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Some kinetic and microstructural aspects during hydrogen-induced phase transformations in Nd₂Fe₁₄B alloys

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Abstract

There are discussed some experimental data on the kinetics and microstructure of direct and reverse hydrogen-induced diffusive phase (HIDP) transformations in the Nd₂Fe₁₄B type alloys (Nd_{34.0}Fe_{64.8}B_{1.2} (wt.%) industrial alloy and original Nd₂Fe₁₄B alloy (Nd_{15.0}Fe_{77.0}B_{8.0} (at.%)). It has been established that a hydrogen-vacuum treatment carried out in accordance with the isothermal kinetic diagrams for HIDP-transformations in these alloys leads to a homogeneous microstructure and allows to avoid abnormal growth processes a main hard magnetic Nd₂Fe₁₄B phase. It is shown that the kinetic factor is one of the main factors determining microstructure features of Nd₂Fe₁₄B type hard magnetic alloys. On the base obtained results, new modified HDDR-treatment scheme based on isothermal kinetic diagrams of HIDP-transformations in Nd₂Fe₁₄B type alloys has been proposed.

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1. Introduction

Currently, permanent magnets made of $R_2Fe_{14}B$ (R–Nd, Er, Pr, Tb, etc.) alloys possess the best magnetic properties with maximum magnetic energies reaching up to 400 kJ/m³ and extremal values of a coercive force and remanence [1]. The improvement of magnet properties magnets will allow to miniaturize user's final products, and therefore constitutes a significant advance in engineering.

There have been proposed several methods to improve magnetic properties, such as powder metallurgy [2], rapid quenching [3], mechanical alloying [4], hot working [5], sintering, etc. However, these methods have some disadvantages [6]. For instance, magnets produced by pulverizing a cast ingot and a subsequent sintering did not show sufficient coercivities [7,8].

To solve this problem during the last three decades there have been proposed some new approaches. For instance, Harris et al. [9] at first proposed the method of hydrogen treatment of hard magnetic alloys, the so-called hydrogen decrepitation (HD) process which led to an increase of a permanent magnets coercivity and also to a considerable decrease of the processing cost of permanent magnets by 16–25% [10].

Takeshita and Nakayama [11–13] suggested the hydrogenation–decomposition–desorption–recombination (HDDR)process based on hydrogen-induced phase and structural transformations in Nd₂Fe₁₄B type alloys, a new method of hydrogen treatment which is a unique method to produce nanocrystalline powders of the Nd–Fe–B type for permanent magnets with improved magnetic properties [13–17].

In last years have been proposed some new modified HDDR-treatment schemes: Sugimoto [18]; Morimoto [19]; Gutfleisch [20]; Kawashita [21].

In Fig. 1 are shown the some following HDDR-treatment schemes: Takeshita's conventional HDDR treatment scheme [13] (Fig. 1a); Ragg et al.'s conventional HDDR treatment scheme [10] (Fig. 1b); modified HDDR scheme so-called 'solid HDDR' (Fig. 1c) proposed by Gutfleisch [22]; modified scheme with intermediate Ar treatment (Fig. 1d) proposed by Kawashita [21].

As can be seen from Fig. 1a and b at conventional HDDR schemes on first stage alloy absorbs hydrogen at room temperature with formation of $Nd_2Fe_{14}BH_x$ compound

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Fig. 1. HDDR-treatment schemes: conventional HDDR schemes—(a) Takeshita's scheme (after Ref. [13]), (b) Ragg et al.'s scheme (after Ref. [10]); modified HDDR schemes—(c) Gutfleisch's "solid HDDR" scheme (after Ref. [22]), (d) Kawashita's scheme with intermediate Ar treatment (after Ref. [21]).

(Hydrogenation) and then on second stage at increasing of temperature up 700–900 °C occurs process of Nd₂Fe₁₄BH_x compound decomposition on NdH₂, α -Fe and Fe₂B phases (Decomposition). Subsequent hydrogen evacuation from decomposed alloy (Desorption) lead to development of recombination process of decomposed phases into initial Nd2Fe14B phase (Recombination). In case of modified HDDR schemes, the alloy is heated up in vacuum to high temperatures (800-875 °C according to Gutfleisch's "solid HDDR" scheme (see Fig. 1c); 700-900 °C according to Kawashita's scheme (see Fig. 1d)) first and then at this constant temperature occurs process of initial alloy decomposition in hydrogen atmosphere during some time (30 min) according to Gutfleisch's "solid HDDR" scheme (see Fig. 1c) and 2.4 h according to Kawashita's scheme (see Fig. 1d). Afterwards, at desorption stage when hydrogen is evacuated (up to 0.1 bar or substitute for Ar) it lead to process of recombination of decomposed phases into initial phase. Finally, alloy powder is being cooled down to room temperature in vacuum. Two last HDDR schemes (see Fig. 1c and d) are very perspectives and allow to obtain highly anisotropic magnet powders.

