_____ STRUCTURE, PHASE TRANSFORMATIONS, _____
AND DIFFUSION

Effect of Hydrogen Pressure on the Kinetics of the Hydrogen-Induced Diffusional Phase Transformation in an $R_2Fe_{14}B$ Alloy

V. A. Gol'tsov*, S. B. Rybalka*, A. F. Volkov*, Yu. G. Putilov**, and V. A. Didus'*

* Donetsk State Technical University, ul. Artema 58, Donetsk, 340066
** Ekspromag OOO, ul. Besedova 29, Dneprodzerzhinsk, 322611
Received April 19, 1999; in final form August 3, 1999

Abstract—The kinetics of the forward phase transformation induced by hydrogen in the alloy of the $R_2Fe_{14}B$ type (R = 32 wt % Nd + Pr and 4.4 wt % intermediate and heavy rare-earth metals) was studied by the magnetometric method. Isotherms of the phase transformation were obtained for temperatures of 710, 730, 750°C and hydrogen pressures of 0.1, 0.15, 0.2 MPa. Kinetic diagrams of this transformation were plotted for hydrogen pressures of 0.1, 0.15, 0.2 MPa. Increasing hydrogen pressure was found to result in a shift of the isolines of the same degree of transformation to the region of shorter times. This indicates that the presence of hydrogen is not only a necessary thermodynamic condition for the occurrence of the diffusional phase transformation but is the most important kinetic factor as well.

INTRODUCTION

At present, a new field of materials science is being developed—hydrogen treatment of materials—which is based on phase transformations induced by hydrogen [1, 2]. A recently developed method of a special hydrogen treatment [3–6] called the HDDR process (Hydrogenation–Decomposition–Desorption–Recombination) is based on the forward and reverse transformations induced by hydrogen in intermetallic alloys of the $R_2Fe_{14}B$ type, where R is Nd, Pr, Sm, Tb, Dy, and other rare-earth elements.

Hydrogen makes the $R_2Fe_{14}B$ alloys thermodynamically unstable. At elevated temperatures (600–900°C), a "forward" phase transformation occurs and causes a diffusional phase decomposition of the initial alloy into phases such as RH_x, α-Fe, and Fe_2B. The removal of hydrogen initiates the "reverse" transformation and the restoration of the original single-phase $R_2Fe_{14}B$ alloy. These forward and reverse transformations give rise to a substantial improvement in the characteristics of permanent magnets made of the $R_2Fe_{14}B$ alloys, such as H_c, B_r, and $(BH)_{max}$ [3–6].

Thus, the HDDR process is based on the forward and reverse phase transformations induced by hydrogen in the $R_2Fe_{14}B$ alloys. It is undoubtful that the study of the kinetics of these transformations is of considerable scientific and technological interest.

The kinetics of the forward hydrogen-induced phase transformation in the alloys of the $Nd_2Fe_{14}B$ and $R_2Fe_{14}B$ types was studied in our previous works [7–9]. Temperature was found to be an important parameter controlling the transformation rate.

In [10–12], the authors studied the effect of the hydrogen pressure on the forward phase transformation in $Nd_2Fe_{14}B$ and $Sm_2Fe_{17-x}Ga_x$ alloys in the course of continuous heating (from room temperature to a temperature of the active development of the transformation) and subsequent isothermal holding at this temperature. Increasing hydrogen pressure was shown to decrease the temperature of the active development of this transformation. The authors of [10–12] concluded that the enhanced hydrogen pressure is expected to accelerate the phase transformation.

In [13], we studied the effect of hydrogen pressure on the forward phase transformation in the $R_2Fe_{14}B$ alloy under isothermal conditions. An increase in the hydrogen pressure was shown to accelerate this transformation.

The aim of this work is to study the effect of hydrogen pressure on the kinetics of the forward phase transformation induced by hydrogen in a commercial $R_2Fe_{14}B$ alloy of a more complex composition as compared to those investigated in [10–12] and in a wider temperature range than in [13].

EXPERIMENTAL

A commercial alloy of the $R_2Fe_{14}B$ type (analog of the $Nd_2Fe_{14}B$ alloy) was investigated. The alloy consisted of 36.4 wt % R, 62.45 wt % Fe, and 1.15 wt % B, where R = 32 wt % Nd + Pr and 4.4 wt % intermediate and heavy rare-earth metals. This alloy was obtained from the intermediate products of processing of the rare-earth concentrate by a special technique.

