Journal of Alloys and Compounds 293–295 (1999) 844–857

Hydrogen treatment (processing) of materials: current status and prospects

V.A. Goltsov

Donetsk State Technical University, 58 Artem street, Donetsk 340000, Ukraine

Abstract

The hydrogen treatment of materials (HTM) as a novel field of Materials Science and Engineering is analysed and reviewed. First, a short history of HTM development is given. Then, the fundamentals of HTM are analysed and it is shown that hydrogen action on materials comprises physical, chemical, physico-chemical and mechanical components. In this aspect, hydrogen-induced phase transformations and their use in HTM are reviewed.

Keywords: Hydrogen treatment of materials; Hydrogen-induced phase transformations

1. Introduction

Historically, Schleicher and Zwicker [1] were the first to conduct experiments and publish papers on the possibilities of using hydrogen for the plastification of titanium alloys and ensuring their hot plastic deformation at lower temperatures. Their idea was based on the fact that hydrogen, as an alloying element, makes the more plastic high temperature β-phase of titanium more stable at lower temperatures. When the plastic deformation was completed, the hydrogen had to be removed from the titanium.

At the time, the work of Schleicher and Zwicker was looked upon as an exception, as some ‘‘funny thing’’. The hydrogen community, numbering already some hundreds of people all over the world, considered hydrogen as a harmful element in steels and any materials. At that time another way of thinking was impossible. In the 1950–1960s, and even before, since the First World War, there were serious accidents and even catastrophes in industry caused by hydrogen, such as unpredicted damage because of hydrogen corrosion in the chemical and petrochemical industry, breaking of rails and energetic equipment because of flakes, aircraft crashes because of hydrogen embrittlement of titanium alloys, etc. There are many such examples in the history of engineering.

Therefore, it was absolutely normal that, in the 1960s, and even in the first half of the 1970s, the concept of hydrogen embrittlement was the only one which was intensively worked on [2]. Almost all investigators were working in this direction and any other possibility of an effect of hydrogen on materials was unthinkable, or, as we say now, was out of the material science paradigm of that time. This is why all information on the interaction of hydrogen and materials generated by the world science community was considered only from one point of view.

In the early 1970s, the hydrogen phase naklep (cold work) phenomenon (HPN) was discovered [3]. This seemed to show, at once, a new possibility of using hydrogen for treating materials (HTM). Indeed, introducing hydrogen into a metal and fulfilling hydride transformation, it was possible to achieve *strong* and *controllable* strengthening of the metal and to change its structure and properties. After removing the hydrogen, one may have the same initial metallic article, but strengthened without changing its dimensions and shape. The wonderful thing was that even metals and metallic materials having no polymorphism could be subjected to such hydrogen treatment. Some outstanding scientists, such as Kurdyumov, Arkharov, Sadovsky, Bogachev, Steinberg, Wert, Smialowsky and others, estimated both the HPN phenomenon and the new ideas following from it. Nevertheless, we needed about 5 years to break down the old way of thinking, to break down the old paradigm, to understand a new possible role of hydrogen in material treatment and to work out a new view on the hydrogen-materials problem.

For the first time, new fundamental tenets in their complete form were formulated and discussed at the All-Union Scientific Conference ‘‘Our Days Problems of Metal Quality Improvement’’ (Donetsk, November 27–29, 1978). In the proceedings of the abstracts of this conference [4] we find (p. 191): ‘‘ . . . hydrogen may be used as a fundamental external agent, providing new effective methods of material treatment. Radical changes in our

PII: S0925-8388(99)00369-2

conception of material treatment are following. It is clear now that the effect of hydrogen on materials is one of the fundamental actions, just as temperature, pressure, fields and streams of particles are''.

Later, on the basis of this formula and the HPN phenomenon, on the basis of the common laws and history of metal science development, a new paradigm of material science was thoroughly elaborated and generalized [5].

Further break-down of the old paradigm was achieved due to the work of many scientists and scientific groups and the hydrogen treatment of materials attracted new adherents [6].

Having no claim to completeness, the new phenomena and effects that have been discovered during the last 25 years and which are now the foundation of HTM are listed in Refs. [7,8]: hydrogen phase ''naklep'' — Goltsov and Timofeev, 1972; hydrogen as a usefull alloying element in aluminium alloys — Erdman-Jesnitzer, 1977; self-stabilization phenomenon of hydride precipitation and polyphase ''naklep'' structures — Goltsov, Timofeev and Machikina, 1978; recrystallization after HPN — Goltsov, Timofeev and Machikina, 1979; hydride shape memory effect — Bushnev, Tyumentsev and Tyumentseva, 1980; hydride TRIP effect — Goltsov and Kirillov, 1980; hydrogen-induced acceleration of diffusive processes, atomic ordering–disordering processes in structural materials — Pokhmursky and Fedorov, 1980–81; hydride- and hydrogen-induced reversible mechanical after-effect — Geld, Spivack, Skryabina and Volyntsev, 1982; hydrogen-induced amorphization of intermetallic compounds — Yeh, Samwer and Johnson, 1983; ''top-hill'' effect — Lewis, 1983; hydrogen- and phase transition-induced shape changes of metallic materials at low (Kuzin, 1986) and high (Shapovalov, 1981) temperatures; development of scientific bases of thermo-hydrogen treatment of titanium alloys — Kolachev and Ilyin, 1987; hydrogen-induced atomic ordering and segregation phenomena — Ponyatovsky, 1981; Sakamoto and Flanagan, 1987; phenomenon of thermo-baro-elastic diffusive phase equilibrium in metal–hydrogen alloys — Goltsov, Artemenko and Vlasenko, 1977–92; improving magnetic properties by HD and HDDR processes — Harris, Takeshita and Fruchart, 1985–95.

The history and development of the HTM of intermetallic materials containing, for example, rare earth elements are of great interest. Some are used to solve problems of hydrogen energy, such as to store and compress hydrogen, to purify it, to use it as an electrode material, etc. Others are widely used as very strong magnetic materials. Since the 1970s, when these materials began to be investigated, two aspects of their interaction with hydrogen have been revealed. When interacting with hydrogen they crack and turn into powder. So, in order to use them for hydrogen storage, it is necessary to make them compact by some method (this problem is out of our discussion), but a very important question from the point of view of HTM theory was to determine whether or not it was possible to control the hydrogen process of powdering of intermetallic materials. Despite the brittleness of the materials, the hydrogen powdering treatment of intermetallic materials, as confirmed experimentally (1984), is a controllable process permitting the regulation of the dispersion of the powders [8]. Another peculiarity of these materials is their decomposition into new phases, one of which is a hydrogen-rich phase (hydride of a strong hydride-forming metal) and the others having a lower hydrogen content or even having no hydrogen at all (pure metals — iron or nickel, for example). For a long time this process was considered to be a ''harmful'' phenomenon leading only to the degradation of hydrogen storage materials but, later, the ideas on this phenomenon were expanded and it is now considered to be a useful, necessary step in the hydrogen treatment of intermetallics to give them the necessary structure and properties. As is now well known, this phenomenon is the basis of a recently discovered method of hydrogen treatment to improve the magnetic properties of rare earth alloys. It is the so-called HDDR process, hydrogenation–disproportionation–desorption–recombination, which allows improvement of the magnetic properties. It is not very difficult to understand that, recently, we witnessed the same break-down of thinking about hydrogen–intermetallic material systems as we did 20 years ago about hydrogen–metallic material systems.

The hydrogen treatment of titanium alloys was being developed on a wider basis than realized by Schleicher and Zwicker in their pioneering work. It turned out that, by temporary hydrogen alloying, it was possible not only to stabilize the β-phase, but to change the mechanism and kinetics of the phase and structural transformations, to have a phase rearrangement of the alloying elements and, finally, to induce by hydrogen, phase transformations which were impossible in alloys having no hydrogen. Much new knowledge has been obtained owing to the work of many scientific groups headed by Kolachev, Ilyin, Ponyatovsky, Kerr, Eylon, (Sam) Froes, Yoshimura, Zhang Shaoqing and others [6,9,10].

In the past few years new possibilities for the hydrogen treatment of steels and alloys based on iron, nickel, etc. have been discovered. These new methods of HTM, based on the hydrogen-induced acceleration of diffusion (Pokhmursky and Fedorov), permit the effective use of hydrogen in chemico-thermal treatment and in coating processes of structural materials (Pokhmursky, Fedorov and Buravlev). The hydrogen treatment of these materials is very long term because of the possibilities of controlling not only the surface properties but also the alloy basic properties (for example, the iron properties — Lunarska) as well as to straighten the control phase and structural transformations [9,10].

