Kinetics of the hydrogen-induced direct and reverse diffusive phase transformation in industrial alloy of $Nd_2Fe_{14}B$ type

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Kinetics of the hydrogen-induced direct and reverse diffusive phase transformation in industrial alloy of $Nd_2Fe_{14}B$ type has been investigated. The isothermal kinetic curves of these transformations were obtained for temperatures from 750 °C to 620 °C under hydrogen pressure of 0.1 MPa and in vacuum about 10^{-2} Torr. The kinetic diagrams for direct and reverse transformation were obtained. These diagrams are similar to those of transformations in steels during heating. It is shown that the investigated direct and reverse phase transformation is a diffusion-controlled one with the nucleation and growth mechanism.

Исследована кинетика индуцированных водородом прямого и обратного фазового превращения в промышленном сплаве типа $Nd_2Fe_{14}B$. Получены изотермические кривые этих фазовых превращений для температур от 750 °C до 620 °C при давлении водорода 0.1 МПа и вакууме до 10^{-2}Торр. Для прямого и обратного превращений получены кинетические диаграммы. Эти диаграммы сходны с диаграммами превращений в стали при нагреве. Показано, что, исследованные прямое и обратное фазовое превращение являются диффузионно-контролируемыми и происходят по механизму зарождения и роста.

Introduction

Phase transformations have always been one of main standpoint area in materials science and engineering. The development of hydrogen treatment of materials as a new field of materials science and engineering confirms that [1,2]. For example, the recently developed HDDR process is based on the hydrogen-induced phase transformation in intermetallic alloys [3]. This process can be used to produce very fine subgrain materials. $Nd_2F_{14}B$ alloy undergoes the reversible phase transition in hydrogen atmosphere and vacuum. In the temperature range between 600 °C and 900 °C in hydrogen atmosphere, $Nd_2F_{14}B$ absorbs hydrogen and undergoes the direct transformation (decomposes into phases: NdH_2, α-Fe and Fe_2B [4]). When hydrogen is desorbed from the system consisting of NdH_2, α-Fe and Fe_2B phases, the reverse transformation takes place and results in the initial $Nd_2F_{14}B$ alloy but just with improved very fine subgrain structure.

This HDDR process is used for preparation of high coercive hard magnetic materials [5,6], e.g. $Nd_2F_{14}B$, $Sm_2Fe_{14}N_x$ and others alloys. The high coercive force H_c (more than 800 kA/m) has been reached in this way. The best isotropic bonded magnets on the base of $Nd_2F_{14}B$ after HDDR treatment show a highest magnetic energy $(BH)_m$ about 80 kJ/m^3 [6].

The kinetics of these transformations in Nd-Fe-B alloys, however, has not been studied up to now. Shape of the isothermal kinetic diagrams and mechanism of these transformations in Nd-Fe-B alloys are unknown.

In the present work, the kinetics of the hydrogen-induced direct and reverse phase transformation in an industrial alloy of $Nd_2Fe_{14}B$ type was studied at isothermal conditions under the pressure of hydrogen P=0.1 MPa and vacuum up to 10^{-2} Torr.

1. Experimental details

The investigated alloy was prepared by melting in an induction furnace. The alloy was homogenized at 1120 °C for 20 h in argon atmosphere and then was crushed into particles from 50 μm to 630 μm size.

The special experimental equipment was made to investigate in the kinetics of the hydrogen-induced phase transformation. This equipment enables to treat the $Nd_2Fe_{14}B$ type compound under hydrogen pressure up to P=1.6 MPa and at temperatures up to 800 °C.

The idea of this method is based on the following fact. The $Nd_2Fe_{14}B$ type alloy is paramagnetic in the range of experimental temperatures (600–750 °C) (Curie temperature T_c=312 °C) but phases of decomposition (α-Fe and Fe_2B) are ferromagnetic.

This fact gives a possibility for magnetic investigation of these phase transitions. The measuring part of experimental equipment before used to study transformations in steels in 30th, was constructed using Sadikov method [8]. The reaction chamber with sample of Nd-Fe-B was placed into alternating magnetic field about 15 kA/m. The bifilar measuring coil was situated around the reaction chamber. Then sample was undergone to the direct and reverse transformation and electromotive force e.m.f was induced. In these cases, values of e.m.f. were proportionally of quantity of the ferromagnetic phases (α-Fe and Fe_2B) in the sample.

