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Kinetics of hydrogen-induced reverse phase transformation in Y_2Fe_{17} hard magnetic alloy

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Kinetics of hydrogen-induced reverse phase transformation, i.e. recombination process of decomposed of YH_2 hydride phase and α-Fe phase of iron in initial phase of Y_2Fe_{17} hard magnetic alloy has been studied. It has been established that, as the temperature increase from 650 to 750°C, a reverse phase transformation significantly accelerates. The activation energy of phase transformation process has been determined from kinetic data (227÷383 kJ/mol) that it is correspond to the values of activation energy of the Fe atoms diffusion in R — T type alloys. It has been shown that the kinetics of hydrogen-induced reverse phase transformation in Y_2Fe_{17} hard magnetic alloy is controlled by the Fe atoms diffusion to growing new Y_2Fe_{17} phase centers.

Keywords: magnetic alloys; intermetallics; gas — solid reactions.

1. Introduction

The intermetallic compounds of R_2M_{17} (R=Er, Sm, Y, Dy, Ho, Gd) type have attracted much attention because of their interesting magnetic properties [1,2]. For instance, R_2M_{17} type compounds demonstrate very interesting magnetic phenomenon during their interaction with interstitial atoms (H, N, C, B) [3—5] and because of this Y_2Fe_{17} compound has great potential applications in the field of high-frequency microwave absorption [6].

New perspective technology well known as a HDDR-process (Hydrogenation-Decomposition-Desorption-Recombination) was applied in R_2M_{17} type alloys (Sm_2Fe_{17}, Sm_2Co_{17} *etc.*) alloys for permanent magnets and allows improve their structure and magnetic properties by hydrogen-induced reversible phase transformations in such type alloys [7]. In particular, the most significant aspect of the HDDR process is that there is a dramatic change in the microstructure alloy from an initial grain size of typically ~150μm to a very fine, uniform grain size of about 100—300 nm [7]. On magnetisation, the HDDR nanocrystalline powder exhibits an appreciable coercivity and this means that, in its simplest net shape form, the powder can be mixed with a thermosetting resin to produce an isotropic and anisotropic permanent magnet by compression moulding. In particular, at HDDR-treatment of the Y_2Fe_{17} alloy undergoes the direct hydrogen-induced phase transformation at temperatures above 500°C with decomposition of initial alloy on hydride YH_2 phase and α-phase of Fe that can be described by the following phase scheme:

$$Y_2Fe_{17} + H_2 \rightarrow YH_2 + \alpha\text{-Fe} \quad (1)$$

The reverse phase transformation takes place during hydrogen evacuation at same temperatures with recombination process of decomposed phases into initial Y_2Fe_{17} matrix phase by the following phase reaction:

$$YH_2 + \alpha\text{-Fe} \rightarrow Y_2Fe_{17} + 2H_2\uparrow \rightarrow Y_2Fe_{17} \quad (2)$$

As a rule, after the completion of recombination stage the treated alloy as a rule consist of the nanocrystalline phase of Y_2Fe_{17}. It is obviously that the clear outstanding of kinetic features of the above hydrogen-induced phase transformations will allow in follows to control microstructure and magnetic properties of this alloy. For instance, investigation of kinetics of such type direct and reverse hydrogen-induced transformations carried out earlier in Sm_2Fe_{17} and $Nd_2Fe_{14}B$ type alloys [8—9], give us possibility to establish the basic features of these transformations: temperature intervals of development of transformations in $Nd_2Fe_{14}B$ type alloys; to establish diffusive-controlled character of transformations; to construct for the first time T-T-T diagrams (Temperature-Time-Transformation or isothermal kinetics diagrams) for transformations; to establish influence of kinetics parameters on microstructure features of alloys [10—11].

Earlier for Y_2Fe_{17} alloy above-mentioned kinetic peculiarities have been established for direct transformation [12] and therefore, the main aim of present paper was to study the features of kinetics of the hydrogen-induced reverse phase transformation (see Eq.(2)) in Y_2Fe_{17} alloy at same temperatures range of 630—750°C in vacuum ~10^{-2} Torr.

