initial $Nd_2Fe_{14}B$-matrix phase being introduced into hydrogen is a thermodynamically instable phase exchanging energy and a substance (hydrogen) with the outer medium. In its motion towards a thermodynamic equilibrium an initial solid undergoes a series of internal phase transformations which according to scheme (2) are divided into two large stages. The first stage is a hydride transformation with the formation of a hydride of the initial matrix phase. The second one is, according to Ref. [8], a hydrogen-induced diffusive phase transformation with the formation of finite phases separated by the interphase boundaries. These alloy phases are in a thermodynamic equilibrium both with each other and the outer medium. Just because of a necessity of a general and local (by hydrogen) thermodynamic equilibrium all finite phases being constituents of a single solid contain equilibrium quantities of a dissolved hydrogen in their interstitial subsystems in such a way that hydrogen thermodynamic potentials in all finite phases were equal:

$$\mu_H(\alpha\text{-}FeH_z) = \mu_H(NdH_{2\pm x}) = \mu_H(Fe_2BH_{z*}) = \mu_H(H_2\text{-gas}). \quad (3)$$

Hence, a very important consequence is following. As known, iron is a hydrogen endothermal occluder. So, hydrogen content in the α-Fe-matrix is little guaranteed ($z = 0.01$–0.1 at.%), for a Fe_2BH_{z*} phase $z*$ is unknown but one can assume that it is a small value too. Nevertheless, when considering thermodynamic, kinetic, structural and other important aspects of the phase transformations under study, one should not neglect the presence of hydrogen dissolved in α-Fe and Fe_2B, as well as participation in hydrogen sorption and hydrogen interphase exchange of these phases (α-Fe and Fe_2B).

From the viewpoint of kinetics and mechanism of solid-state transformations, hydrogen-induced phase transformations under discussion need a diffusion transport of hydrogen from the outer medium, a diffusion rearrangement of hydrogen among new forming phases, an obligatory condition of this type of transformation being the presence of a long-range diffusion of Fe, Nd, B atoms. The latter is the most important factor.

Just because of such a diffusive specific character these transformations were classified in Refs. [2–4,6] among the classic phase transformations as 'hydrogen-induced diffusive phase transformations'. According to Ref. [6] these transformations are kinetically possible at $T \geq 0.45T_m$, where T_m is a melting point of an initial alloy (for the alloys $Nd_2Fe_{14}B$ $T_m \approx 1180$ °C). In reality a HIDP transformation in the $Nd_2Fe_{14}B$ alloy is fully braked because of kinetic reasons at $T \sim 0.5T_m$.

Thus, kinetics and mechanism of HIDP transformations are determined by a necessity of hydrogen, boron, iron and neodium diffusion. Hydrogen diffusion coefficients are larger than those of other interstitial atoms (C, B, N and others) by 10^{12} times, and are larger than the coefficients of self-diffusion and diffusion of substitutional atoms (Fe, Nd and other substitutional atoms) by 10^{20}–10^{30} times. So, there is no doubt that the rate of development of HIDP transformations is fully controlled by a long-range diffusion transport of substitutional atoms (Fe, Sm, Nd and others). Speaking figuratively, diffusion of intermetallic component atoms fully and simply defines a kinetic 'face' of HIDP transformations.

For a further analysis, in Refs. [2–4] the Johnson–Mehl–Avrami phenomenological kinetic theory of phase transformations was used [7]. According to this theory a degree of transformation ξ can be described by the following expression:

$$\xi = 1 - \exp(-kt^n), \quad (4)$$

where t is the transformation time, k and n are constants.

As an example for the $Nd_2Fe_{14}B$ alloy the values of n equal to 0.8–1.0 for direct transformations [4]. According to the Johnson–Mehl–Avrami theory [7] these values of n correspond to the diffusive-controlled transformations proceeding by the mechanism of nucleation and growth.