At first, at 750 °C the full 100 % decomposition of the sample was obtained. On that base the measuring part of equipment was graduated for temperatures from 750 °C to 600 °C. That has made it possibile to determine the transformation degrees within the whole experimental temperature interval.

For direct transformation experimental procedure was as follows. The samples (m=1.46 g) were placed into a reaction chamber at room temperature. Then they were heated to a temperature in the interval 750–600 °C in vacuum (10^{-2} Torr). The temperature was measured by a chromel-alumel thermocouple. Then the reaction chamber was filled with hydrogen under 0.1 MPa pressure. From this time the moment on, the formation and growth of ferromagnetic phases (α-Fe and Fe_2B) were measured continuously.

Experimental investigation of the reverse transformation was carried out as follows. At first, each sample (m=1.46 gram) was undergone to the direct transformation in hydrogen atmosphere of 1 bar at the temperature 750 °C up to full decomposition. Then the sample was cooled down to a temperature from interval 750–620 °C, and after this, hydrogen was evacuated from the reaction chamber. From this time moment on, the decrease of the ferromagnetic phases content in the sample (α-Fe and Fe_2B) was measured continuously.

All experimental results were obtained under strictly isothermal conditions.

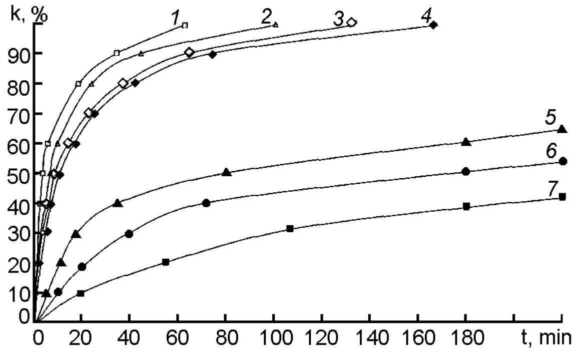

Fig.1. Kinetic curves of the direct phase transformation in $Nd_2Fe_{14}B$ alloy type obtained under hydrogen pressure of 0.1 MPa and different constant temperatures: 1 — 750 °C; 2 — 730 °C; 3 — 710 °C; 4 — 700 °C; 5 — 680 °C; 6 — 650 °C; 7 — 620 °C.

2. Results and discussion

Fig.1 shows the isothermal kinetic curves for hydrogen-induced direct phase transformation in the $Nd_2Fe_{14}B$ type alloy. At T=750 °C the direct phase transformation has very high rate and is finished in 65 min (curve 1). Decreasing of the isothermal temperature to 720 °C induces a slowing down of the phase transformation rate. At this temperature, the full decomposition has completed in 105 min (curve 2). At 710 °C (curve 3) and 700 °C (curve 4), the direct phase transition was completed in 140 and 180 min, respectively.

A further temperature decreasing made transformation to be more and more slow, so phase decomposition was not finished in 220 experimental minutes. At 680 °C phase transformation reached 64 % only (curve 5). At 650 °C (curve 6) and 620 °C (curve 7) it reached 53 % and 41 %, respectively.

Fig.2 shows the kinetic curves for reverse phase transformation in $Nd_2Fe_{14}B$ type alloy. At temperature 750 °C, NdH_2, α-Fe and Fe_2B phases transform to $Nd_2Fe_{14}B$ phase in 75 min (curve 1′). The isothermal temperature decrease to 720 °C induces a slowing-down of the reverse transformation rate. At this temperature, the full transformation was completed in 110 min (curve 2′). At the further temperature decrease to 710 ° (curve 3′) and 700 °C (curve 4′), the reverse transition was completed in 150 and 190 min, respectively. The rate of reverse transformation decreases as the isothermal temperature is lowered. In temperature interval from 680 °C to 620 °C transformations were not finished in 220 experimental minutes. So, at 680 °C (curve 5′) phase transition reached 60% only. At 650 °C (curve 6′) and 620 °C (curve 7′) it reached 50% and 30%, respectively.

It is important that at all temperatures there was a small but distinct incubation period of the phase transition for direct and reverse transformation. For direct transition at temperatures from 750 °C to 720 °C, this incubation period was about 30-75 sec., but at 620 °C, it amounted about 90 second. For reverse transformation this period demands a longer time. In this case, the incubation period was from 2 min up to 5 min.