It is very important from the technological point of view that casting processes may be significantly improved by hydrogen. This kind of HTM is based on the fundamental laws of the crystallization of liquid metals and alloys saturated with hydrogen (Erdman-Jesnitzer, Borisov and Shapovalov). The HTM of catalytic, membrane and functional materials will provide great opportunities in the near future (Pielaszek, Goltsov, Timofeev and Gryaznov) [9,10].

So, the scientific and engineering achievements of HTM during the last two decades are amazing. This is a new, rapidly developing field of materials science and engineering.

On the other hand, in spite of the above achievements, *the logical synthesis of knowledge of such a scale has not yet been done, which could permit us to formulate the most fundamental HTM laws and principles which would be general for all materials*.

2. The specific character of the hydrogen action on materials and the fundamental bases of HTM

The first principles of HTM are the result of the fundamental knowledge of the interaction of hydrogen with materials, which is formed by the work of physicists, chemists, physico-chemists and others.

The hydrogen treatment of materials is based on the specific peculiarities of hydrogen, giving the possibility of a *strong and controllable* action on materials. This action is *reversible* in the sense that the hydrogen can be removed from a material even at very low temperatures. Hydrogen action on materials comprises physical, chemical, physico-chemical and mechanical components.

A *physical component* of hydrogen action shows itself as a change in a material's electron structure, possible changes in a phonon spectrum of a matrix crystal lattice, increase of an equilibrium concentration of vacancies and in a diffusive mobility of substitutional and interstitial atoms in the hydrogen interaction with crystal defects and in a change of their stability and mobility, etc.

A *chemical component* of hydrogen action is conditioned, in particular, by the fact that hydrogen (especially its ionized and atomic forms) is a very strong chemical reductant and a highly active reagent, the latter allowing it to modify a material's surface layers and its special coats, to act on body structural components, and to carry out nondirect alloying of a matrix due to reactions with oxides, carbides and other chemical compounds introduced into a material or making contact with it.

A *physico-chemical component* of hydrogen action causes a disturbance of the thermodynamic conditions of existence of a material and its separate phases. As a result, a thermodynamic necessity appears in hydride- and other hydrogen-induced phase transformations. This is the so-called ''artificial'' hydrogen-induced polymorphism. The thermodynamic conditions for the realization of a natural polymorphism of materials change, and as a result some phases stabilize themselves and extend their sphere of existence. Critical points, the mechanism and kinetics of phase transitions, and the morphology of transformation products change.

Because of the different affinity of hydrogen for individual atoms — components of a material — and because of the different affinity of hydrogen for different phases of a material, there is a thermodynamic necessity for different types of material decomposition (being first a solid solution, intermetallic or chemical compound,etc.) into separate phases or even into separate parts, having a different affinity for hydrogen.

A *mechanical component* of hydrogen action is conditioned by the fact that hydrogen dissolved in a material causes a great dilatation of the crystal lattice. Any nonhomogeneities and rearrangements, any concentration gradients caused by external or internal factors, results in the appearance of ''hydrogen'' internal mechanical stresses. These stresses cause a new hydrogen rearrangement. Thus, a material's crystal subsystem and hydrogen subsystem interconditionally and synergetically react upon any changes of external and internal factors. Therefore, all changes of a hydrogen subsystem are carried out diffusively only, while changes of the metallic matrix are carried out at low temperatures mainly by a cooperative shift mechanism. All this results in an entire spectrum of diffusive–cooperative phenomena in a material: elastic–diffusive, diffusive–plastic, brittle and afterplastic destruction, respectively, if hydrogen stresses are lower than the limit of the matrix elasticity, higher that it, or exceed an ultimate strength.

When analysing the fundamental bases of HTM, one should take into account these four components of hydrogen action on materials. However, in a great number of practical cases two components are the most important for HTM: physico-chemical and mechanical. The former determines thermodynamically necessary and kinetically possible phase and structural transformations, caused by the introduction or removal of hydrogen into or from a material as well as by a combination of these actions and other fundamental actions such as temperature, pressure, fields and streams of particles. The latter determines the specific character of the phase–structural rearrangement of a material which is conditioned by internal hydrogen stresses working under the conditions of synergetic interrelationality of any changes in the hydrogen subsystem and in a material matrix taking place in the process of hydrogen treatment.

3. Hydrogen-induced phase transformations and their use in HTM

Let us look at hydrogen-induced phase transformations from the viewpoint of the fundamental fact that hydrogen-material systems consist of two subsystems which differ greatly in their diffusivity (up to 10^{20}–10^{30}).

Hydrogen diffusive mobility is very high and cannot be suppressed even at very low temperatures. On the contrary, large atoms' diffusive mobility is suppressed completely at low temperatures: $T < (0.20–0.45)T_m$, where T_m is the material melting point.

At elevated temperatures ($T > (0.20–0.45)T_m$) large atoms' diffusive mobility is great enough to guarantee thermodynamically needed rearrangements of the material structure on the *micro and macro scale*. At moderate temperatures ($T \approx (0.20–0.45)T_m$) large atoms' diffusive mobility is not suppressed completely, but it is very low. So, at these temperatures thermodynamically needed rearrangements of the material structure are possible only on the atomic scale. So, many materials become thermodynamically unstable under hydrogen action. From the kinetic viewpoint it is very important that hydrogen greatly accelerates material atom diffusion. Therefore, the hydrogen-induced diffusive rearrangement of the atomic, micro and macro structure of materials might be achieved at much lower temperatures than before.

This fundamental knowledge is very important for understanding the nature of hydrogen-induced phase transformations, for their classification and use in HTM.

3.1. Hydride (diffusive–cooperative) phase transformations

Transformations of this class take place in hydride-forming materials usually *at low temperatures*: $T < (0.20–0.45)T_m$. At these temperatures the diffusivity of material large atoms is completely suppressed. The most distinctive feature of transformations of this class is that any kind of hydrogen redistribution in the interstitial subsystem is achieved diffusively. But, interconditionally, rearrangements of a crystal lattice or amorphous matter take place only by a cooperative, shift mechanism. In metallic materials it is similar to the martensite mechanism.

The significant feature of hydride transformations is that specific internal stresses (the so-called hydrogen stresses) play important roles in material–hydrogen systems. Near the critical point of transformation, hydrogen-induced elastic stresses are first generated by small hydrogen inhomogeneities (for instance, those caused by fluctuations of hydrogen). Elastic coherent nuclei of the hydride phase are produced under supercooling or elevation of hydrogen pressure. In metallic materials during the process of nuclei growth the coherency is lost at some moment and *plastic deformation of the matrix takes place*. In turn, this gives rise to a redistribution of hydrogen, etc. In other words, the loss of coherency and further growth of hydrogen precipitates trigger the mechanisms of hydrogen phase naklep (cold work).

So, the appearance and relaxation of very strong internal ''hydrogen'' stresses induced by hydrogen gradients and differences in the specific volumes of transforming phases are very important for understand the nature of this class of phase transformation. Thermo(baro)-elastic-diffusive braking of the transformation or even equilibrium of transforming phases are realized during hydride transformations. In this class of transformation the diffusive–cooperative nature of hydrogen-material systems appears in the most pronounced way. A synthesis of the knowledge of hydride transformations is given in Ref. [11]. The kinetics and morphology of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transformations for this class of hydride transformation can be found in Refs. [12–18].

3.2. Hydrogen treatment of materials based on hydride transformations

The phase transformations of this class serve as the basis of many kinds of HTM: strengthening of materials by hydrogen phase naklep, recrystallisation after the above treatment, technology of production of hydride TRIP alloys and of alloys with a hydride memory effect, technology of powdering and activating intermetallic storage and magnetic materials, etc. Examples of HTM based on hydride transformations are given below.

3.2.1. Hydrogen treatment of metals based on the HPN phenomenon

The hydrogen phase naklep phenomenon (HPN phenomenon) is a result of the influence of hydrogen and diffusive–cooperative (hydride) phase transformations which cause the controllable process of internal plastic deformation (relaxation) and controllable strengthening of metals. Here, some basic changes in the structure and properties of the metal also occur.

Unlike the internal cold work occurring during the martensitic transformation in steel and iron alloys, the HPN phenomenon is caused not only by the internal plastic deformation taking place due to differences in the specific volumes of the transferred phases, but also by the development of processes of the interaction of solute hydrogen, generating hydrogen-containing stable and metastable phases and generating defects in the crystal lattice. Hydrogen stresses and mechanisms of their interaction play a critically important role in the HPN phenomenon.

Two examples of treatment with HPN are given here. The mechanical properties of palladium specimens (wire of diameter 0.5 mm) in an annealed state and after HPN treatment are summarized in Fig. 1 [3]. Hydrogen phase naklep was achieved by direct and reverse $\alpha \rightarrow \beta \rightarrow \alpha$ hydride transformations, taking place during thermocycling in hydrogen ($20° \rightarrow 250° \rightarrow 20°C$). In the last stage of treatment the specimens were fully degassed. It can be seen (Fig. 1) that during the HPN treatment we have strong and controllable strengthening of palladium: the strength properties increase about three times and the plastic properties decrease accordingly.

