PERGAMON

International Journal of Hydrogen Energy 24 (1999) 913–917

International Journal of HYDROGEN ENERGY

Kinetics of the hydrogen-induced diffusive phase transformation in Nd–Fe–B industrial alloy

V.A. Goltsov*, S.B. Rybalka, A.F. Volkov

Donetsk State Technical University, 58 Artem Street, Donetsk 340000

Abstract

The kinetics of the hydrogen-induced diffusive phase transformation in industrial alloy Nd–Fe–B has been investigated. The isothermal kinetic curves were received for temperatures from 750 to 620°C at the hydrogen pressure 0.1 MPa. An isothermal kinetics diagram was obtained. This diagram is similar to the ones of the transformations in steels during heating. It is shown that the investigated phase transformation is a diffusion-controlled one with the mechanism of nucleation and growth.

Nomenclature

$(BH)_m$	Maximal magnetic energy (kJ/m^3)
HDDR	Hydrogenation-decomposition-desorption-recombination
T	Temperature (°C)
T_c	Curie temperature (°C)
H_c	Coercive force (A/m)
k	Degree of transformation
t	Time (min)
d, n	Constants
e.m.f.	Electromotive force
P	Hydrogen pressure (MPa)

1. Introduction

Phase transformations have always been the main standpoint area of 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. In the temperature range between 600 and 900°C in gaseous hydrogen the compounds $Nd_2Fe_{14}B$ absorbs hydrogen and decomposes into phases: NdH_x, α-Fe and Fe_2B [4]. When hydrogen is desorbed from the alloy consisting NdH_2, α-Fe and Fe_2B phases, the reverse transformation takes place and gives the initial $Nd_2Fe_{14}B$ alloy, but with improved very fine subgrain structure. This HDDR-process is used for preparation of high coercive hard magnetic materials [5, 6], e.g. $Nd_2Fe_{14}B$, $Sm_2Fe_{14}N_x$ and other alloys. The high H_c might have been reached (more than 800 kA/m) in this way. The best isotropic bonded magnets on the base of $Nd_2Fe_{14}B$ HDDR-powders might have maximum energy $(BH)_m$, which is about 80 kJ/m^3 [6].

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

In the present study the kinetics of the hydrogen-induced direct phase transformation in industrial alloy of $Nd_2Fe_{14}B$ type has been investigated at isothermal conditions and under the pressure of hydrogen $P = 0.1$ MPa.

2. Experimental details

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

The experimental special equipment for the inves-

* Corresponding author

0360-3199/99/$20.00
PII: S0360-3199(98)00167-0

tigation of the kinetics of the hydrogen-induced phase transformation was made. This equipment enables us to treat the alloy Nd–Fe–B under pressure of hydrogen up to $P = 1.6$ MPa and at temperatures up to 800°C.

The idea of this method is based on the next fact. In the interval of experimental temperatures (600–750°C), Nd–Fe–B alloy is paramagnetic ($T_c = 312$°C), but phases of decomposition (α-Fe and Fe_2B) are ferromagnetic.

This fact gives a possibility for magnetic investigation of this phase transition. The measuring part of experimental equipment, which had been used for investigation of transformations in steels in 30th, was constructed by the Sadikov method [8]. A sample of Nd–Fe–B was placed in alternating magnetic field about 15 kA/m. The bifilar measuring coil was situated around the reaction chamber, cooled by water. The sample was put into chamber. Then it was subjected to hydrogen, and *e.m.f.* was induced. In this case, the values of *e.m.f.* were proportional to the quantity of the ferromagnetic phases in the sample (α-Fe and Fe_2B).

First, at 750°C the full 100% decomposition of the sample was obtained. On that basis, the measuring part of equipment was graduated for the temperatures from 750 to 600°C. That gave the possibility to determine the degrees of decomposition for the whole experimental temperature interval.

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 the temperature in the interval 750–600°C in vacuum (10^{-2} Torr). Temperature was measured by a chromel-alumel thermocouple; the reaction chamber was then filled with hydrogen under the pressure of 0.1 MPa. From this time the formation and growth of ferromagnetic phases (α-Fe and Fe_2B) was measured continuously. All experimental results were obtained under strictly isothermal conditions.