Let us discuss the obtained experimental results. The hydrogen-induced direct phase transformation in $Nd_2Fe_{14}B$ alloy can be represented as [7]:

$$Nd_2Fe_{14}B+H_2 \rightarrow$$
$$\rightarrow Nd_2Fe_{14}BH_x \rightarrow NdH_2+\alpha\text{-}Fe+Fe_2B$$

The reverse transformation induces evacuation of hydrogen from NdH_2 occurs by the following scheme in accordance with [7]:

$$NdH_2+\alpha\text{-}Fe+Fe_2B \rightarrow Nd_2Fe_{14}B+H_2\uparrow$$

It is obvious that for these phase transformations the diffusive transfer of large atoms (Nd, Fe and B) is necessary.

It is known that there are diffusive phase transitions of two types: spinodal decomposition and phase transformation of nucleation and growth.

The spinodal decomposition necessitates the diffusive transfer of alloy component atoms through small distances. Therefore, the spinodal decomposition occurs at relatively low temperatures and its rate is high. The phase transition of nucleation and growth demands the diffusive transfer of atoms through long distances (much longer then atomic distances). So, this phase transformation occurs at higher temperatures, and a longer time is necessary for its completion.

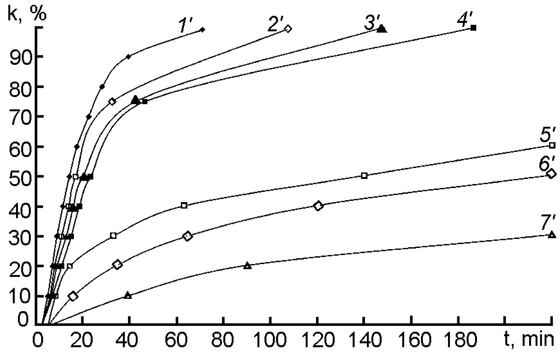

Fig.2. Kinetic curves of the reverse phase transformation in $Nd_2Fe_{14}B$ alloy type obtained in vacuum 10^{-2} Torr at different constant temperatures: 1′ — 750 °C; 2′ — 730 °C; 3′ — 710 °C; 4′ — 700 °C; 5′ — 680 °C; 6′ — 650 °C; 7′ — 620 °C.

As can be seen from Fig.1 and Fig.2, this type of kinetic curves with gradual reduction of transformation rate at T<700 °C indicates that these transitions are developed according to the nucleation and growth mechanism.

It is known that phase transformations occurring through nucleation and growth mechanism, which were well studied for steels have two types of isothermal kinetic diagrams [9].

When lowering the temperature and increasing the supercooling from the critical point, the new phases nucleation rate dominates at first and then the diffusion control begins to dominate. In this case, diagrams of transformation have a C-shape type.

The other types of transformations (for example, the ferrite→austenite transformation in steels during heating) have another type of kinetic diagrams. In this case, both factors act along and the phase transformation becomes accelerated with temperature elevation.

The kinetic diagrams of the hydrogen-induced phase transformations in $Nd_2Fe_{14}B$ type alloy are showed in Fig.3 (direct transformation) and Fig.4 (reverse one). It is obvious that investigated phase transformations have the kinetic diagram of the second type (from above mentioned).

The diffusion coefficients of Nd, Fe and B atoms increase as the temperature becomes higher. This is an important factor. But, so fast rise of the phase transformation rate (about two orders of magnitude) in the temperature interval only 130 °C (from 620 °C and to 750 °C) cannot be attributed to increasing of diffusion coefficients only

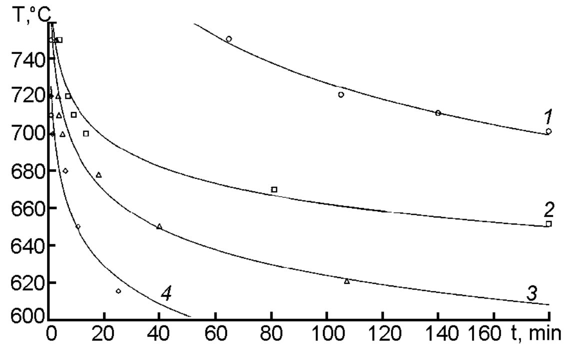

Fig. 3. Isothermal kinetic diagrams of the hydrogen-induced direct phase transformation in $Nd_2Fe_{14}B$ type alloy. Curves are 1 — 100 %, 2 — 50 %, 3 — 30 %, 4 — 10% of direct phase transformation.