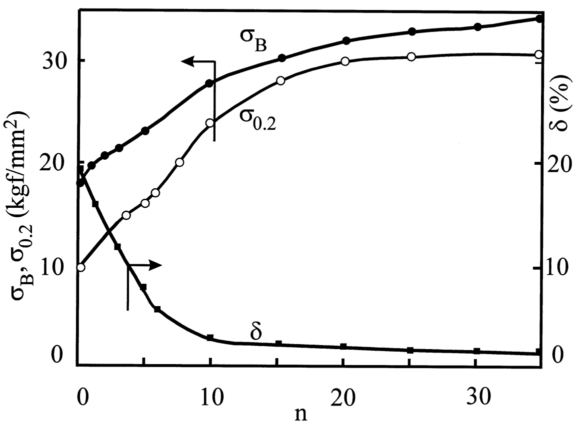

Fig. 1. Effect of strengthening of annealed palladium induced by hydrogen treatment based on the HPN phenomenon [3].

So, as shown in Fig. 1, hydrogen treatment allows us to controllably and greatly strengthen a metal *having no polymorphism without changing its dimensions and shape*. Without using HTM this aim cannot be achieved.

HPN treatment without complete degassing results in the formation of superstrength hydrogen–metal alloys having high plasticity (hydride TRIP effect). Here, the most wonderful result given in Fig. 2 [11] was achieved by a double treatment. First, 90% plastic deformation of a palladium wire was induced until a finished diameter of 0.5 mm was achieved. The palladium had very high strength properties (points a and b, Fig. 2) and very low plastic properties (point c, Fig. 2). The specimens were then HPN-treated. Hydride $\alpha \rightarrow \beta \rightarrow \alpha$ transformations were achieved by a number (n) of barocycles (0.2 MPa→1.33 Pa→0.2 MPa) in hydrogen at 100°C. The specimens were not degassed at all and we obtained a new hydrogen–palladium material. One can see (Fig. 2) the wonderful result. This new hydrogen-containing material ($n = 1$–2) is many times stronger and, concurrently, more plastic than pure, annealed palladium. The nature of HPN-strengthened metals having hydride TRIP plasticity is discussed in Ref. [11], where a review and detailed analysis of the hydrogen treatment of metals and metallic materials based on hydrogen phase naklep is presented. Strengthening and structure changes of niobium during HPN treatment are given in Refs. [19,20].

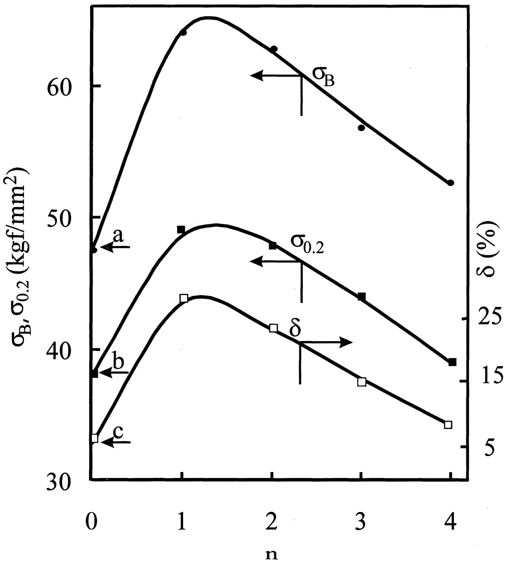

Fig. 2. Strengthening and TRIP effect of PdH alloys produced by HPN treatment of hardly cold worked palladium [11].

So, in metals and metallic materials having a larger plasticity resource under hydrogen action and hydride transformations, the HPN phenomenon is observed. The mechanism of this phenomenon ensures a permanent, partial relaxation of internal hydrogen stresses by internal plastic deformation and generation of dislocations. As a result, HPN shows itself in the strengthening of the material and the changing of its structure and properties. Materials actively reacting with hydrogen, forming hydrides but not having a high plasticity resource, act in another way. For example, it has been known for a long time that many intermetallics destruct when interacting with hydrogen. Such destruction is associated with the fact that a parameter of the crystal lattice (the specific volume) of hydrides is much larger than that of the initial intermetallics. Internal stresses, produced during hydrogen saturation and diffusive–cooperative (hydride) transformations, have no possibility of relaxing by hydrogen phase naklep. Therefore, they achieve ultimate strength and destroy the material. Up to the first half of the 1980s the destruction of intermetallics was considered to be a noncontrollable process.

3.2.2. Controllable powdering intermetallics

In Ref. [21], $LaNi_5$ alloys were used to illustrate that intermetallics — materials brittle in nature — can be *controllably* treated with hydrogen. As a result of this treatment powders of these materials may be obtained with a previously determined average particle size and the required dispersivity arrangement.

So, particles of $LaNi_5$ of roughly the same initial size were placed in the reaction chamber of a special device and activated by heating and cooling in vacuum (20°→300°→20°C). Hydrogen was then introduced into the reaction chamber at 20°C at a specific rate and up to a specific pressure. After reaching a specific hydrogen pressure, the $LaNi_5$ samples were held at this pressure for different periods of time. The samples were then heated from 20 to 300°C, the hydrogen was removed and the samples cooled. This constituted one hydrogen treatment cycle. The number of treatment cycles was also varied. Characteristic results of the experiments are summarized in Fig. 3, where one can see that the average size of the particles and the dispersivity of the powders, obtained after hydrogen treatment of $LaNi_5$, can be controlled entirely and on a large scale. The main parameters of HTM to obtain intermetallic powders with a designed dispersivity

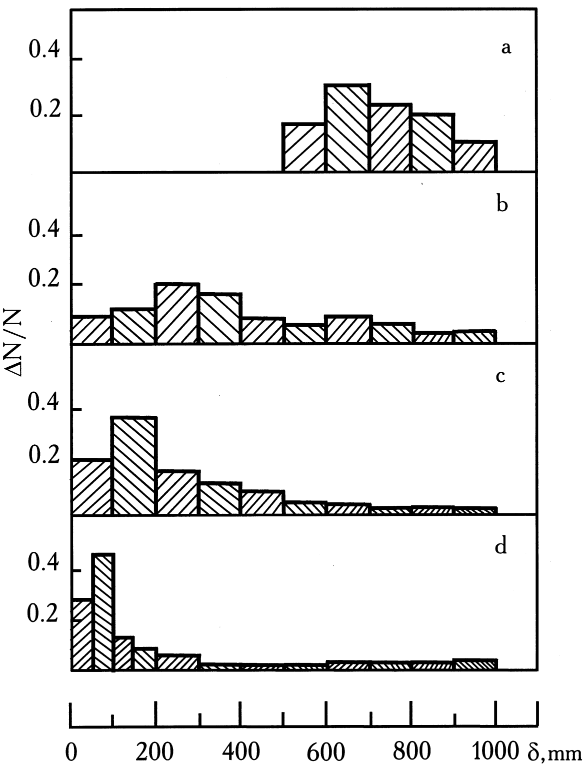

Fig. 3. Powdering of LaNi$_5$ particles and changes in their distribution by linear size (δ) as a function of the rapidity (ν) of hydrogen pressure increase: $\Delta N/N$, proportion of particles having sizes inside the region ($\Delta\delta$) near the δ of interest. (a) Initial distribution; (b) $\nu = 1.1 \times 10^{-3}$; (c) $\nu = 2 \times 10^{-2}$; (d) $\nu = 1.0$ MPa c^{-1} [21].

are: rapidity of hydrogen feed, hydrogen pressure, duration of action and number of treatment cycles.

A cracking and partial powdering process based on diffusive–cooperative (hydride) transformations is now widely used in permanent magnet manufacture. This process is called hydrogen decrepitation (HD process). The main technical advantages of the HD process are summarized in Ref. [22].

3.3. Hydrogen-induced diffusive phase transformations

Transformations of this class take place because of the different affinity of hydrogen for individual atoms — components of a material. For example, a material may consist of strong hydride-forming and non-hydride-forming elements. Such a material being saturated with hydrogen loses its thermodynamic stability and transforms into the nonequilibrium state. At low temperatures this hydrogen-containing material exists in a frozen, nonequilibrium or metastable state. At elevated temperatures ($T > (0.2–0.45)T_m$), when the diffusion of large atoms of the material becomes possible, the diffusion phase transformation takes place.

Many such metallic and intermetallic materials are now known, but the nature of the hydrogen-induced diffusive phase transformations of this class, their mechanisms, kinetics and morphology have not been investigated in detail. Let us look at the typical hydrogen-induced diffusive phase transformations in Nd–Fe–B-type alloys, which, being hard magnetic materials, have been studied much more than others because of their industrial importance.