3. Results and discussion

Figure 1 shows the isothermal kinetic curves for hydrogen-induced phase decomposition of the $Nd_2Fe_{14}B$ type compound. At $T = 750$°C the phase transformation has very high-rate, and it was finished in 65 min. Decreasing of isothermal temperature to 720°C induces slowing down the speed of the phase decomposition. At this temperature, full decomposition was accomplished in 105 min. At the temperatures 710 and 700°C phase transitions were completed in 140 and 180 min, respectively.

Further decreasing of the temperature made transformation slower. The phase decomposition was not finished (in 3 experimental hours). At 680°C, the phase

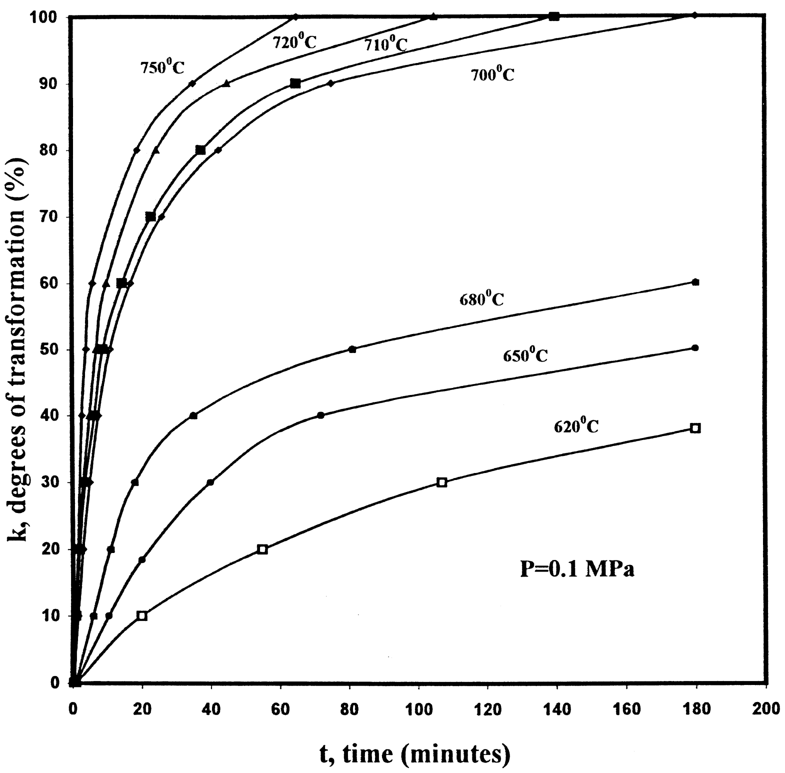

Fig. 1. The kinetic curves of the phase decomposition of Nd–Fe–B alloy at hydrogen pressure $P = 0.1$ MPa and different constant temperatures.

transformation reached only 60%. At 650 and 620°C, it was as low as 50 and 38%, respectively.

It is important, that at all temperatures, there was a small but distinct incubation period of the phase transition. At temperatures from 750 to 720°C this incubation period was about 30–75 s, but at 620°C this period was about 90 s.

Hydrogen-induced phase transformation in Nd–Fe–B alloys occurs by the following scheme [7]:

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

It is obvious that for this phase transformation 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 at small distances. Because of that, the spinodal decomposition occurs at relatively low temperatures and its speed is high. The phase transition of nucleation and growth demands diffusive transfer of atoms at long distances (much longer than atomic distances). So, this phase transformation occurs at higher temperatures, and it is necessarily a long time for its finishing.

As may be seen from Fig. 1, the type of kinetic curves with gradual slowing down of transformation speed at the $T < 700$°C indicates that this transition develops by mechanism of nucleation and growth.

It is known that phase transformations of nucleation and growth, that have been investigated in steel, have two types of isothermal kinetic diagrams [9].

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

The other types of transformations (e.g., the ferrite → austenite transformation in steels during heating) have other kinetic diagrams. In this case both factors act, and with the increasing temperature, only phase transformation accelerates.

The isothermal kinetics diagram of the hydrogen-induced phase transformation in alloy Nd–Fe–B is shown in Fig. 2. It is obvious that the investigated phase transformation has the kinetic isothermal diagram of the second type.