The kinetics of the forward phase transformation in the intermetallic compound was studied using a special
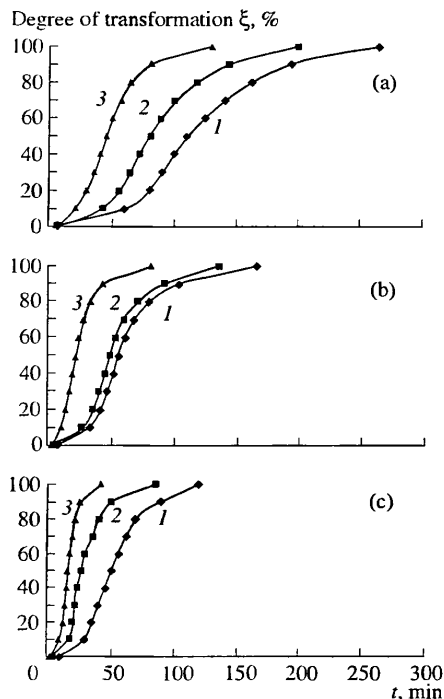
Degree of transformation ξ, %

Fig. 1. Development of the hydrogen-induced forward phase transformation as a function of the isothermal holding time at temperatures of (a) 710, (b) 730, (c) 750°C, and hydrogen pressures of (*1*) 0.1, (*2*) 0.15, and (*3*) 0.20 MPa.

hydrogen-vacuum apparatus. It enabled us to perform treatment both in hydrogen (up to 0.2 MPa) and in vacuum (up to 10^{-2} Torr) at temperatures up to 800°C. The technique of detecting the new phases (α-Fe and iron boride) formed upon the phase decomposition is based on the fact that the $R_2Fe_{14}B$ alloy is paramagnetic (T_C = 315°C) at the experimental temperatures (710–750°C), while α-Fe and iron boride are ferromagnetic. This allowed us to observe the appearance and growth of these phases by the magnetometric method. The measuring part of the experimental unit, previously described in detail [8, 9], was made similar to that of Sadikov's unit used to study the kinetics of phase transformations in steels [14].

The experimental technique used for the investigation was as follows. Small (1.017-g) specimens of the $R_2Fe_{14}B$ alloy were placed in the reaction chamber evacuated to 10^{-2} Torr. Under continuous pumping-out, the specimens were heated at an average rate of 20 K/min to a specified temperature in a range of 710–750°C. After isothermal conditions were established in the chamber, hydrogen was let into the system up to a given pressure (0.1, 0.15, or 0.2 MPa). Further, we kept the pressure constant and under the isothermal condi-

tions continuously watched on the development of the forward phase transformation by an increase in the amount of the ferromagnetic phases (α-Fe and iron boride). The data obtained were used to plot kinetic curves.

RESULTS AND DISCUSSION

Using the technique described above, we studied the kinetics of the forward phase transformation induced by hydrogen in the $R_2Fe_{14}B$ alloy at temperatures of isothermal holding equal to 710, 730, 750°C and hydrogen pressures P_{H_2} = 0.1, 0.15, and 0.2 MPa.

Figure 1a shows the kinetic curves of the forward phase transformation induced by hydrogen in the commercial alloy of the $R_2Fe_{14}B$ type at T = 710°C under hydrogen pressures of 0.1, 0.15, and 0.2 MPa. As seen, the phase transformation is completed in 265 and 200 min at 0.1 MPa (curve *1*) and 0.15 MPa (curve *2*), respectively. An increase in P_{H_2} to 0.2 MPa (curve *3*) results in the completion of the transformation in 130 min.

Figure 1b shows the isothermal development of the forward phase transformation at T = 730°C. Under a pressure of 0.1 MPa (curve *1*), the transformation is over in 165 min. At hydrogen pressures of 0.15 MPa (curve *2*) and 0.2 MPa (curve *3*), the process was over in 135 and 80 min, respectively.

Figure 1c demonstrates the development of the forward phase transformation at 750°C. It is seen that under a pressure of 0.1 MPa the transformation finishes in 120 min (curve *1*). An increase in pressure to 0.15 MPa (curve *2*) causes an acceleration of the transformation. It is completed now in 85 min. Under a pressure of 0.2 MPa (curve *3*), the transformation is completed in 42 min.

Thus, as Figs. 1a–1c show, a twofold increase in the hydrogen pressure results in a significant acceleration of the phase transformation (by a factor of 2 to 3).