In Ref. [23] the phase diagram of the hydrogen–Nd$_2$Fe$_{14}$B system was proposed (Fig. 4). One can see temperature–hydrogen pressure fields where Nd$_2$Fe$_{14}$B alloy is thermodynamically stable or unstable. So, Nd$_2$Fe$_{14}$B alloy, being in a hydrogen atmosphere, first undergoes a hydride phase transformation and transforms into a hydride phase state (Nd$_2$Fe$_{14}$BH$_x$); then Nd$_2$Fe$_{14}$BH$_x$ alloy, heated in accordance with pointer 1→2 in Fig. 4, will undergo a direct phase transformation in conformity with the scheme: $Nd_2Fe_{14}BH_x + H_2 \rightarrow NdH_{\sim 2} + Fe_2B + \alpha\text{-}Fe$. The multi-phase alloy may undergo a reverse phase transformation and transform into its initial Nd$_2$Fe$_{14}$B mono-phase state (see pointers 2→3 and 3→4 in Fig. 4).

The kinetics of the hydrogen-induced phase transformation in Nd$_2$Fe$_{14}$B-type industrial alloy was studied in Ref. [24]. The experimental procedure was as follows. The alloy was homogenized at 1120°C for 20 h in an argon atmosphere and was then crushed into particles of sizes from 50 to 630 μm. The samples (1.46 g) were placed in the reaction chamber of the special equipment at room temperature. The samples were then heated to a temperature within 750–600°C in vacuum (10^{-2} Torr). The reaction chamber was then filled with hydrogen ($P_{H_2} = 0.1$ MPa). From this time the formation and growth of ferromagnetic phases (α-Fe and Fe$_2$B) were measured continuously by the magnetic method. All experimental results were obtained under strict isothermal conditions.

Fig. 5 shows isothermal kinetic curves for the phase transformation under investigation. One can see that, at

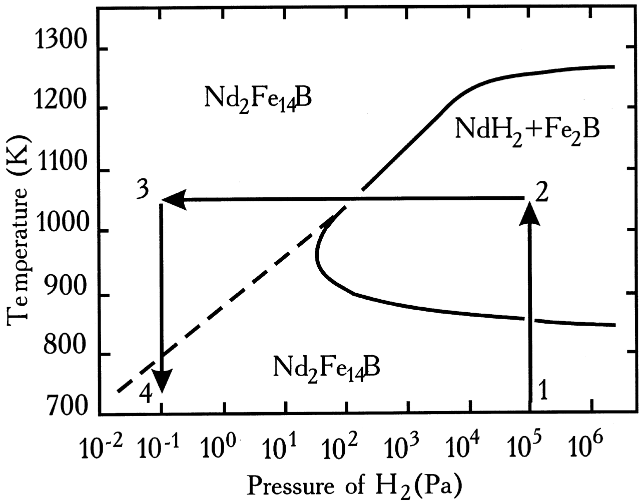

Fig. 4. Phase diagram of the hydrogen–Nd$_2$Fe$_{14}$B system (after Ref. [23]).

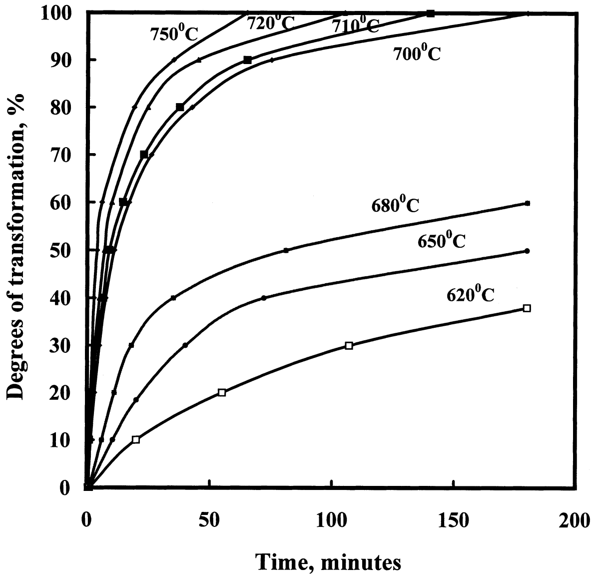

Fig. 5. Kinetic curves of the hydrogen-induced diffusive phase transformation in Nd–Fe–B-type alloy at hydrogen pressure $P = 0.1$ MPa and different constant temperatures [24].

750, 720, 710 and 700°C, phase transformations were fully completed in 65, 105, 140 and 180 min, respectively. At 680, 650 and 620°C, the phase transformation was not completed in 3 h and reached 60, 50 and 38%, respectively. At all temperatures there was a transformation incubation period (30–90 s).

Analysis of the mechanism of the transformation was carried out using the Avrami theory, according to which the phase transformation can be described by:

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

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

The results were plotted in coordinates: $\ln \ln[1/(1 - k)] - \ln t$. The curves were parallel straight lines, the slope of which gave $n = 1.06$. By the Avrami theory, if $n = 1$–1.5, the transformation has a nucleation and growth mechanism with diffusion-controlled growth of particles of new phases. This result is very important and it confirms that hydrogen-induced phase transformations at elevated temperatures ($T > (0.2$–$0.45)T_m$) have a classical mechanism of nucleation and growth and are controlled by long-range diffusion of material atoms. Therefore, they may be classified as hydrogen-induced *diffusive* phase transformations.

It is known that phase transformations of nucleation and growth, which have been well investigated for steels, have two types of isothermal kinetic diagram. When lowering the temperature and increasing the supercooling from the critical point the rapidity of nucleation of new phases first dominates and then diffusion control begins to dominate. In this case the transformation diagrams are C-shaped. The other types of transformation (for example, the ferrite→austenite transformation in steels during heating) have different kinetic diagrams. In this case both factors act along and with increasing temperature the phase transformation accelerates only.

An isothermal kinetic diagram of a hydrogen-induced phase transformation in $Nd_2Fe_{14}B$-type alloy is shown in Fig. 6. It is clear that this class of phase transformation has a kinetic isothermal diagram of the second type. This is an important fact. High growth in the rapidity of a phase transformation (about two order of magnitude in the temperature range from 620 to 750°C, 130°C only!) cannot be attributed to increasing growth of the diffusion coefficients only (even in view of the fact that hydrogen accelerates the diffusive processes in a condensed matter). This means that the rapidity of the generation of centers of new phases (NdH_2, α-Fe, Fe_2B) also greatly increases. The same laws as above were established for the reverse hydrogen-induced diffusive phase transformations in the $Nd_2Fe_{14}B$-type industrial alloy–hydrogen system and in other systems.

The morphological peculiarities of direct and reverse hydrogen-induced diffusive phase transformations in Sm_2Fe_{17} alloy were investigated by transmission electron microscopy in Ref. [25]. After a direct phase transformation at 600°C in hydrogen atmosphere, spherical or rod-like SmH_2 phases several nanometers in diameter were observed in the α-Fe matrix phase. The spherical SmH_2 particles of 20–100 nm diameter in the α-phase were the result of a direct transformation at 775°C. A further increment of temperature accelerateed the growth of SmH_2 precipitates in the α-Fe matrix. These were 50–100 nm at 850°C for 4 h in hydrogen. It is very important from a

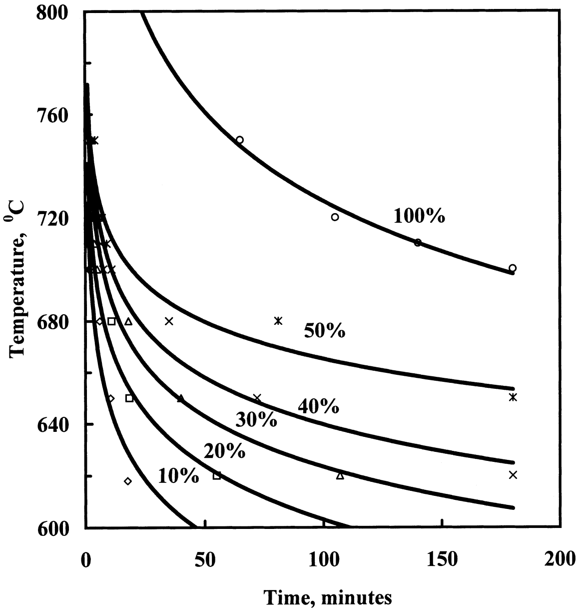

Fig. 6. Isothermal kinetic diagram of a hydrogen-induced diffusive phase transformation in Nd–Fe–B-type alloy [24].