2. Materials and methods

Original samples of Y_2Fe_{17} alloy were prepared by arc melting in an argon atmosphere of high purity. The raw materials of

Y, Fe were at least 99.9% pure. The arcmelted ingots were wrapped in molybdenum foil, sealed in a steel tube, annealed at 1273 K for 24 h in a highly-purified argon atmosphere and then quenched to room temperature, resulting in a single-phase compound of the 2:17-type structure.

Kinetics investigations of reverse hydrogen-induced phase transformation has been carried out on special hydrogen-vacuum equipment using a special magnetometric Sadikov's method [8]. Samples of Y_2Fe_{17} alloy as powders (~50 μm, ~1.2 g) were placed into a reaction chamber which was evacuated up to ~0.1 Pa vacuum. Then Y_2Fe_{17} alloy was heated in vacuum to temperature 750°C and then filled by hydrogen at pressure of 0.1 MPa that was accomplished by Y_2Fe_{17} alloy decomposition on YH_2 and α-Fe phase. After establishing some isothermal conditions (in temperature interval from 630 up to 750°C), from reaction chamber with sample has been evacuated hydrogen by vacuum pump up to vacuum ~10^{-2} Torr and from this time moment the evolution of hydrogen-induced reverse phase transformation in Y_2Fe_{17} alloy was monitored continuously by meaning the decrease of the amount of α -Fe ferromagnetic phase in the sample. Then, in accordance with obtained data, the isothermal kinetic curves of phase transformation have been plotted. XRD-analysis was performed using of DRON-3 difractometer in Fe-Kα radiation.

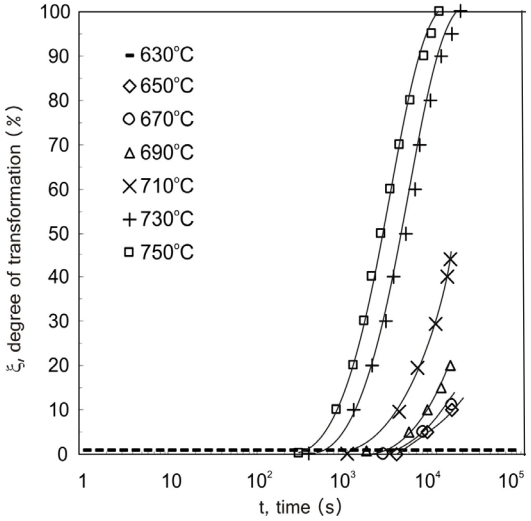

Fig. 1. The kinetic curves of reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy at temperatures from 630 to 750°C and in vacuum ~ 10^{-2} Torr.

3. Results and discussion

Thus, hydrogen evacuation from decomposed Y_2Fe_{17} alloy results in development of reverse phase transformation leading to recombination of a hydride YH_2 phase and α-Fe phase (see the Eq.(2)) into initial Y_2Fe_{17} phase which was confirmed by XDR data.

In Fig.1 results of research of kinetics of hydrogen-induced reverse phase transformation in Y_2Fe_{17} alloy are generalized in form of kinetic curves.

As can be seen from Fig.1, at temperature 630°C reverse transformation does not develop for transformation time. Further, at temperatures 650, 670, 690 and 710°C hydrogen-induced reverse phase transformation not has been completed for transformation time of ~1.8×10^4 s. In this case, at lower temperatures the reverse phase transformation is not finished completely for experimental time with reaching at 650°C only ~10% of completeness for 1.5×10^4 s, then at 670°C — 11% for 1.5×10^4 s, 690°C — 20% for 1.44×10^4 s, 710°C — 44% for 1.44×10^4 s. Further, at increase of temperature up to 730 and 750°C transformation has been completed for 1.8×10^4 s and 1.11×10^4 s, respectively.

Thus, as follows from Fig.1, with increasing of transformation temperature in narrow interval (120°C) from 630°C up to 750°C the reverse phase transformation lead to very strong acceleration of transformation in some order of magnitude.

In addition, because of this, it is necessary also to note, that at all temperatures there is a noticeable incubation period of a reverse phase transformation (from 0.72×10^4 s at 650°C to 0.0228×10^4 s at 750°C).