It is important to note the existence at all temperatures and pressures of an induction ("incubation") period preceding the start of the phase transformation as registered from the earliest signs of the appearance of magnetic phases. The duration of this period changed from 3 min (T = 750°C, P_{H_2} = 0.3 MPa) to 7.5 min (T = 710°C, P_{H_2} = 0.1 MPa). It is significant that the incubation period shortens by 2.5 times with the rise of the transformation temperature and pressure.

In solving processing problems, it is convenient to use kinetic diagrams [15]. Figures 2a–2c display segments of such diagrams plotted from the data of Fig. 1 for the hydrogen-induced forward phase transformation of the $R_2Fe_{14}B$ intermetallide. Note that the diagrams obtained for the forward phase transformation in the $R_2Fe_{14}B$ alloy under consideration are of the same type as those for the $Nd_2Fe_{14}B$ alloy [7, 8]. Figure 2

shows that a twofold increase in the hydrogen pressure (from 0.1 to 0.2 MPa) result in a substantial increase in the transformation rate. Therefore, the "isopercentage" kinetic curves (corresponding to the same degree of transformation) are shifted to the region of shorter times.

Let us discuss the potential causes of this strong effect of hydrogen pressure on the transformation rate. As is known, the hydrogen-induced forward phase transformations studied in this work (this problem was most extensively investigated in the $Nd_2Fe_{14}B$ alloy) occurs at $P_{H_2} = 0.1$ MPa and $T = 600-900°C$ by the following reaction [3–5]:

$$Nd_2Fe_{14}B + H_2 \longrightarrow \alpha\text{-Fe} + NdH_2 + Fe_2B.$$
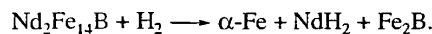
The phase transformations of this type [7–9] occur by the nucleation-and-growth mechanism and are controlled by diffusion of the alloy components (Nd, Fe, B). As was experimentally shown in 1951 [16], even a small amount of interstitial atoms (carbon atoms in [16]) results in a rather marked increase in the iron self-diffusivity in the γ-Fe crystal lattice. More recently, Krivoglaz and Smirnov [17] theoretically showed that an increase in the concentration of interstitial atoms must give rise to a grown in the metal self-diffusivity. The cause is that an increase in the concentration of interstitial impurity results in a rise of the equilibrium vacancy concentration in metals [18–19]. The experimental data indicating the acceleration of diffusion of substitutional atoms under the effect of dissolved hydrogen were generalized in [20]. A dramatic increase in the equilibrium vacancy concentration at high temperatures and hydrogen pressures was observed by Fukai [21], which inevitably resulted in the acceleration of the diffusion decomposition of the alloys (by several orders according to [21]). The theoretical aspects of this problem were considered in [22, 23].

Thus, we can state that an increase in the vacancy concentration and the acceleration of diffusion of substitutional atoms under the effect of dissolved hydrogen can apparently be considered as general physical phenomena that are characteristic of many materials. It can be assumed that a similar mechanism is operative in our case as well. The content of hydrogen dissolved in the $R_2Fe_{14}B$ alloy increases with increasing hydrogen pressure. Therefore, it is reasonable to suppose that this increases the diffusivities of the alloy components (R, Fe, B) and a substantial acceleration of the phase transformation. In other words, the increase in the amount of dissolved hydrogen increases the number of equilibrium vacancies and, correspondingly, the rate of diffusional transport of atoms to the nuclei of the new phases (RH_2, α-Fe, Fe_2B). It is also possible that the rate of nucleation of new phases also depends on the hydrogen content in the alloy. However, the latter problem needs to be investigated in more detail. Along with the above-indicated kinetic causes of the strong effect of hydrogen pressure on the kinetics of these transfor-
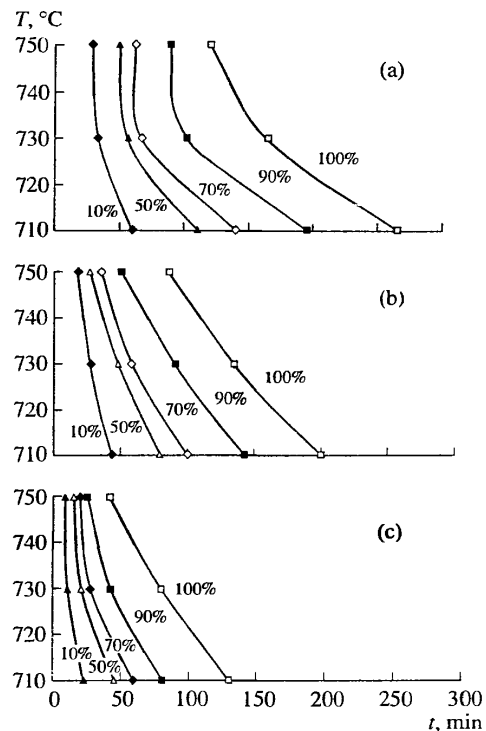