Materials Science point of view that the two new phases are faced along each closed packed plane [25]:

α-Fe$\{110\}\|$Sm$H_2\{111\}$

α-Fe$\{111\}\|$Sm$H_2\langle 110\rangle$

The reverse phase transformation was induced by desorbing hydrogen in vacuum at 775°C. When the alloys undergo vacuum heat treatment, hydrogen atoms start to diffuse from SmH_2 particles and iron atoms, in contrast, diffuse into the SmH_2 phase. Within a very short time of vacuum treatment (775°C, 9 min) the alloy consists of the $Sm_{2-\delta}Fe$ phase and the α-Fe phase. Complete reverse transformation gave the initial Sm_2Fe_{17} alloy, but with improved very fine grains (150–300 nm) and high coercivity.

This thorough investigation [25] leads to a very important understanding of the peculiarities of the direct and reverse diffusive phase transformations and their role in the process of improving the structure and magnetic properties of hard magnetic materials. The mechanism of the direct transformations in Sm_2Fe_{17} alloy is that of nucleation and growth. But according to Ref. [25] there is no nucleation of the Sm_2Fe_{17} phase during a reverse phase transformation. Precipitates of the SmH_2 phase are first transformed by hydrogen and iron atom diffusion into $Sm_{2+\delta}Fe_{17}$, and then these growing particles are transformed into homogenized $SmFe_{17}$ alloy by diffusion. Therefore, the grain structure of hydrogen–vacuum-treated Sm_2Fe_{17} alloy greatly depends on both the direct and reverse phase transformations.

3.4. HTM based on diffusive phase transformations

The typical practical use of hydrogen-induced diffusive phase transformations is the so-called HDDR process, permitting improvement of the structure and properties of hard magnet materials of $Nd_2Fe_{14}B_x$ and $Sm_2Fe_{17}N_x$ types and others.

A review of the HD and HDDR processes in the production of Nd–Fe–B permanent magnets is given in Refs. [22,23]. Fig. 7 [22] shows a scheme of a standard HDDR processing procedure. HDDR is an abbreviation of the stages of the process: hydrogenation, disproportionation, desorption and recombination [22,23].

Magnet industrial alloys of the Nd–Fe–B type have such a chemical composition that they consist of two phases: a $Nd_2Fe_{14}B$ basic phase and a Nd-rich phase. Therefore, in a hydrogen atmosphere (Fig. 7) the alloy absorbs hydrogen in two stages. First, the hydrogen reacts with the Nd-rich phase at close to room temperature. Then, at around 160°C, the $Nd_2Fe_{14}B$ matrix phase absorbs hydrogen. As stated above these are hydride transformations and they lead to cracking and partially powdered material. This stage of the process (Fig. 7), called decrepitation, takes place at low temperatures and is already very widely used in industry [22].

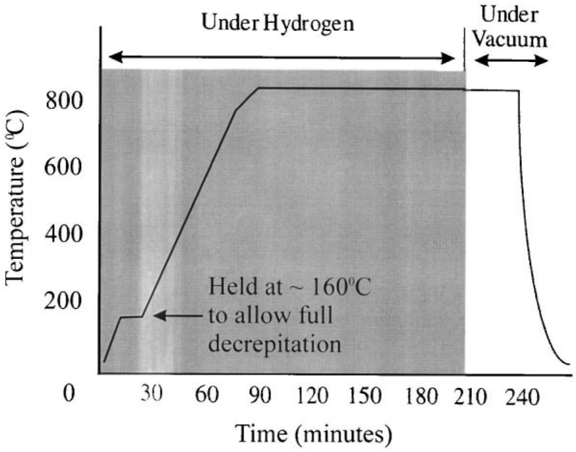

Fig. 7. Schematic diagram of a standard HDDR procedure (after Ref. [22]).

At elevated temperatures (Fig. 7) the HDDR process takes place. At $T > 600$°C, Nd–Fe–B alloy continues to absorb additional amounts of hydrogen from the hydrogen atmosphere (‘‘hydrogenation’’ stage). Then, the $Nd_2Fe_{14}B$ phase of the alloy undergoes the direct diffusive phase transformation discussed above (this stage of the process is called ‘‘disproportionation’’). The next step of the process is fulfilled under vacuum at elevated temperatures. Hydrogen desorbs from the alloy (‘‘desorption’’ stage). The alloy undergoes reverse diffusive phase transformations (this stage of the process is called ‘‘recombination’’).

On completion of the recombination stage the usual procedure is to cool the material rapidly whilst still under vacuum (Fig. 7). Rapid cooling prevents excessive grain coarsening, which can occur readily amongst sub-micron grains. Following the HDDR procedure, the material emerges as a coarse, magnetically coercive powder, which may be crushed readily into a fine powder suitable for bonding [22].

The influence of technological parameters of the hydrogen–vacuum HDDR treatment on the demagnetisation loops and the coercivity of Nd16–Fe7–B8 alloy was described in Ref. [22]. In the same work all critical factors in the HDDR process were analysed.

3.5. Hydrogen-induced intermediate phase and structural transformations

The transformations of this class take place in materials at moderate temperature ($T \approx (0.2–0.45)T_m$). So, the intermediate phase and structure transformations have characteristic peculiarities similar to those of diffusive high temperature transformations and of diffusive–cooperative (hydride) low temperature transformations.

The thermodynamic necessities of the transformations of this class are of two kinds. First, the initial material is thermodynamically stable at moderate temperatures. But under the action of hydrogen it becomes thermodynamically unstable. Second, the initial material is thermodynamically unstable at moderate temperatures, but it is in the frozen state. Hydrogen greatly accelerates the diffusive processes in a condensed matter and makes the kinetic processes possible at moderate temperatures (from the old point of view, rather low for diffusion migration of matrix atoms). The latter is very important for understanding the main peculiarities of hydrogen-induced intermediate transformations. At intermediate temperatures structures with very small differences of free energy with very small atomic rearrangements may be realized by hydrogen action on materials.

So, at intermediate temperatures in hydrogen–material systems, such kinds of phases and structures may be realized, for which atomic scale rearrangement is needed, such as, for example, long- or short-distance atomic ordering, atomic segregation, amorphization, etc.

There is no doubt that hydrogen internal stresses, their generation and relaxation play a great role in intermediate transformations, the same as they play in diffusive–cooperative (hydride) transformations. Plastic metallic materials undergo hydrogen phase naklep during intermediate transformations at temperatures lower than the onset of recrystallization. Brittle intermetallic materials will undergo cracking and powdering, etc.

Let us look at some hydrogen-induced intermediate phase and structural transformations.

Hydrogen-induced atomic ordering and hydrogen-induced atomic segregation phenomena were discovered by the Ponyatovsky group for some palladium alloys in the early 1980s.

It was shown [26] that, for $Pd_{0.6}Cu_{0.4}$ alloy in the temperature range from 523 to 623 K at 2 GPa hydrogen pressure, the f.c.c. lattice distorted to a tetragonal lattice. At the same time the alloy was partly ordered. After complete removal of the hydrogen in vacuo at 573 K, the alloy was still ordered but, after annealing at 623 K, disordering took place and the alloy lattice rearranged to a f.c.c. structure. In Ref. [27], a hydrogen-induced ordering transformation was found in $Pd_{0.5}Ag_{0.5}$ alloy at 470 K under a hydrogen pressure of $P_{H_2} = 2.8$ GPa.

Recently, an initially disordered f.c.c. $Pd_{0.81}Au_{0.19}$ alloy was shown [28] to partially order under the influence of hydrogen heat treatment (HHT) at 473 K and a hydrogen pressure of 7.0 MPa. Superlattice reflections in the electron diffraction pattern confirmed that the long-range order resulted from the HHT. When the ordered alloy resulting from HHT was annealed in vacuo at the same temperature at which it was prepared, it returned to its initially disordered state. This means that the long-range ordered state is not thermodynamically stable in the bulk $Pd_{0.81}Au_{0.19}$ alloy. More information about hydrogen-induced ordering of alloys can be found in Ref. [28].

So, if dissolved hydrogen makes the interaction of different atoms stronger than the interaction of the same atoms there will be atomic ordering of the alloy of proper composition under the action of hydrogen. On the contrary, if dissolved hydrogen makes the interaction of the same atoms stronger, then there will be atomic segregation in such an alloy.

Hydrogen-induced segregation as a phenomenon was first reported in Ref. [29]. At 623 K and $P_{H_2} = 2$ GPa, $PdNi_x$ alloys ($x = 0.2$, 0.4, 0.6, 0.8) segregated into two phases which closely corresponded to nickel hydride and a palladium-rich nickel alloy hydride. The segregated alloys returned to their initial states after annealing in vacuo at above 673 K. $PdPt_x$ alloys (from $x = 0.15$ to $x = 0.60$) were found [30] to segregate into palladium-rich and palladium-poor phases at $P_{H_2} = 2$–6.5 GPa and at $T \geq 523$ K.