Thus, all above-mentioned proposed schemes are based on empirical approaches where treatment in hydrogen and vacuum occurs at different temperatures and processing time (from 30 min up to 2.6–3 h in hydrogen and from 30 min up to 1 h in vacuum). In some cases when some abovedescribed HDDR schemes were applied to $Nd_2Fe_{14}B$ type alloys with various chemical composition it can lead to the abnormal grains growth processes of a hard magnetic $Nd_2Fe_{14}B$ Φ -phase up to tens-hundreds μ m [23,24] and coercivity decrease.

On the other hand, as it was shown in our previous works the HDDR process is based on the hydrogen-induced diffusive phase (HIDP) transformations in solid state and evolution of these transformations depends on temperature and hydrogen pressure [25–28].

Further, investigations in papers [6,9,20] have been shown that coercivity of Nd₂Fe₁₄B permanent magnets is a function the transformation time and temperature during hydrogeninduced transformations in the Nd₂Fe₁₄B type alloy.

Therefore, in order to optimise magnetic properties it is necessary to control the reaction rates during HIDPtransformations in $Nd_2Fe_{14}B$ type alloys.

From this point of view in metal physics and physical metallurgy [29,30] in respect to treatment of metals and alloys there is well known approach based on establishment of following relationship—"treatment conditions—microstructure features—physical properties". In other words, this approach includes the following important stages: investigation of kinetics features of transformations during treatment and then construction of isothermal kinetics diagrams (also well known as transformation–temperature–time (T–T–T) diagrams); investigation of microstructure features at different transformation conditions in accordance with T–T–T diagrams; study of relationship between obtained microstructure and some physical properties (mechanical, magnetic, etc.) of a treated alloys.

This approach has been successfully applied not only in respect of treatment of many metals and steels but also in hard magnetic alloys such as SmCo₅, Sm₂Fe₁₇, Al–Ni–Co, Co–Cu–Ce and others alloys [31–33].

Thus, application of above-mentioned approach concerning to HDDR-process in $Nd_2Fe_{14}B$ hard magnetic alloys should be included following main stages: (i) study of kinetics features and construction of isothermal kinetics diagrams for hydrogen-induced transformations (ii) investigation of microstructure after different transformation conditions carried out in accordance with isothermal kinetics diagrams (iii) establishment of relationship between microstructure and magnetic properties of $Nd_2Fe_{14}B$ alloys.

Consequently, establishment of relationship "isothermal kinetic diagrams-microstructure-magnetic properties" for $Nd_2Fe_{14}B$ type alloys is important goal and it may be assumed that realisation of this aim will lead to new improved HDDR-technology.

One of the above-mentioned goal (i) has been solved earlier in previous works [25–28] where some kinetic features of HIDP-transformations in the $Nd_2Fe_{14}B$ alloys were established and isothermal kinetics diagrams were constructed at first.

Therefore, the main goal of this work is to establish some relationship between HIDP-transformations kinetics and microstructure in the $Nd_2Fe_{14}B$ alloys.

2. Experimental

Experiments in this work were performed on two Nd₂Fe₁₄B type alloys: industrial alloy of Nd_{34,0}Fe_{64,8}B_{1,2} (wt.%) (UkrNIIspetsstal, Zaporozh'ye, Ukraine) and original Nd₂Fe₁₄B alloy (CNRS, Grenoble, France) of a nominal composition (Nd_{15.0}Fe_{77.0}B_{8.0} at.%). All alloys were prepared by arc melting in a high pure argon atmosphere and then crushed into powders with a particle size $50-600 \,\mu\text{m}$. All alloys have been treated by scheme proposed below in hydrogen atmosphere of 0.1 MPa and vacuum \sim 1 Pa. In our case has been used treatment scheme which is similar with "solid-HDDR" scheme. Treatment procedure was the following: the Nd₂Fe₁₄B alloys are heated in vacuum to necessary temperature (700-750 °C) first; then, at same constant temperature the reaction chamber is filled with hydrogen to develop a direct HIDP-transformation; afterwards, when the direct HIDP-transformation is completed, hydrogen is evacuated from the chamber, this hydrogen evacuation leading to the development of reverse HIDP-transformation; finally, when reverse HIDPtransformation development is completed the Nd₂Fe₁₄B alloy powder is being cooled down to room temperature in vacuum.