Fig. 2. Diagrams of the hydrogen-induced isothermal phase transformation in the alloy of the $R_2Fe_{14}B$ type at hydrogen pressures of (a) 0.1, (b) 0.15, and (c) 0.20 MPa.

mations induced by accelerated diffusion, it can be supposed that a thermodynamic factor discussed in [10–12] also affects the kinetics. Indeed, an increase in the hydrogen content decreases the Gibbs free energy of formation of RH_x rare-earth hydrides. As a result, the "driving force" of the transformation increases. This must cause the acceleration of phase transformations induced by hydrogen.

Thus, it is the mutual effect of the above factors, i.e., a kinetic factor caused by the acceleration of diffusion of atoms of the metal matrix with increasing hydrogen pressure and a thermodynamic factor related to the decrease in the Gibbs free energy of RH_x formation, that results in this significant acceleration of the phase transformation (by a factor of 2 to 3 in this work) with the rise of the hydrogen pressure only from 0.1 to 0.2 MPa.

Finally, we can conclude that the hydrogen effect generating phase transformations in the $R_2Fe_{14}B$ alloys is not only a necessary thermodynamic condition but also a rather strong kinetic factor that determines the transformation rate.

CONCLUSION

1. The effect of hydrogen pressure on the kinetics of the forward phase transformation induced by hydrogen in the alloys of the $R_2Fe_{14}B$ type was studied. An increase in the hydrogen pressure from 0.1 to 0.2 MPa was found to result in a two- to threefold acceleration of the transformation.

2. Kinetic diagrams were plotted for the forward isothermal diffusional phase transformation in the $R_2Fe_{14}B$ alloy at hydrogen pressures of 0.1, 0.15, and 0.2 MPa. An increase in the hydrogen pressure is shown to result in a shift of the kinetic curves (isolines corresponding to the same degree of transformation) to the region of shorter durations.

3. It was established that the hydrogen effect, initiating the phase transformations in the $R_2Fe_{14}B$ alloys, is not only a necessary thermodynamic condition for these transformations to develop, but also a very important kinetic factor determining the transformation rate.

REFERENCES

1. Goltsov, V.A., History, Ideology and Prospects of the Hydrogen Treatment of Materials.—Opening Address, *Int. J. Hydrogen Energy*, 1997, vol. 22, no. 2/3, pp. 115–117.

2. Goltsov, V.A., Fundamentals of Hydrogen Treatment of Materials and Its Classification, *Int. J. Hydrogen Energy*, 1997, vol. 22, no. 2/3, pp. 119–124.

3. Takeshita, T., Present Status of the Hydrogenation-Decomposition-Desorption-Recombination Process as Applied to the Production of Magnets, *J. Alloys Compd.*, 1993, vol. 193, pp. 231–234.

4. Takeshita, T., Some Applications of Hydrogenation-Decomposition-Desorption-Recombination (HDDR) and Hydrogen-Decrepitation (HD) in Metals Processing, *J. Alloys Compd.*, 1995, vol. 231, pp. 51–59.

5. Ragg, O.M., Keegan, G., Nagel, H., and Harris, I.R., The HD and HDDR Processes in the Production of Nd–Fe–B Permanent Magnets, *Int. J. Hydrogen Energy*, 1997, vol. 22, no. 2/3, pp. 333–342.

6. Fruchart, D., Bacmann, M., de Rango, P., Ishard, O., Liesert, S., Miraglia, S., Obbade, S., Soubeyroux, J.-L., Tomey, E., and Wolfers, P., Hydrogen in Hard Magnetic Materials, *J. Alloys Compd.*, 1997, vols. 253–254, pp. 121–127.

7. Rybalka, S.B., Volkov, A.F., and Gol'tsov, V.A., Effect of Temperature on the Kinetics of Diffusional Phase Decomposition of Alloys of the Nd–Fe–B Type upon Hydrogen Treatment, *Materialy 5-i mezhdunarodnoi nauchno-tekhnicheskoi konferentsii "Mashinostroenie i tekhnosfera na rubezhe 21 veka"* (Proc. 5th Int. Conf. "Machine Building and Technosphere on the Turn of the 21th Century), Donetsk: Mashinostroenie, 1998, vol. 3, no. 6, pp. 47–49.