Hydrogen-induced segregation in palladium-rich Pd–Pt, Pd–Ni and Pd–Rh alloys and its influence on hydrogen absorption was studied by Flanagan et al. (review given in Ref. [28]). It is shown that $Pd_{0.9}Pt_{0.1}$, $Pd_{0.85}Ni_{0.15}$ and $Pd_{0.8}Rh_{0.2}$ segregated at moderate temperatures into palladium- and second metal-rich regions. Usually, after segregation the hydrogen plateau pressures are greatly reduced and the hysteresis may have changed. Most significantly, the hydrogen capacity of the alloys decreases. Therefore, ‘‘diagnostic’’ hydrogen isotherms at low temperatures measured before and after HHT were the principal means employed in these works to determine whether lattice changes had occurred in the alloys [28].

Therefore, these authors [28] used the measurement of hydrogen solubility as a method to study structural changes in metallic materials. It should be noted that, for the same purpose, hydrogen penetration was used in the 1960s and 1970s to study atomic ordering and other structural changes in Fe-rich, Ni-rich and Pd-rich alloys [31,32]. Such methods of investigation of materials are possible because of the very high sensitivity of the hydrogen atom to the rearrangement of the metal atoms around it.

It is interesting that, in the case of Pd–Pt and Pd–Ni alloys, both thermodynamic and kinetic actions of hydrogen take place. In the Pd–Rh system [28] there is a miscibility gap below 845°C, but these quenched homogeneous f.c.c. alloys are metastable, frozen up to relatively high temperatures for long periods of time (at 600°C for 1 year). Therefore, in these alloys hydrogen acts mostly like *a kinetic factor* strongly fastening the ‘‘native’’ required segregation.

The scale of the fastening is so great that it was hardly imaginable before reported in Ref. [33]. Under hydrogenation in 5 GPa of fluid hydrogen [33], $Pd_{0.8}Rh_{0.2}$ alloy was segregated into Pd-rich hydride and Rh-rich metal at about 500°C *during only a few minutes*. Precipitates of the second phase were found to be distributed at an average distance of approximately 0.1 μm. According to Ref. [33] the observed acceleration of diffusivity was four to five orders of magnitude.

Hydrogen-induced amorphization (HIA), as a physical phenomenon, was discovered by Yeh et al. in 1983 [34]. They, using the action of hydrogen at 180°C, transformed the crystal Zr_3Rh alloy into its amorphous state. From the very beginning it was absolutely clear that this phenomenon is very important both for a fundamental understanding of the interaction of hydrogen with condensed matter and for future novel kinds of hydrogen treatment of materials. The HIA phenomenon attracted the attention of many scientists and scientific groups.

Below, in brief, we concentrate on only those peculiarities of the HIA phenomenon which are important from the viewpoint of the hydrogen treatment of materials.

The common conditions of HIA taking place *in solid state* materials were formulated in the middle of the 1980s [11]:

1. Initial $A_nB_m(A_{n-x}C_xB_{m-y}D_y)$-type intermetallic alloys must consist of atoms with a large difference in their affinity for hydrogen. Atom A must be a hard hydride-forming element (Zr, Ti, etc.) and B must be a non-hydride forming element (Fe, Co, Ni, Rh, Al, Ga, etc.).
2. This intermetallic alloy in an homogenized crystal state should be able to absorb hydrogen at low to moderate temperatures and *form a hydride which is less stable than the hydride of element A.*
3. Such a $A_nB_mH_x$ hydride alloy is thermodynamically unstable. At elevated temperatures, when enhancement of diffusivity takes place, the $A_nB_mH_x$ hydride alloy will undergo a diffusive phase transformation and will be transformed from the mono-phase state to a poly-phase state. Usually, one of these phases is the hydride of element A or a phase based on it. The other phase without hydrogen or with a low hydrogen content is based on the crystal phase of element B. As mentioned above the hydrogen-induced diffusive phase transformation needs the long-range diffusion of metal atoms. Therefore, *for kinetic reasons they cannot be fulfilled at low and moderate temperatures*.
4. Under the above conditions there must exist some moderate or low to moderate temperature interval where short (atomic)-range diffusion only is possible. At this moderate temperature under the same thermodynamic driving force, short-range diffusive rearrangements of the structure might be realized and unstable (but frozen) or metastable structural states will be formed. Therefore, *HIA is one of those intermediate transformations leading to the formation of an amorphous structure*.

Since the publication of Ref. [34] many investigations have been conducted (see, for example, Refs. [35,36]) and the understanding of HIA is now much deeper. Already, more than 70 intermetallics have been amorphized by HIA treatment [35]. They are intermetallics of the following types: A_3B with $L1_2$ (f.c.c.) crystal structure (Zr_3Rh, etc.) and with $D0_{19}$ crystal structure (Ti_3Ga, etc.); A_2B with C_{23} crystal structure (Y_2Al, etc.) and with $B8_2$ crystal structure (Zr_3Al, etc.); AB_2 with C15 crystal structure ($CeFe_2$, etc.).

A very important investigation of HIA and its analysis was reported in Refs. [35,36]. Not all compounds with the crystal structures mentioned above amorphize on hydrogenation. For example, the C15 Laves phase RM_2 (R: rare earth metal; M: Fe, Co, Ni) amorphizes on hydrogenation around 400–500 K. On the contrary, ZrV_2, $ZrMo_2$ and others absorb hydrogen, retaining the crystalline state. The authors of Refs. [35,36] concluded that HIA is controlled not only by the crystal structure but also by other factors. In Ref. [35] a large group of C15 Laves phases amorphizing by hydrogenation was analyzed. The atomic size ratio is the decisive factor controlling the occurrence of HIA in C15 Laves phases, and those with a ratio >1.37 amorphize by hydrogenation. The stability of the initial C15 Laves phase is another important factor in HIA. The authors of Ref. [35] concluded that the structure of the amorphous alloys prepared by hydrogenation of stable $GdNi_2$ is homogeneous rather than that prepared from the less stable ones (for example, $GdFe_2$ or $GdCo_2$).

On the other hand, amorphous alloys of this kind transform into a crystalline structure forming different phases: GdH_2 and $GdNi_5$ in the case of $GdNi_2$ amorphous alloy; GdH_2 and Fe, GdH_2 and Co in the case of $GdFe_2$ and $GdCo_2$, respectively.

HIA is an exothermic process which means that the amorphous structure being, in principal, unstable is at the same time more stable than the hydride of the initial alloy. The nature of the thermodynamic driving force for HIA in C15 Laves compounds is considered [35] to be the enthalpy difference resulting from the different occupation sites in the two states of the alloys.

From the viewpoint of this review a very important result of the analysis of Ref. [35] is that T_h/T_m, T_a/T_m and T_x/T_m for many C15 Laves phases are constant with values 0.28, 0.4 and 0.5, respectively (Fig. 8). Here, T_h, T_a and T_x are the temperatures of hydrogen absorption (h), amorphization (a) and crystallization (x). Of course, it is necessary to mention that T_h/T_m, T_a/T_m and T_x/T_m are not the exact constant values, but have approximate values around 0.28, 0.4 and 0.5, respectively.

One can see from Fig. 8 that $T_a/T_m \approx 0.4$ is inside the moderate temperature interval ($0.2T_m < T < 0.45T_m$), where the hydrogen-induced intermediate phase and structural rearrangements take place. This confirms once more that hydrogen-induced amorphization in diffusional and kinetic aspects is a transformation of the same kind as hydrogen-induced ordering and segregation.

All these transformations are of great interest for the hydrogen treatment of materials as a new field of Materials Science and Engineering. They permit us to transform the structure and properties of materials in previously unpredictable ways: to order initially non-ordered metals and alloys, to produce metallic alloys with a segregated atomic

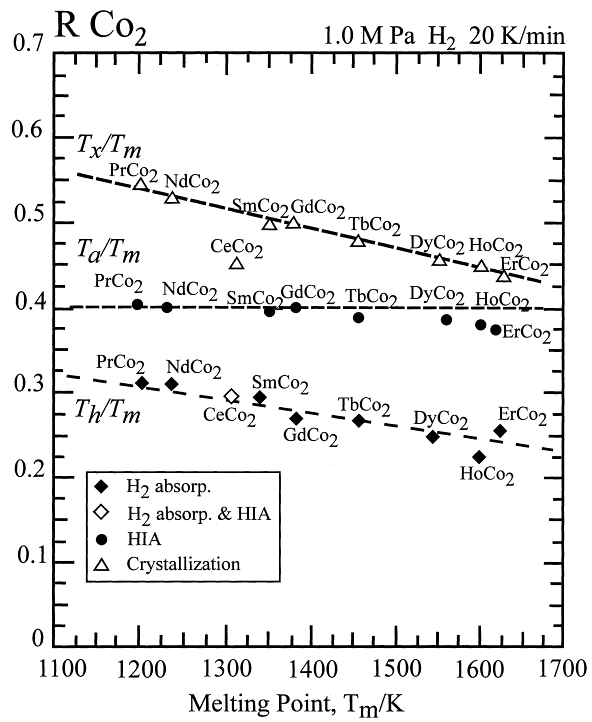

Fig. 8. The ratio T_t/T_m vs. T_m for RCo_2 compounds (after Ref. [35]).

structure, to transfer intermetallic alloys from the crystalline to the amorphous state.