As can be seen in Fig.1, the shape of the kinetic curves with a gradual slowdown of the transformation rate with decrease temperature and also dependence of the incubation period on the temperature let us suggest [13] that phase transformations develop by the mechanism of nucleation and growth. It is necessary to note that the results obtained in this work are similar to the our earlier data [8,9], where the kinetics of hydrogen-induced phase transformations in $Nd_2Fe_{14}B$ and Sm_2Fe_{17} alloys was studied; direct and reverse phase transformations in these alloys greatly accelerates as the temperature increases within 610°C — 750°C, too.

On the other hand, as well known from classic kinetic theory of phase transformations in condensed state [13], in particular in accordance with Becker-Döering model of nucleation kinetics [14—15] if plots dependence $\ln t_\xi$ on 1/T, where t_ξ is the transformation time, which it is necessary for reaching of some degree of transformation ξ and T is the transformation temperature, we can determine an effective energy of reverse phase transformation process. For this goal experimental data from Fig.1 were re-plotted in co-ordinates $\ln t_\xi$ versus 1/T which are shown in Fig.2. The slopes of the straight lines give us the values of the effective activation energies for hydrogen induced reverse phase transformation in Y_2Fe_{17} alloy [13,15].

As a result, obtained values of activation energy determined for some degrees of reverse transformation varying from 227 up to 383 kJ/mol. The above-mentioned obtained values of activation energy correspond to the values of an activation energy of the Fet atoms diffusion in R — T alloys (where R is a rare-earth metal, T — a transition metal) ~250 kJ/mol [16] and self-diffusion of Fe atoms in α-Fe phase of iron [17,18], whereas activation energy for hydrogen atoms diffusion in R_2Fe_{17} type alloys is ~ (31±10) kJ/mol [19].

Because of this the obtained activation energy for reverse phase transformation is similar with activation energy for hydrogen-induced direct phase transformation in the same Y_2Fe_{17} alloy (163÷242 kJ/mol [12]).

Therefore, it is believed that the above investigated reverse hydrogen-induced phase transformations in Y_2Fe_{17} alloy are controllable by diffusion of iron atoms to growing Y_2Fe_{17} phase new centers in our case.

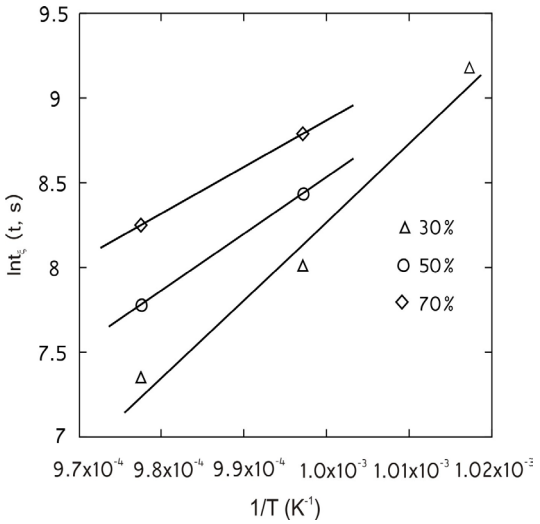

Fig. 2. Dependence $\ln t_\xi$ on $1/T$ for reverse phase transformations in Y_2Fe_{17} alloy for 30, 50 and 70 % of degrees of phase transformation.

4. Conclusions

In this work, in Y_2Fe_{17} alloy it is established experimentally that with increase of temperature (from 650°C up to 750°C) the development process of hydrogen-induced reverse phase transformations accelerates too. At lower temperature (630°C) reverse transformation does not develop for experimental time. In addition, it is established that at all transformation temperatures there is noticeable incubation period of transformation (from 0.72×10^4 s at 650°C to 0.0228×10^4 s at 750°C).

Activation energy of transformation process determined from kinetic data varying from 227 up to 383 kJ/mol that it is correspond to the values of activation energy of the Fe atoms diffusion in R — T type alloys.

Analysis of results carried out on the base of classic kinetic theory of phase transformations in condensed state allow made conclusion that hydrogen-induced reverse phase transformations in Y_2Fe_{17} alloy occur by the mechanism of nucleation and growth.

In addition, it is shown that reverse phase transformations kinetics is controllable by diffusion of iron atoms to growing new Y_2Fe_{17} phase centers.

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