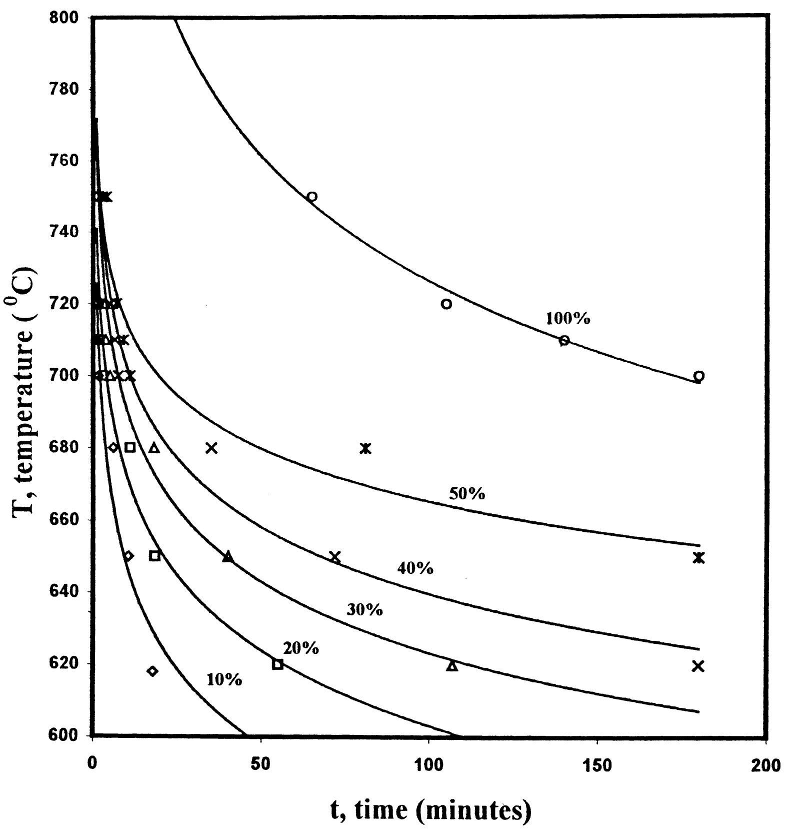

Fig. 2. The isothermal kinetics diagram of the hydrogen-induced phase transformation in Nd–Fe–B industrial alloy.

The diffusion coefficients of Nd, Fe and B atoms increase as the temperature becomes higher. This is an important factor. But, so rapid rise of the speed of the phase transformation (about two orders of magnitude) into the interval of temperatures only 130°C (from 620 and to 750°C) cannot be attributed to increasing of the diffusion coefficients alone (even in view of the fact that hydrogen accelerates the diffusive processes in solid body). It means that the speed of the generation of the centers of new phases (NdH_2, α-Fe and Fe_2B) also increased.

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

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

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

Our results were plotted by following coordinates: $lnln[1/(1-k)] - lnt$. Figure 3 shows these curves. As it is evident from Fig. 3, these curves are straight lines. The slope of the lines gives $n = 1.06$. Using the Avrami theory [10], if $1 < n < 1.5$ that means that the transformation is of nucleation and growth mechanism with diffusion-controlled growth of particles. This fact confirms once more that investigated phase transformations of this kind are diffusion-controlled mechanisms. They may be classified as hydrogen-induced *diffusive* phase transformations.

4. Conclusion

The first investigation of the kinetics of the hydrogen-induced diffusive phase transformation in $Nd_2Fe_{14}B$ type was fulfilled.

- Decreasing the temperature of phase transformation in interval from 750 to 620°C incudes a slowing down of the speed of the transformation by two orders of magnitude.
- The isothermal kinetics diagram of the phase transformation was obtained. This diagram is similar to the diagrams of the transformations in steels during heating.