8. Goltsov, V.A., Rybalka, S.B., and Volkov, A.F., Kinetics of the Hydrogen-Induced Direct and Reverse Diffusive

9. Goltsov, V.A., Rybalka, S.B., Volkov, A.F., Subbotin, V.V., and Putilov, Yu.G., Kinetics of the Hydrogen-Induced Forward and Reverse Diffusional Phase Transformation in an $R_2Fe_{14}B$ Hard Magnetic Alloy, *Phys. Met. Metallogr.*, 1999, vol. 87, no. 6, pp. 543–546.

10. Gutflish, O. and Harris, I.R., Hydrogen Assisted Processing of Rare-Earth Permanent Magnets, *Proc. 15th Workshop on Rare-Earth Magnets and Their Application*, Dresden, 1998, p. 487.

11. Kubis, M., Muller, K.-H., and Schultz, L., Hydrogenation and Disproportionation of $Sm_2Fe_{17-x}Ga_x$ at High Hydrogen Pressures, *J. Appl. Phys.*, 1998, vol. 83, pp. 6905–6907.

12. Handstein, A. *et al.*, Thermoanalytical Investigations on the Hydrogen Absorption Behavior of $Sm_2Fe_{17-x}Ga_x$ at Hydrogen Pressures, *Proc. 15th Workshop on Rare-Earth Magnets and Their Application*, Dresden, 1998, p. 563.

13. Gol'tsov, V.A., Rybalka, S.B., Volkov, A.F., Subbotin, V.V., and Putilov, Yu.G., Effect of Hydrogen Pressure on the Kinetics of the Hydrogen-Induced Diffusional Phase Decomposition of $R_2Fe_{14}B$ Alloys, *Fiz. Tekh. Vys. Davl.*, 1999, vol. 9, no. 1, pp. 76–80.

14. Livshits, B.G., *Fizicheskie svoistva chernykh metallov i metody ikh ispytanii* (Physical Properties of Ferrous Metals and Methods of Their Testing), Moscow: Otd. Nauchn. Tekh. Inform., 1937.

15. Popova, L.E. and Popov, A.A., *Diagrammy prevrashcheniya austenita v stalyakh i β-rastvorakh titana. Spravochnik* (Time-Temperature-Transformation Diagrams for the Transformation of Austenite in Steels and Titanium β Solutions), Moscow: Metallurgiya, 1991.

16. Gruzin, P.L., Kornev, Yu.V., and Kurdjumov, G.V., Effect of Carbon on Iron Self-Diffusion, *Dokl. Akad. Nauk SSSR*, 1951, vol. 80, pp. 49–51.

17. Krivoglaz, M.A. and Smirnov, A.A., Effect of Interstitial Atoms of Self-Diffusion in Metals, *Dokl. Akad. Nauk SSSR*, 1954, vol. 96, no. 3, pp. 495–498.

18. Smirnov, A.A., *Molekulyarno-kineticheskaya teoriya metallov* (Kinetic Theory of Metals), Moscow: Nauka, 1966.

19. Krivoglaz, M.A. and Smirnov, A.A., Effect of Interstitial Impurities on Alloy Decomposition, *Zh. Fiz. Khim.*, 1955, vol. 29, no. 8, pp. 1532–1534.

20. Pokhmurs'kii, V.I. and Fedorov, V.V., *Vpliv vodnyu na difuziini protsesi v metalakh* (Effect of Hydrogen on Diffusional Processes in Metals), Lviv, 1998.

21. Fukai, Y., Formation of Superabundant Vacancies in Metal Hydrides at High Temperatures, *J. Alloys Compd.*, 1995, vol. 231, pp. 35–40.

22. Smirnov, A.A., Theory of Vacancies in Interstitial Alloys, *Ukr. Fiz. Zh.* (Russ. Ed.), 1992, vol. 37, no. 8, pp. 1188–1212.

23. Bugaev, V.M. *et al.*, Impurity-Induced Host-Lattice Vacancies in Metals and Interstitial Alloys, *Int. J. Hydrogen Energy*, 1999, vol. 24, no. 2/3, pp. 135–140.

Phase Transformation in Industrial Alloy of $Nd_2Fe_{14}B$ Type, *Funct. Mater.*, 1999, vol. 6, no. 2.