Usually in HTM it is possible either to evacuate the hydrogen from the treated materials or to leave it there: the properties after such treatment may be very different and unpredictable, as shown in the case of treatment using hydride transformations [3,11].

Finally, it is well known [3] that, for new phenomena, for new kinds of treatments, novel uses for them needed by industry need to be developed. This task is now very important for the future development of hydrogen treatment based on a hydrogen-induced intermediate phase and structure transformations.

3.6. Control by hydrogen phase transformations and their use in engineering

Transformations of this class take place in metals such as Ti and Zr and in alloys based on such metals. The above-discussed phase and structural transformations of different classes might also take place in these materials. But these materials (without hydrogen and by their nature) are polymorphic, and there are ‘‘nature’’ phase transformations such as, for example, β→α→β transformations in titanium. Titanium, titanium alloys and the principles of their alloying, phase transformations, structure and properties constitute the large and very important field of Materials Science and Engineering [1,37,38].

Titanium is a polymorphic metal with critical point $T_c = 882.5$°C. At $T > T_c$, the high-temperature β-phase is stable, at $T < T_c$ the low-temperature α-phase is stable. Therefore, upon slow cooling and heating around T_c there are diffusive β→α and α→β phase transformations. Some alloying elements (Al, etc.) make the α-Ti-phase more stable. Others (V, etc.) make the β-Ti-phase more stable. The third group of alloying elements (Zr, etc.) does not affect the difference in stability of the α- and β-phases much. Therefore, titanium industrial alloys have to be divided into groups on the basis of their phase structure at room temperature: α-type alloys (Ti–5Al, Ti–5Al–25Sn), pseudo-α-type alloys (Ti–7Al–0.8Mo–1.0Nb–3.7Zr–2.8Sn–0.15Si), (α + β)-type alloys (Ti–6.0Al–4.0V), β-type alloys (Ti–10Cr–8Mo–3Al).

In titanium alloys, instead of a critical point T_c there is a critical interval of temperatures where the α- and β-phases coexist. Usually, in poly-component titanium alloys this interval is below T_c and there may not be only α- and β-phases but other phases also (see Refs. [1,38]). If titanium alloys are quenched there are some types of martensite transformations. At moderate temperatures, phase and structural rearrangements of many kinds take place. So, polymorphism of titanium and poly-component alloying lead to the possibility of obtaining many industrial alloys with a very wide spectrum of structure and properties, which may be improved by heat treatment, plastic deformation, etc. This has helped to solve many problems in the space, aircraft, chemical and other industries.

Reversible hydrogen action on titanium alloys (temporary alloying) provides the possibility of improving the existing technologies and of creating many novel ones for treating titanium alloys and for producing industrial constructions [37,38]. Let us summarize hydrogen actions on titanium alloys. Hydrogen as an alloying element makes the β-phase more stable and its solubility is much higher in the β-phase than in the α-phase. The region of α- and β-phase coexistence under the influence of hydrogen phases changes and moves to lower temperatures. So, the alloy may even change its structural class and transform from an α-alloy to an (α + β)-alloy, or from an (α + β)-alloy to a β-alloy. So, dissolved hydrogen changes the thermodynamic and kinetic conditions of all the transformations in titanium alloys (diffusive, martensite, etc.). The mechanism and morphology of these transformations also changes under hydrogen action.

At elevated and moderate temperatures hydrogen leads to the redistribution of the alloying elements between the α-, β- and other phases for the same thermodynamic reasons as discussed above for hydrogen-induced diffusive and intermediate transformations in material–hydrogen systems.

For example, in Ti–7Al–0.8Mo–1.0Nb–3.7Zr–2.8Sn–0.15Si alloy at 650°C there is a redistribution of aluminum, and its content in the α-phase becomes higher (7.2→9.3%) when the hydrogen content is 0.4% (by weight). Because of this, and by the direct influence of hydrogen, the α-phase becomes an ordering phase and transforms into its ordered state. There will now be two kinds of α-phase in the alloy: an ordered α_2-phase and a disordered α_1-phase transformed from the β-phase and having the same chemical composition as the β-phase.

There is no great difference between the specific volumes of the α- and β-phases of titanium and its alloys. But the β-phase usually has a slightly smaller specific volume than the α-phase. Hydrogen influences the specific volume of the phases. It increases the specific volume of the β-phase and at some hydrogen content the specific volumes of the α- and β-phases will be the same and then the specific volume of the β-phase will be larger. So, there is the possibility of controlling the internal stresses and phase cold work during $\beta \rightarrow \alpha \rightarrow \beta$ transformations and of controlling the morphology and properties of the α- and β-phases.

Another situation is hydride (diffusive–cooperative) phase transformations in titanium alloys. The specific volume of the hydride phase is much greater (13–17%) than that of the α-phase. So, a large hydrogen phase naklep (cold work) may take place in titanium alloys and recrystallization treatment might then be fulfilled. With a combination of hydrogen and other actions it is possible in this way to obtain ultra-fine grain structures (about 1 μm). One can see such a structure in Fig. 9 [39]. The alloy with such a structure has an excellent superplastic elongation as large as 1000% at 850°C [39].

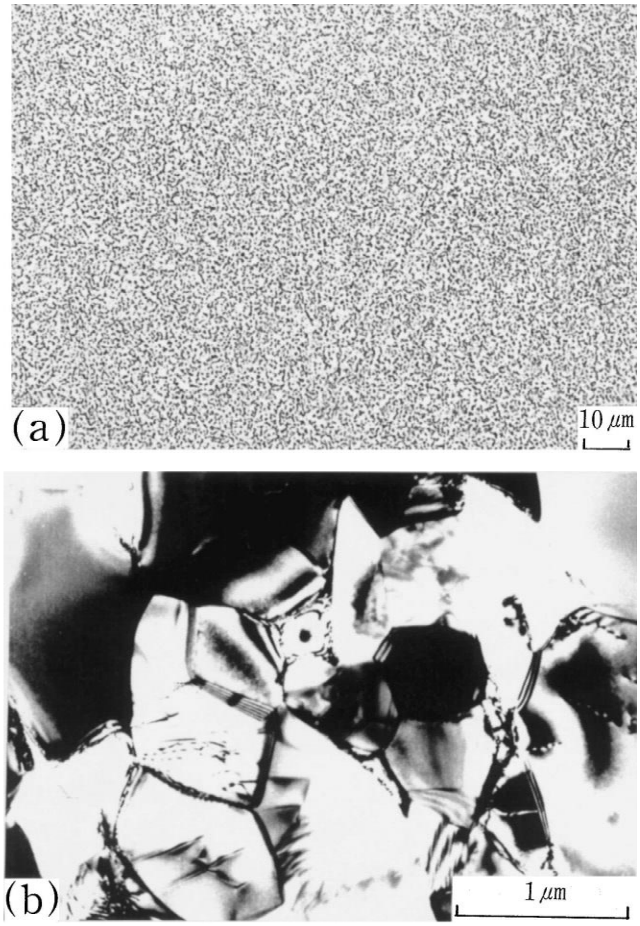

Fig. 9. Optical (a) and transmission electron micrographs (b) of Ti–6Al–4V alloy subjected to treatment: hydrogenation (0.2 mass% H), β-quenching, hot rolling by 60% at the α+β two-phase, and dehydrogenation (after Ref. [39]).

There are many ways of hydrogen heat treatment to produce titanium alloys with a fine structure and they are the most useful for casting technologies in which there is no plastic deformation stage of the treating materials [37,38].

So, one can see the evident situation that the hydrogen action on titanium alloys is a fundamental one, permitting the control of all phase and structural transformations, the control of technological and service properties, etc.

Hydrogen technologies for titanium alloys based on temporary alloying by hydrogen have three stages. First is saturation of the material to the required hydrogen content. The second includes heat treatment, plastic deformation or any other technological operation. The third is vacuum annealing to desorb hydrogen until the content is not dangerous for practical use. Reviews of hydrogen plastification, hydrogen heat treatment, and other hydrogen technologies for titanium alloys can be found in Refs. [37,38].

Thus, hydrogen treatment of materials as a novel field of Material Science and Engineering permits us to realize the goals of improving existing and creating new technologies, of improving material structure and properties and of obtaining new hydrogen-containing materials with unique properties.

