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KINETICS OF THE HYDROGEN-INDUCED DIRECT DIFFUSIVE PHASE TRANSFORMATION IN INDUSTRIAL ALLOY OF $R_2Fe_{14}B$ TYPE

The kinetics of the hydrogen-induced direct diffusive phase transformation in industrial alloy of $R_2Fe_{14}B$ type is studied. The isothermal-kinetics curves of this transformation are obtained for temperatures from 690 to 760°C under hydrogen pressure of 0.15 MPa. The kinetics diagram for direct transformation is obtained. This diagram is similar to ones for the transformations in steels during heating. It is shown that the studied direct phase transformation is a diffusion-controlled one by the mechanism of nucleation and growth.

Досліджено кінетику ініційованого воднем прямого фазового перетворення у промисловому сплаві типу $R_2Fe_{14}B$. Отримано ізотермічні кінетичні криві цього фазового перетворення для температур від 690 до 760°C під тиском водню 0,15 МПа. Для прямого перетворення отримано кінетичну діаграму. Ця діаграма подібна до діаграм перетворень у сталях при нагріванні. Виявлено, що досліджене пряме фазове перетворення є дифузійно контрольованим та відбувається за механізмом зародження та росту.

Исследована кинетика индуцированного водородом прямого фазового превращения в промышленном сплаве типа $R_2Fe_{14}B$. Получены изотермические кривые этого фазового превращения для температур от 690 до 760°C при давлении водорода 0,15 МПа. Для прямого превращения получена кинетическая диаграмма. Эта диаграмма сходна с диаграммами превращений в стали при нагреве. Показано, что исследованное прямое фазовое превращение является диффузионно-контролируемым и происходит по механизму зарождения и роста.

Key words: *hydrogen-induced phase transformation, kinetics, nucleation and growth, $R_2Fe_{14}B$.*

1. Introduction

Phase transformations have always been of 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—6]. This process can be used to produce very fine subgrain materials. The alloy of $Nd_2F_{14}B$ type undergoes to the direct and reverse phase transformation in hydrogen and vacuum atmosphere. In the temperature range between 600 and 900°C in hydrogen atmosphere the compounds $Nd_2F_{14}B$ absorbs hydrogen and it undergone to 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 gives 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 has been reached (more than 800 kA/m) in this way. The best isotropic bonded magnets on the base of $Nd_2F_{14}B$ after HDDR treatment have maximal magnetic energy $(BH)_{max}$, which is about 80 kJ/m^3.

Kinetics of these transformations in R–Fe–B alloys, however, is not studied up to now. The kinetics diagram and the mechanism of these transformations in R–Fe–B alloys are unknown.

In the present work the kinetics of the hydrogen-induced direct and reverse phase transformation in industrial alloy of $R_2Fe_{14}B$ type was investigated at isothermal conditions and under the pressure of hydrogen $P = 0.15$ MPa.

2. Experimental Details

The components of the investigated alloy were prepared by special technology. Then they were melted in an induction furnace. The composition of this alloy is: R—36.4 wt.%, Fe—62.45 wt.%, B—1.15 wt.%, where R—32.0 wt.% of Nd+Pr and 4.4 wt.% of others rare earth metals.

The experimental special equipment for the investigation of the kinetics of the hydrogen-induced phase transformation was made. This equipment enables to treat the $R_2Fe_{14}B$ type compound under pressure of hydrogen up to $P = 0.2$ MPa and at temperatures up to 800°C.

The idea of this method is based on the next fact. The $R_2Fe_{14}B$ type alloy is paramagnetic (Curie temperature $T_c = 312$°C) in the interval of experimental temperatures (690–760°C), but phases of decomposition (α-Fe and Fe_2B) are ferromagnetic.

This fact gives a possibility for magnetic investigation of these phases transitions. The measuring part of experimental equipment, which had been used for investigation of transformations in steels in 30th, was constructed by Sadikov method [7]. The reaction chamber with sample of $R_2Fe_{14}B$ was placed into alternating magnetic field about 15 kA/m. The bifilar measuring coil was situated around reaction chamber. Then sample was undergone to the direct transformation and electromotive force (e.m.f.) was induced. In this case, values of e.m.f. were proportionally of quantity of the ferromagnetic phases in the sample (α-Fe and Fe_2B).