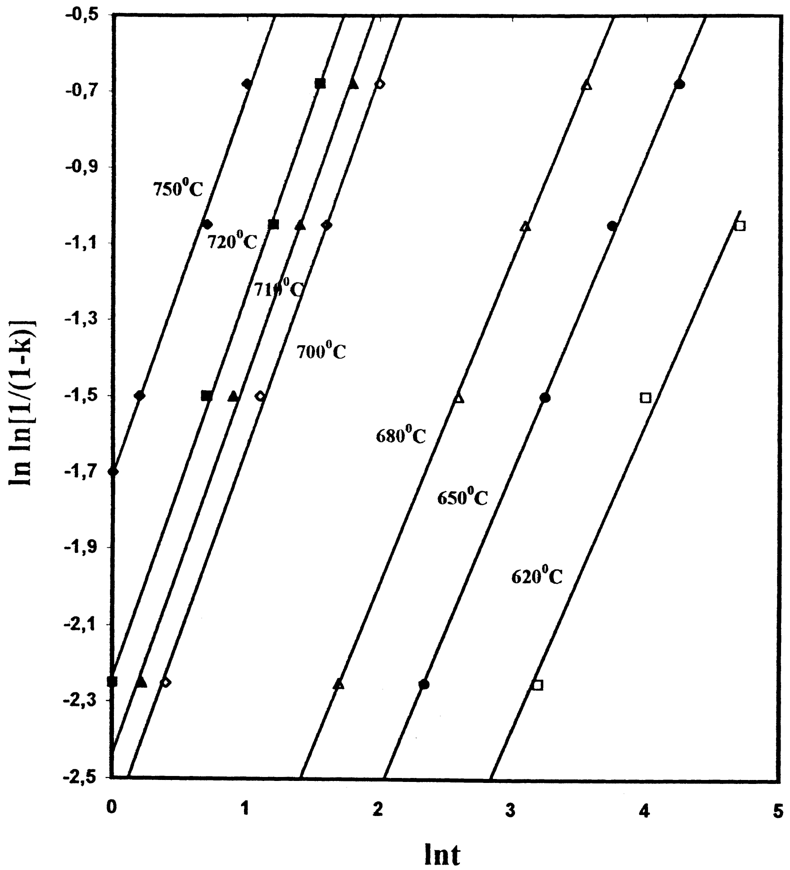

Fig. 3. The kinetic curves of investigated transformation in accordance with the Avrami equation.

- The investigated phase decomposition is described well by the Avrami equation, with $n = 1.06$. It is diffusion-controlled phase transition, developed by the mechanism of nucleation and growth. So, this kind of $Nd_2Fe_{14}B$ decomposition can be classified as a hydrogen-induced *diffusive* phase transformation.

References

[1] Goltsov VA. History, ideology and prospects of the hydrogen treatment of materials—Opening Address. International Journal of Hydrogen Energy 1997;22(2/3):115–7.

[2] Goltsov VA. Fundamentals of hydrogen treatment of materials and its classification. International Journal of Hydrogen Energy 1997;22(2/3):119–24.

[3] Fruchart D, Bacmann M, de Rango P, Isnard O, Liesert S, Miraglia S, Obbade S, Soubeyroux J-L, Tomey E, Wolfers P. Hydrogen in hard magnetic materials. Journal of Alloys and Compounds 1997;253–4:121–7.

[4] Takeshita T. Some applications of hydrogenation-decomposition-desorption-recombination (HDDR) and hydrogen-decrepitation (HD) in metals processing. International Journal of Hydrogen Energy 1997;22(2/3):51–9.

[5] Takeshita T. Present status of the hydrogenation-decomposition-desorption-recombination process as applied to the production of magnets. Journal of Alloys and Compounds 1993;193:231–4.

[6] Takeshita T, Nakayama R. Proc. 11th Int. Workshop on Rare-Earth Magnets and their Applications. Pittsburgh, PA, 21–24 October 1990, p. 49.

[7] Ragg OM, Keegan G, Nagel H, Harris IR. The HD and HDDR processes in the production of Nd–Fe–B permanent magnets. International Journal of Hydrogen Energy 1997;22(2/3):333–42.

[8] Livshits BG. Fizicheskie svoistva chernykh metallov i metody ikh ispytany, ONTI NKTR SSSR, Moskva-Leningrad, 1937.

[9] Popova LE, Popov AA. Diagrams of austenite transformation in steels and β-solution in titanium alloys. Metallurgia, Moscow, 1993.

[10] Christian JW. The Theory of Transformations in Metals and Alloys, part 1. Mir, Moscow, 1978.