4. Conclusion

Hydrogen treatment (processing) of materials (HTM) is based on the specific peculiarities of hydrogen, providing the possibility of a *strong and controllable* action on materials. This action is reversible in the sense that the hydrogen can be removed from the material at low temperatures. Hydrogen action on materials comprises physical, chemical, physico-chemical and mechanical components. From the point of view of HTM the most important factor is that hydrogen action causes a disturbance of the thermodynamic conditions of existence of a material and its separate phases. As a result there appears a thermodynamic necessity in hydrogen-induced phase transformations. This is the so-called ''artificial'' hydrogen-induced polymorphism. The thermodynamic conditions for the realization of the natural polymorphism of materials can also be changed by hydrogen. The kinetic factor of the hydrogen action on materials is of great importance. Being dissolved, hydrogen accelerates the diffusion processes of atoms — components of the material. All phase and structural transformations become much faster and under the action of hydrogen they might be attained at much lower temperatures than thought possible before such transformations controlled by large atoms' diffusion.

Hydrogen-induced phase and structural transformations are classified into three large classes: hydride (diffusive–cooperative) phase transformations, diffusive phase transformations and intermediate phase transformations. This classification is based on the atomic peculiarities of the transformation mechanism and the temperature intervals where they take place.

Hydride (diffusive–cooperative) phase transformations take place in hydrogen–material systems at low temperatures ($T < (0.2\text{–}0.45)T_m$). They have a diffusive–cooperative mechanism: all rearrangements in the hydrogen subsystem have a diffusive mechanism, and interconnected rearrangements of the material subsystem have a cooperative, shift mechanism. In hydrogen–metal systems this cooperative mechanism is very similar to the martensite one. Hydrogen treatment based on this class of transformation permits the preparation of stronger metals, the production of fine structure metallic materials, super strong materials with high TRIP plasticity, materials with a memory shape effect, the production of intermetallic material powder and makes the powdering easier (HD process, etc.).

Hydrogen-induced diffusive phase transformations take place at elevated temperatures ($T > (0.2\text{–}0.45)T_m$). They have a mechanism of nucleation and diffusion-controlled growth. There must be a long-range diffusion of atoms — components of a material. Processes based on transformations of this class permit the production of materials with a changed phase structure, with the finest grain and subgrain structure, etc. For example, this class of hydrogen-induced transformation is the basis of a very well known HDDR process permitting the production of high coercive magnetic materials of the Nd–Fe–B type.

Hydrogen-induced intermediate transformations take place at moderate temperatures ($0.2T_m < T < 0.45T_m$). Their mechanisms have some characteristic features of the mechanisms of elevated temperature diffusive transformations and low temperature hydride (diffusive–cooperative) transformations. The main peculiarity of this class of transformation is that only short-range (atomic scale) rearrangements of atoms — components of a material — take place. Dissolved hydrogen changes the interaction of atoms — components of a material. Thus, if under the action of hydrogen the interaction of different atomic species becomes stronger there might be an atomic ordering transformation. On the contrary, if the interaction of the same atoms becomes stronger there might be an atomic segregation transformation. Hydrogen-induced amorphization is a transformation of the same class, where material transforms into a metastable or unstable (frozen) amorphous state. The transformations of this class provide the possibility of improving the structure and properties of metallic and intermetallic materials.

Hydrogen-controlled phase transformations in polymorphic metals and alloys may be considered as a special very wide class of transformations. This class of transformations is rather well studied in titanium alloys. They are the basis of many hydrogen technologies permitting improvement of the structure and properties of many titanium alloys, the improvement of industrial technologies of production of deformed and cast in articles and constructions.

References

[1] U. Zwicker, Titan und Titanlegierungen, Springer, Berlin, 1974.
[2] Hydrogen in Metals, Proceedings of the 2nd International Congress, Paris, 1977.
[3] V.A. Goltsov, Mater. Sci. Eng. 42 (1981) 109.
[4] V.A. Goltsov, in: Our Days Problems of Improving of Metal Quality, Collection of Abstracts of the All-Union Science Conference, Donetsk, 1978, p. 189.
[5] V.A. Goltsov, in: Metal–Hydrogen Systems, Proceedings of an International Symposium, Miami, 1981, 1982, p. 211.
[6] Proceedings of selected papers of the 1st International Conference on Hydrogen Treatment of Materials, Donetsk, 1995, Int. J. Hydrogen Energy 22(2/3) (1997).
[7] V.A. Goltsov, Int. J. Hydrogen Energy 22 (1997) 115.
[8] V.A. Goltsov, Int. J. Hydrogen Energy 22 (1997) 119.
[9] Hydrogen Treatment of Materials, Proceedings of the 2nd International Conference, Ukraine, Collection of Abstracts, Donetsk, 1995, Part 1, 124 pp. Part 2, 83 pp.
[10] Hydrogen Treatment of Materials, Proceedings of the 2nd International Conference, Ukraine, Collection of Abstracts, Donetsk, 1998, 235 pp.
[11] V.A. Goltsov, in: Vzaimodeistvie Vodoroda s Metallami (Metal–Hydrogen Interactions), A.P. Zakharov (Ed.), Nauka, Moscow, 1987, p. 264, Chapt. 9.
[12] V.A. Goltsov, Yu.A. Artemenko, Fiz. Met. Metalloved. (2) (1991) 181.
[13] V.A. Goltsov, Yu.A. Artemenko, Fiz. Met. Metalloved. (10) (1991) 160.
[14] V.A. Goltsov, Yu.A. Artemenko, Phys. Met. Metallogr. 76 (1993) 77.
[15] V.A. Goltsov, Yu.A. Artemenko, Phys. Met. Metallogr. 78 (1994) 432.
[16] Yu.A. Artemenko, M.V. Goltsova, V.I. Zaitsev, Int. J. Hydrogen Energy 22 (1997) 343.
[17] M.V. Goltsova, Yu.A. Artemenko, V.I. Zaitsev, Phys. Met. Metallogr. 84 (1997) 418.
[18] J. Bloch, M.H. Mintz, J. Alloys Comp. 253/254 (1997) 529.
[19] V.A. Goltsov, V.M. Dekanenko, N.N. Vlasenko, Mater. Sci. Eng. A 129 (1990) 239.
[20] V.A. Goltsov, N.N. Vlasenko, Int. J. Hydrogen Energy 22 (1997) 151.
[21] V.A. Goltsov, A.F. Volkov, L.I. Smirnov, E.I. Grinchenko, in: Fizika Tverdogo Tela, Vysshaya Shkola, Kiev, 1986, p. 57.
[22] O.M. Ragg, G. Keegan, H. Nagel, I.R. Harris, Int. J. Hydrogen Energy 22 (1997) 333.
[23] T. Takeshita, J. Alloys Comp. 231 (1995) 51.
[24] V.A. Goltsov, A.F. Volkov, S.B. Rybalka, Int. J. Hydrogen Energy 24 (1999) 913.
[25] M. Okada, K. Saito, H. Nakamura, S. Sugimoto, M. Homma, J. Alloys Comp. 231 (1995) 60.
[26] V. Degtyareva, V. Antonov, I. Belash, E. Ponyatovskii, Phys. Status Solidi A 66 (1981) 77.

[27] A. Irodova, V. Glaskov, I. Kurchatov, V. Antonov, E. Ponyatovskii, Z. Phys. Chem. 163 (1989) 53.

[28] T.B. Flanagan, H. Noh, J. Alloys Comp. 231 (1995) 1.

[29] V. Antotnov, T. Antonova, I. Belash, E. Ponyatovslii, V. Rashupkin, V. Thiessen, Phys. Status Solidi A 77 (1983) 71.

[30] V. Antonov, T. Antonova, I. Belash, E. Ponyatovslii, V. Rashupkin, Phys. Status Solidi A 78 (1983) 137.

[31] V.A. Goltsov, G.E. Kagan, in: Hydrogen in Metals, Proceedings of the 1st International Congress, Paris, 1972, p. 249.

[32] V.A. Goltsov, in: The Problems of Atomic Science and Technique, Atomic Hydrogen Energy, Vol. 1(2), 1977, p. 65.

[33] Y. Fukai, J. Alloys Comp. 231 (1995) 35.

[34] X.L. Yeh, K. Samwer, W. Johnson, Appl. Phys. Lett. 42 (1983) 242.

[35] K. Aoki, T. Masumoto, J. Alloys Comp. 231 (1995) 20.

[36] K. Mori, K. Aoki, T. Masumoto, J. Alloys Comp. 231 (1995) 29.

[37] A.G. Bratukhin, B.A. Kolachev et al., Technology of Production of Titanium Aircraft Constructions, Mashinostroenie, Moscow, 1995, 448 pp.

[38] A.A. Ilyin, Mechanism and Kinetics of Phase and Structure Transformations in Titanium Alloys, Nauka, Moscow, 1994, 304 pp.

[39] H. Yoshimura, K. Kimura, M. Hayashi, M. Ishii, T. Hanamura, Jin-ichi Takamura, Mater. Trans., JIM 35 (1994) 266.