The experimental procedure was as follow. The samples (m = 1.016 gram) with size of particles from 0.1 to 1.2 mm were placed into a reaction chamber at room temperature. Then they were heated to the temperature in the interval 760–690°C in vacuum up to 10^{-2} Torr. Temperature was measured by a chromel–alumel thermocouple. Then reaction chamber was filled with hydrogen under the pressure of 0.15 MPa. From this time the formation and growth of quantity of ferromagnetic phases (α-Fe and Fe_2B) were measured continuously.

All experimental results were obtained under strictly isothermal conditions.

3. Results and Discussion

Figure 1 shows the isothermal kinetic curves of the hydrogen-induced direct phase transformation in the $R_2Fe_{14}B$ type alloy. As may be seen from Fig. 1 at isothermal temperature $T = 760$°C the direct phase transformation has very high-rate, and was finished in 65 min (curve *1*). Decreasing of isothermal temperature to 750°C induces slowing down of the phase transformation rapidity. At this temperature, full decomposition was completed in 85 min (curve *2*). At the temperatures 730°C (curve *3*) and 710°C (curve *4*) phase transformation was completed in 135 and 200 min, respectively. Further decreasing of the temperature made transformation to be more and more slow. So, at the temperature 690°C (curve *5*) phase transformation was finished in 340 min. It is important that at all temperatures there was distinct incubation period of the phase transformation. At the temperatures from 760 to 690°C this incubation period was equal from 3 up to 15 min.

Let's discuss obtained experimental results. The hydrogen-induced direct phase transformation in $Nd_2Fe_{14}B$ alloy can be represented as [6]:

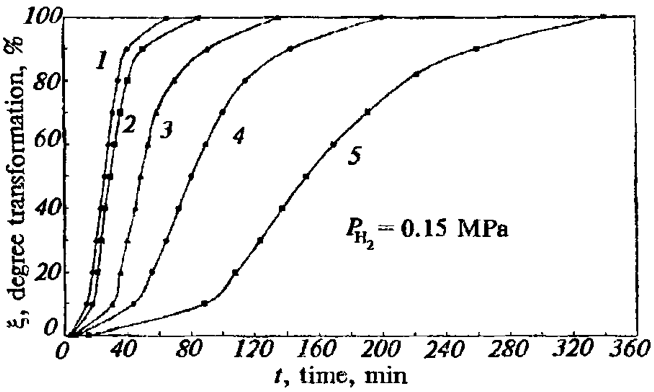

Fig. 1. The kinetic curves of the direct phase transformation in alloy of $R_2Fe_{14}B$ type obtained under hydrogen pressure of 0.15 MPa and different constant temperatures: *1*—760; *2*—750; *3*—730; *4*—710; *5*—690°C.

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

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

As may be seen from Fig. 2, this type of kinetic curves with gradual slowing down of transformation rate at the $T < 730$°C indicates that this transformation develop by the mechanism of nucleation and growth.

It is known that phase transformations by mechanism of nucleation and growth, being well investigated in steels, have two types of isothermal kinetic diagram [8].

When lowering the temperature and increasing the supercooling from critical point the growth of speed of new phases nucleation dominates at first 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 (for example the ferrite→austenite transformation in steels during heating) have another type of kinetic diagrams. In this case both factors act along and with the increasing of temperature phase transformation accelerates.

The kinetics diagram of the hydrogen-induced direct phase transformation in $R_2Fe_{14}B$ type alloy is showed in the Fig. 2. It is obvious that investigated phase transformations have the kinetic diagram of the second type (from above mentioned). It is interesting that the shape of the kinetics diagram, showed in Fig. 2, is similar to the diagram such direct transformation in industrial alloy of Nd—Fe—B-type, which was investigated in work [9]

The diffusion coefficients of Fe, Nd, Pr, B and others atoms are increasing as the temperature become higher. This is an important factor. But, so rapid rise of the speed of the phase transformation (about five times) into the interval of temperatures only 70°C (from 690 and to 760°C) can not be attributed to increasing of the diffusion coefficients only (even in view of the fact that hydrogen accelerates the diffusive processes in solid body). It means that the rate of the generation of the centers of new phases (NdH_2, α-Fe and Fe_2B) increased too.