It is of interest to analyse what type of the isothermal diagram is typical for HIDP transformations for alloys of the $Nd_2Fe_{14}B$ type. Such a diagram for the $Nd_2Fe_{14}B$ alloy plotted by the experimental data is given in Fig. 1 [4]. As follows from Ref. [1], the alloy $Nd_2Fe_{14}B$ in hydrogen atmosphere at $P_{H2} = 0.1$ MPa and $T > 1000$ °C is thermodynamically stable. In this connection in Fig. 1 there is marked a critical point for a direct HIDP-transformation, viz. $T_c \approx 1000$ °C ($P_{H2} = 0.1$ MPa).

On the another hand if we plot the dependence $\ln t_\xi$ on $1/T$ (where t is the transformation time, ξ is the degree of transformation and T is the exposure temperature) we can determine activation energy of process [7]. This dependence plotted by experimental data from Fig. 1 is shown in Fig. 2. As can be seen from Fig. 2 the dependence $\ln t_\xi$ on $1/T$ has two line fields: from 670 up to 800 °C and from 800 up to 860 °C. Thus, the activation energy values in low temperature range (670–800 °C) change from 214 up to 265 kJ/mol and in high temperature range (800–860 °C) change from −146 up to −215 kJ/mol. The low temperature activation energy values have a good agreement with the activation energy of self-diffusion of Fe atoms in α phase of Fe ($Q_{\alpha\text{-}Fe} = 251.2$ kJ/mol) [8]. The activation energy values in high temperature range have a good agreement with heat of formation of NdH_2 rare-earth hydride ($H_{NdH2} = -187.7$ kJ/mol) [9]. Thus, in low tem-

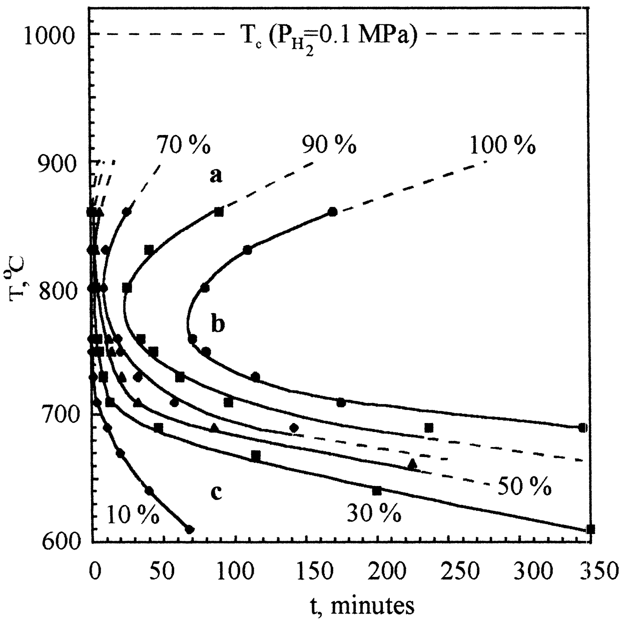

Fig. 1. Isothermal kinetic diagram of a direct HIDP transformation in $Nd_2Fe_{14}B$ alloy at hydrogen pressure of 0.1 MPa.

perature field (field c in Fig. 1) the evolution process of direct phase transformation is controlled by diffusion of Fe atoms. In a high temperature field (field a in Fig. 1) the evolution process of direct phase transformation is controlled by growth of NdH_2 hydride phase. In field b (700–800 °C) is an optimum combination of the growth rates of α-Fe phase and NdH_2 phase and therefore a transformation rate is maximum. At $T < 600$ °C a transformation does not progress because of a full kinetic braking. At temperatures about 900 °C transformation slows down before NdH_2 hydride becomes thermodynamically unstable at these temperatures. Thus, it is quite evident that direct transformations in alloys of the $Nd_2Fe_{14}B$ type are characterized by the isothermal kinetic diagrams of the C-type.