The microstructure was studied by using an optical microscope NEOPHOT-21 with digital camera Casio-350 and scanning electron microscope (SEM) JSM T300 with the device for the local analysis Link 860–500. SEM images processing have been performed using special programs for the microanalysis ZAF-4/FSL and SIA.

3. Results and discussion

Thus, from the viewpoint of the solid-state physics and materials science, the HDDR process is based on the following direct and reverse hydrogen-induced diffusive phase (HIDP) transformations as it was shown in previous works [25–28].

 Direct HIDP-transformation: in a hydrogen atmosphere (~0.1 MPa) at 600–900 °C, a hydrogen-induced direct phase transformation (decomposition) proceeds by a following phase scheme [26]:

$$Nd_2Fe_{14}B + H_2 \rightarrow NdH_2 + \alpha - Fe + Fe_2B$$
 (1)

(2) Reverse HIDP-transformation: a reverse phase transformation (recombination) occurs at hydrogen evacuation at ~1 Pa proceeds in accordance with a following phase scheme [26]:

$$NdH_2 + \alpha - Fe + Fe_2B \rightarrow Nd_2Fe_{14}B$$
 (2)

Below are discussed some kinetic and microstructural results in accordance to conception that the HDDR-treatment in $Nd_2Fe_{14}B$ type alloys is based on the above-mentioned HIDP-transformations.

3.1. Kinetics and microstructure in $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy

The results of the kinetic investigation of HIPDtransformations in the $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy obtained in our previous work are shown in Fig. 2 [28]. Fig. 2a presents kinetic results in the form of isothermal kinetic diagram for a direct HIPD-transformations (see Eq. (1)) carried out at hydrogen pressure of 0.1 MPa in accordance with the treatment scheme described in experimental part. The isothermal kinetic diagram for a reverse HIPD-transformation (see Eq. (2)) carried out in vacuum according to the treatment scheme described in experimental part.

In Fig. 3, there is shown the optical microscope images of microstructure of the $Nd_{34.0}Fe_{64.8}B_{1.2}$ alloy before and after direct and reverse HIPD-transformations. The results of a microstructure investigation of the initial ascast $Nd_{34.0}Fe_{64.8}B_{1.2}$ alloy before HIPD-transformations are shown in Fig. 3a.

In Fig. 3b, there is shown the one of a samples of the Nd_{34.0}Fe_{64.8}B_{1.2} alloy processed at first to a direct HIDPtransformation (at temperature 710 °C and hydrogen pressure 0.1 MPa during 140 min according to the isothermal kinetic diagram data in Fig. 2a that ensure a completion (100%) of a direct transformation in the sample) and then a reverse HIDPtransformation (at same temperature 710 °C and vacuum ~1 Pa during 150 min that ensure a full 100% completion of a reverse transformation according to data of Fig. 2b).

As can be seen from Fig. 3a, microstructure of an initial $Nd_{34.0}Fe_{64.8}B_{1.2}$ alloy has dendritic structure because of processes of dendritic segregation during alloy



Fig. 2. Isothermal kinetic diagrams of HIDP-transformations in $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy: (a) direct HIDP-transformations, (b) reverse HIDP-transformations (after Ref. [28]).

crystallisation that is typical for as-cast alloys. On contrast, in case when hydrogen treatment is carried out $Nd_{34.0}Fe_{64.8}B_{1.2}$ with the HIDP-transformation scheme (Fig. 1) in accordance with kinetic data from the isothermal kinetic diagrams of the HIDP-transformations in the $Nd_{34.0}Fe_{64.8}B_{1.2}$ alloy (see Fig. 2), this leads to a homogeneous microstructure of the $Nd_{34.0}Fe_{64.8}B_{1.2}$ alloy with fine grains of a $Nd_2Fe_{14}B$ hard magnetic phase (grey regions, A in Fig. 3b).

Thus, investigation of microstructure in $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy has been shown that when a hydrogenvacuum treatment was carried out with taking into account of transformation rates during HIDP-transformations in accordance with data from the isothermal kinetic diagrams it avoid the abnormal grains growth processes and results in homogenisation of microstructure in this alloy.