The Avrami theory [10] for further analyses of mechanism of this transformation was used. According to this theory the phase transformation may be described by the following equation:

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

where ξ is a degree of transformation, k, n are constants, t is a time.

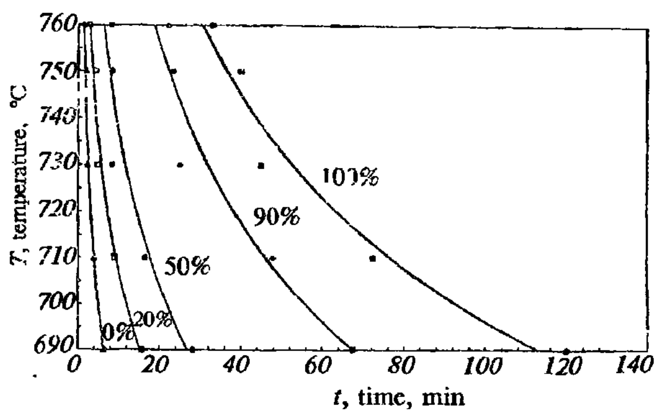

Fig 2. The isothermal kinetics diagram of the hydrogen-induced direct phase transformation in alloy of $R_2Fe_{14}B$ type.

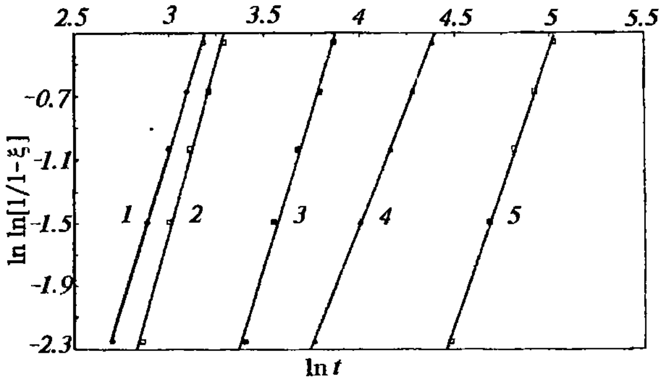

Fig. 3. The kinetics curves plotted by the Avrami equation for degrees of direct transformation from 10% up to 50% at the different constant temperatures: *1*—760; *2*—750; *3*—730; *4*—710; *5*—690°C.

The experimental results (from Fig. 1) were plotted in the following co-ordinates: $\ln\ln[1/(1-\xi)] - \ln t$, where $\xi = 0.1 - 0.5$, *i.e.* from 10% up to 50% of degree of the direct transformation. As may be seen from Fig. 3, these curves are straight lines. The slope of the lines gives $n = 3.98$, on average. In case of hydrogen-induced direct phase transformation in Nd—Fe—B alloy [9] n was equal 1.06. By Avrami theory [10], if $1 < n < 4.0$ than transformation occurs by the 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 mechanism. They may be classified as hydrogen-induced *diffusive* phase transformations.

4. Conclusions

The investigation of the kinetics of the hydrogen-induced direct diffusive phase transformation in industrial alloy of $R_2Fe_{14}B$ type is fulfilled.

♦ Decreasing of the isothermal temperature of the direct phase transformation in interval from 760 to 690°C induced slowing down of the transformation rate in approximately five times.

♦ The kinetics diagram of this phase transformation was obtained. This diagram is similar to the diagrams of the transformations in steels during heating and hydrogen-induced direct phase transformation in alloy of Nd—Fe—B type.

♦ The investigated phase transformation is described well by the Avrami theory. This phase transformation is developing by the mechanism of nucleation and growth with diffusion-controlled growth of particles.

So, this kind of transformations in industrial alloy of $R_2Fe_{14}B$ type is needed to be classified as hydrogen-induced *diffusive* phase transformations.

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