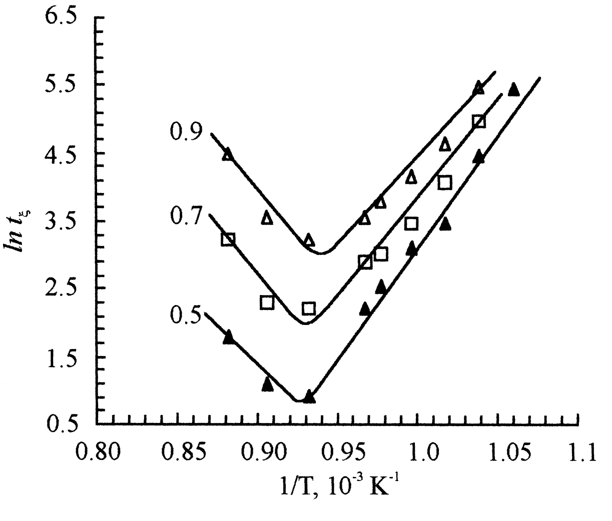

Fig. 2. $\ln t_\xi$ versus $1/T$ dependence for direct HIDP transformation in $Nd_2Fe_{14}B$ alloy for various degrees of transformation.

3. The reverse hydrogen-induced phase transformations

An experimental investigation of a reverse HIDP transformation in $Nd_2Fe_{14}B$ type alloys is given in Refs. [4,10,11]. If an alloy of the $Nd_2Fe_{14}B$ type which has undergone a direct HIDP transformation is subjected to degassing by a special vacuum treatment at temperatures above 600 °C, a reverse HIDP transformation will develop in the alloy and it will lead to the recovery of an initial phase composition of the alloy, the latter having an improved, more ground structure.

Phase transformations in this case can be presented by the following structural scheme:

$$\begin{aligned}&\alpha\text{-FeH}_z(\text{MP}) + \text{NdH}_{2\pm x}(\text{HP}) +\\&\text{Fe}_2\text{BH}_{z*}(\text{BP}) \to [\text{degass.}] \to \alpha\text{-Fe(MP)} + \text{Nd-phase} +\\&\text{Fe}_2\text{B(BP)} + \text{H}_2\uparrow \to [\text{HIDP trans.}] \to \text{Nd}_2\text{Fe}_{14}\text{B (RMP)},\end{aligned} \tag{5}$$

where MP, HP, BP have the same meaning as in scheme (2), RMP is a refined matrix phase.

So, in its moving to a thermodynamic equilibrium an initial polyphase alloy undergoes a series of phase and structural transformations which according to (5) can be conventionally divided into two large stages. The first stage is an alloy degassing and hydrogen evacuation into a gaseous phase. The second stage is a proper reverse HIDP transformation with the formation of a structurally refined matrix phase $Nd_2Fe_{14}B$. In principle the first and second stages can be fully separated in time and by temperature under certain conditions. Under the usual conditions, the second stage as a rule is put over the first one, and a reverse HIDP transformation starts to progress before hydrogen is fully evacuated from the alloy.

By its nature a reverse HIDP transformation is also a diffusive one and its rate is limited by the diffusion of atoms of the alloy components (Nd, Fe, B). Now we can only add that this means a fluctuational, activated new phase nucleation. For example, one can imagine that near a phase boundary ($NdH_{2\pm x}$ and α-FeH_z) or at the joint of three phases ($NdH_{2\pm x}$, α-FeH_z and Fe_2BH_{z*}) nuclei of the $Nd_2Fe_{14}B$ type occur under alloy degassing. They are separated by an interphase boundary from initial phases and are larger than a critical size. Then these nuclei grow due to a long-range diffusion of Nd, Fe and B atoms and, hence, their boundary 'motion' is observed. The fact that kinetics of reverse HIDP transformations is well described by the Johnson–Mehl–Avrami phenomenological theory favours this mechanism. As an example for the $Nd_2Fe_{14}B$ alloy, $n = 1.18$–1.4 [7], which corresponds to a diffusion-