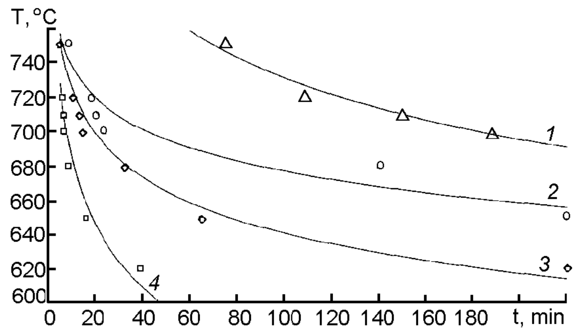

Fig.4. Isothermal kinetic diagrams of the hydrogen-induced reverse phase transformation in $Nd_2Fe_{14}B$ type alloy. Curves are 1 — 100 %, 2 — 50 %, 3 — 30 %, 4 — 10% of reverse phase transformation.

(even in view of the fact that hydrogen accelerates diffusive processes in solid body). It means that the generation rate of centers of new phases (NdH_2, α-Fe and Fe_2B) increases too.

For further analysis of mechanism of this transformation, the Avrami theory [10] was used. According to this theory, the phase transformation can be described by the following equation:

$$k = 1 - \exp(-dt^n),$$

where k is degree of transformation; d, n, constants; t, time.

The obtained experimental results (from Fig.1 and Fig.2) were plotted in the following coordinates: lnln $[1/(1-k)]$ - ln$t$. These curves are straight lines. The slope of the lines gives n=1.06 and n=1.81 for direct and reverse transformation, respectively. According to Avrami theory [10], if $1<n<2.5$ than transformation occurs by the nucleation and growth mechanism with diffusion-controlled growth of particles. This fact confirms once more that the investigated phase transformations of this kind are diffusion-controlled ones. They may be classified as hydrogen-induced *diffusive* phase transformations.

Conclusions

The kinetics of the hydrogen-induced direct and reverse diffusive phase transformation in $Nd_2Fe_{14}B$ type alloy has been first studied.

– Decreasing of the isothermal temperature of the direct and reverse phase transformation in interval from 750 °C to 620 °C induced a reduction of the transformation rate by two orders of magnitude.

– The kinetic diagrams of these phase transformations were obtained. These diagrams are similar to those of transformations in steels during heating.

– The investigated phase transformations are well described by the Avrami theory. These phase transitions are developed by the nucleation and growth mechanism with diffusion-controlled growth of particles.

So, this kind of transformations in industrial alloy of $Nd_2Fe_{14}B$ type is to be classified as hydrogen-induced diffusive phase transformations.

References

1. V.A.Goltsov, *Int.J. Hydrogen Energy*, **22**, 115 (1997).
2. V.A.Goltsov, *Int.J. Hydrogen Energy*, **22**, 119 (1997).
3. D.Fruchart, M.Bacmann, P.de Rango et al., *J. of Alloys and Compounds*, **253/254**, 121 (1997).
4. T.Takeshita, *J. Alloys and Compounds*, **231**, 51 (1995).
5. T.Takeshita, *J.Alloys and Compounds*, **193**, 231 (1993).
6. T.Takeshita, R.Nakayama, in: Proc. 11th Int. Workshop on Rare-Earth Magnets and their Applications, Pittsburgh, PA, 21-24 October 1990, p.49.
7. O.M.Ragg, G.Keegan, H.Nagel, I.R.Harris, *Int.J. Hydrogen Energy*, **22**, 333 (1997).
8. B.G.Livshits, Physical Properties of Iron Metals and Their Test Methods, ONTI, Moscow-Leningrad (1937) [in Russian].
9. L.E.Popova, A.A.Popov, Diagrams of Austenite Transformation in Steels and β-Solution in Titanium Alloys, Metallurgia, Moscow (1993) [in Russian].
10. J.W.Christian, The Theory of Transformations in Metals and Alloys, Part 1, Pergamon Press, Oxford (1975).