3.2. Kinetics and microstructure in $Nd_{15.0}Fe_{77.0}B_{8.0}$ alloy

In previous part are described experimental results obtained in $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy. Further investigations were carried out in original $Nd_2Fe_{14}B$ alloy.



Fig. 3. Optical microscope image of $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy: (a) initial alloy before HIDP-transformations; (b) after direct and reverse HIDP-transformations in accordance with kinetic data of isothermal kinetic diagrams in Fig. 2. (A) a main hard magnetic $Nd_2Fe_{14}B$ phase; (B) an intergranular Nd-rich phase.

Fig. 4 presents results of the kinetic investigation of HIPDtransformations in the $Nd_2Fe_{14}B$ alloy have been obtained earlier [25,26]. Fig. 4a presents kinetic results of direct HIPDtransformations carried out at hydrogen pressure of 0.1 MPa in accordance with the treatment scheme described in experimental part. The isothermal kinetic diagram for a reverse HIPD-transformation carried out in vacuum according to the treatment scheme described in experimental part is shown in Fig. 4b.

Fig. 5 shows the SEM image of microstructure of the $Nd_2Fe_{14}B$ alloy in secondary electrons mode before and after direct and reverse HIPD-transformations. The results of a microstructure investigation of the initial as-cast $Nd_2Fe_{14}B$ alloy before HIPD-transformations are shown in Fig. 5a.

In Fig. 5b there is shown the one of a samples of the Nd₂Fe₁₄B alloy processed at first to a direct HIDP-transformation (at temperature $730 \,^{\circ}$ C and hydrogen pressure 0.1 MPa during 115 min according to the isothermal kinetic diagram data in Fig. 4a that ensure a completion of a direct transformation in the sample) and then a reverse HIDP-transformation (at same temperature 730 $^{\circ}$ C and vacuum ~1 Pa during 95 min that ensure a full



Fig. 4. Isothermal kinetic diagrams of direct (a) and reverse (b) HIPD-transformations in the $Nd_2Fe_{14}B$ alloy (after Ref. [26]).

completion of a reverse transformation according to data of Fig. 4b).

As can be seen from Fig. 5a, microstructure of an initial $Nd_2Fe_{14}B$ alloy has dendritic structure with the insufficient magnetic isolation of a $Nd_2Fe_{14}B$ hard magnetic Φ -phase (grey regions, A in Fig. 5a) by Nd-rich intergranular phase (white regions, B in Fig. 5a), that is typical for as-cast alloys. A comparison between microstructure in this alloy and microstructure observed in $Nd_{34.0}Fe_{64.8}B_{1.2}$ industrial alloy (see Fig. 3a) shows that its microstructures have a similar dendritic type.

In contrast to above-described case, in case if hydrogen treatment is carried out by controlling of the transformation rates in accordance with kinetic data from the isothermal kinetic diagrams of the direct and reverse HIDPtransformations in the Nd₂Fe₁₄B alloy (Fig. 4), this leads to formation of morphological ordered homogeneous microstructure in Nd₂Fe₁₄B alloy with fine grains of a Nd₂Fe₁₄B hard magnetic phase (grey regions, A in Fig. 5b)



Fig. 5. SEM image of $Nd_2Fe_{14}B$ alloy before (a) and after (b) direct and reverse HIPD-transformations in secondary electrons mode: (A) a main hard magnetic $Nd_2Fe_{14}B$ phase; (B) an intergranular Nd-rich phase; (C) a Fe phase.

with a high degree of its magnetic isolation by Nd-rich boundary phase (white fields in Fig. 5b). Because of thus, comparing microstructure presented in Fig. 5a and b shows that carrying out the HIDP-transformations leads to decreasing of amount of a Fe phase (dark regions, C in Fig. 5) in Nd₂Fe₁₄B alloy that is positive factor for coecivity permanent magnets increase [34–36].

It's interesting that above-described microstructural results have good agreement with results in work [37] where similar microstructure was obtained in HDDR-treated Nd₂Fe₁₄B type alloy with high coercivity by way doping of Dy and Co elements to bulk alloy and Nd₂Fe₁₄B type alloy alloying by Co, Zr and Ga elements where HDDR-treatment was carried out in accordance to scheme in Fig. 1d [21].

Thus, proposed approach based on isothermal kinetic diagrams of HIDP-transformations in $Nd_2Fe_{14}B$ type alloys result in microstructure formation that is necessary for permanent magnets with high coercivity without very complicated and expensive of alloying procedures or additional treatment in Ar atmosphere.