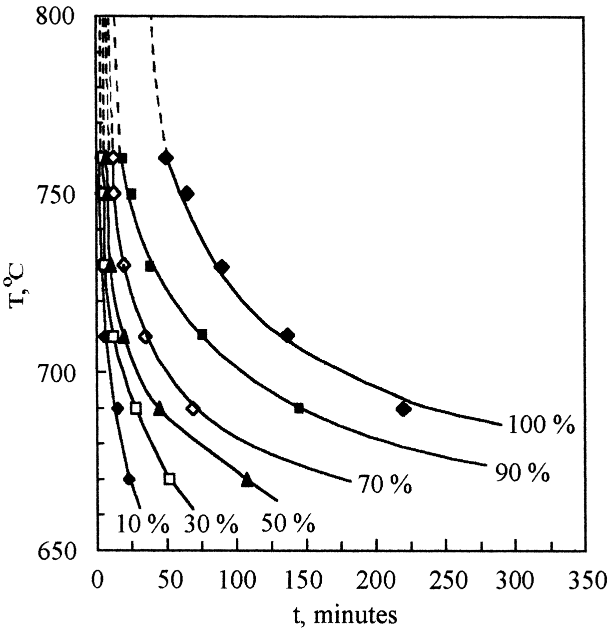

Fig. 3. Isothermal kinetic diagram of a reverse HIDP transformation in $Nd_2Fe_{14}B$ alloy at initial hydrogen pressure of 0.1 MPa and vacuum up to 10^{-2} Torr.

controlled transformation proceeding by the mechanism of nucleation and growth.

A reverse transformation kinetically differs from a direct one by the character of an isothermal kinetic diagram. The isothermal kinetic diagrams for reverse transformation in $Nd_2Fe_{14}B$ alloy is shown in Fig. 3 [4]. As can be seen from this figure within the temperature range from 650 °C up to 760 °C a reverse transformation accelerates. Further increasing of temperature up to 860 °C results in acceleration of reverse transformation evolution [12].

The dependence $\ln t_\xi$ on $1/T$ plotted by experimental data from Fig. 3 is shown in Fig. 4. Thus, the activation energy values change from 221 up to 248 kJ/mol. These values of the activation energy have a good agreement with the activation energy of diffusion of Fe atoms in matrix of α-Fe ($Q_{\alpha\text{-Fe}} = 259.54$ kJ/mol) [8]. Thus, the process of reverses phase transformation is controlled by diffusion of Fe atoms. Thus, as temperature raises, kinetics of reverse transformations proceeding by this mechanism has only to increase. One should notice that for a reverse transformation (after heating above 600 °C and removing a kinetic braking) there are no critical temperatures above which the transformation does not proceed. This is a direct consequence that a phase mixture obtained at a direct transformation after hydrogen desorption (see structure scheme (5)) is thermodynamically unstable within the whole interval of the alloy existence up to a melting temperature. Some experimental data on structure forming after direct and reverse HIDP transformations in $Nd_2Fe_{14}B$ alloy are given in Ref. [13]. Microstructure investigations of the $Nd_2Fe_{14}B$ alloy after direct and reverse-phase HIDP transformations showed that such treatment made on the base of isothermal kinetic diagrams led to homogenization of microstructure of this alloy [14]. This fact creates the necessary prerequisites for improving of the magnetic properties of the isotropic permanent magnets.

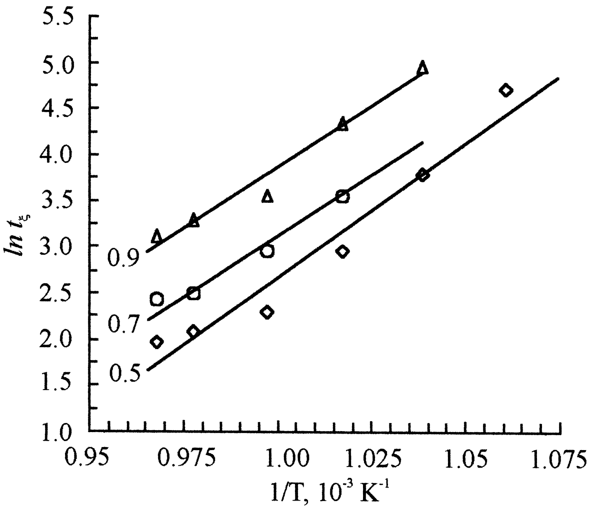

Fig. 4. $\ln t_\xi$ vs. $1/T$ dependence for reverse HIDP transformation in $Nd_2Fe_{14}B$ alloy for various degrees of transformation.

4. Conclusions

Hard magnetic alloys of the $R_2Fe_{14}B$ type (where R is Nd, Pr, Dy and other rare-earth metals) under hydrogen influence become thermodynamically unstable and undergo decomposition into a rare-earth metal hydride and α-Fe and Fe_2B. From the viewpoint of chemistry this reaction is classified as ‘hydrogenolysis of a chemical compound’.

But in the case of the $Nd_2Fe_{14}B$-type alloys a possibility was found to improve their structure and magnetic properties by using reactions of this type. Also, the so-called HDDR process (hydrogenation–decomposition–desorption–recombination) was developed. From the viewpoint of metals physics the HDDR process is based on hydrogen-induced diffusive phase transformations. Under hydrogen influence at temperatures of $0.45T_m \leq T < T_c$ in an alloy of the $Nd_2Fe_{14}B$ type a direct transformation develops. As a result, a monophase alloy undergoes a phase transformation going into a polyphase state: α-FeH_z (matrix), a hydride $NdH_{2\pm x}$ phase and a boride phase Fe_2BH_{z*}. It is well determined that this phase transformation proceeds by the mechanism of nucleation and growth. Diffusion of substitutional atoms is a necessary condition for the development of phase transformations of this class. That is why they are classified as hydrogen-induced *diffusive* phase transformations.

Kinetics of this transformation is described by the C-shaped kinetic diagram. A little bit below critical temperature ($T < T_c$) this phase transformation is controlled by the rate of growth of nucleation of NdH_2 phases. In low temperature field (600–700 °C) the evolution process of direct phase transformation is controlled by diffusion of Fe atoms. At temperatures of 700–800 °C there is an optimum combination of the growth rates of α-Fe phase and NdH_2 phase and therefore a transformation rate is maximal. Below the definite temperature (T~600 °C) a HIDP transformations in alloys of the $Nd_2Fe_{14}B$ type are fully braked by kinetic reasons.

A decomposed polyphase alloy (α-FeH_z, $NdH_{2\pm x}$, Fe_2BH_{z*}) being subjected to degassing undergoes at $T \geq 0.45T_m$ a reverse diffusive phase transformation with the formation of the monophase alloy $Nd_2Fe_{14}B$ but with an improved structure and magnetic properties. A long-range (in comparison with interatomic) diffusion of atoms (Nd, Fe, B) is a necessary condition for the development of these transformations. That is why these transformations are also classified as *diffusive*. Under degassing there is no critical points and a transformation is thermodynamically possible within the whole range of temperatures up to a melting one. At present it is admissible that a reverse transformation can proceed both by the mechanism of nucleation and growth and by the homogenizational mechanism. As well as direct transformations, at low temperatures ($T \leq 0.45T_m$) these transformations do not proceed by the kinetic reasons (the diffusion of substitutional atoms is fully suppressed). As temperature rises, diffusion accelerates. Other possible factors operate in this direction. Thus, kinetic diagrams for reverse transformations differ in principle from those for direct transformations. As temperature rises, reverse transformations accelerate only.

Thus, temperature is not only a necessary thermodynamic factor which makes the evolution of HIDP transformations possible, but it is also a very strong kinetic factor which (in parallel with hydrogen) determines the rate of the development of these transformations, the type of their kinetic diagrams and other specific features of phase transformations of this type in a solid.

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