Because of this, hydrogen treatment of the Nd₂Fe₁₄B alloys carried out by proposed scheme in accordance with the isothermal kinetic diagrams allows to avoid abnormal grains growth processes and it also results in the microstructure formation corresponding to permanent magnets with high coercivity. This fact is a prerequisite for improving coercivity of permanent magnets [1,34–36] made of a powder treated by this way.

Let's discuss further another important aspect following from obtained results. As can be seen from Figs. 2 and 4, transformation rates of the direct and reverse HIDPtransformations also strongly depend on chemical composition of alloy. This fact allows explain processes of abnormal growth of Nd₂Fe₁₄B hard magnetic phase. As it has been shown in previous works [25-28] transformations of this type Nd₂Fe₁₄B type alloys proceeds by mechanism of nucleation and growth. From this viewpoint, it is obviously that in some Nd₂Fe₁₄B type alloys with chemical composition differ from ordinary Nd₂Fe₁₄B alloy the direct HIDPtransformation may be not completed for treatment time that is recommended by HDDR-treatment scheme. As a result, alloy should consist from the following polyphase structure: undecomposed Nd₂Fe₁₄B phase, α -Fe phase, NdH₂ hydride phase and Fe₂B boride phase (see Eq. (1)). Further, at reverse HIDP-transformation stage the undecomposed Nd₂Fe₁₄B phases will be act as preferable site for nucleation of new Nd₂Fe₁₄B phases that will be grow with very high speed in contrast to other ordinary Nd₂Fe₁₄B centres. Consequently, obtained microstructure should consist from many numbers of Nd₂Fe₁₄B grains with small sizes and with not numerous large Nd₂Fe₁₄B grains. Really, the above-described microstructure was observed experimentally in some Nd₂Fe₁₄B type alloys during HDDR-treatment [9,23,24].

Hence, kinetic factor is one of the main factors determining microstructure features of $Nd_2Fe_{14}B$ type hard magnetic alloys.

Thus, above-described results allow propose a new modified HDDR-treatment scheme based on isothermal kinetic diagrams of HIDP-transformations in Nd₂Fe₁₄B type alloys. This scheme is shown in Fig. 6. In this scheme, the Nd₂Fe₁₄B alloy is heated up in vacuum to high temperatures first (stage I in Fig. 6), and then at this constant temperature the reaction chamber is filled with hydrogen to develop a direct HIDP-transformation (stage II in Fig. 6). Then, when the direct HIDP-transformation is completed (processing time at this stage it is necessary to choose from isothermal diagrams for direct HIDP-transformation in each a specific Nd₂Fe₁₄B type alloy, 1 in Fig. 6), hydrogen is evacuated from the chamber, this hydrogen evacuation leading to the development of reverse HIDP-transformation (stage III in Fig. 6). At the final stage, when reverse HIDP-transformation development is completed the $Nd_2Fe_{14}B$ (processing time at this stage it is necessary to choose from isothermal diagrams for direct HIDP-transformation in each a specific Nd₂Fe₁₄B type alloy, 2 in Fig. 6) alloy powder is being cooled down to room temperature in vacuum (stage IV in Fig. 6).

Hence, in contrast to others HDDR-treatment schemes proposed scheme should include as a indispensable condition the carrying out a investigation of kinetics of HIDPtransformations for each a specific $Nd_2Fe_{14}B$ type alloy.

In summary, in future proposed approach may be extended by carrying out more detailed microstructural investigations



Fig. 6. Scheme of HDDR-treatment based on HIPD-transformations in $Nd_2Fe_{14}B$ type alloys.

and establishment of a such HIDP-treatment conditions that is a necessary for obtaining not only isotropic homogeneous microstructure but also microstructure with high degree of anisotropy a corresponding to the permanent magnets with high remanence.

4. Conclusions

Thus, there has been shown hydrogen-vacuum treatment carried out in accordance with the HIDP-transformations scheme based on isothermal kinetic diagrams in the $Nd_2Fe_{14}B$ type alloys leads to homogeneous microstructure of the $Nd_2Fe_{14}B$ alloys with sub-micron grains of a $Nd_2Fe_{14}B$ hard magnetic phase and avoid abnormal grains growth processes. This is a necessary condition for production of permanent magnets with high coercivity.

Hence, *kinetic factor* is shown to be one of the main factors determining microstructure features of $Nd_2Fe_{14}B$ type hard magnetic alloys.

On the base obtained results new modified HDDRtreatment scheme based on isothermal kinetic diagrams of HIDP-transformations in $Nd_2Fe_{14}B$ type alloys has been proposed.

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