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Severe plastic deformation and hydrogenation of the titanium aluminides

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ABSTRACT

Severe plastic deformation (mechanical activation in a hydrogen atmosphere and shear under pressure) effects on the hydrogenation of two titanium aluminides Ti_3Al and TiAl-type alloy (B2) have been studied. It is shown that a conventional hydrogenation of the bulk samples allows forming the hydrides with high hydrogen content and high desorption temperature: TiAl (773 K, 1.76 mass%) and Ti_3Al (1043 K, 2.94 mass%). In comparison with the conventional hydrogenation, the mechanical activation in a hydrogen atmosphere at room temperature allows one to obtain the hydrides of the TiAl (B2) and Ti_3Al alloys with the reduced desorption temperature: TiAl (453 K, 1.96 mass%) and Ti_3Al (531 K, 2.6 mass%). The shear under pressure has been applied to the sample before hydrogenation also leads to a reduction of the desorption temperature; however, it produces the phase transformation in the Ti_3Al intermetallic compounds, which lowers the observed a maximum hydrogen content.

1. Introduction

Metal hydrides have a large range of applications, among which the hydrogen storage becomes more attractive today. The Ti–Al system is a potential hydrogen absorber because of hydride-forming lightweight components Ti and Al. Hydrogen absorption/desorption by titanium aluminides with the B2 (β_0-phase, TiAl) superstructure has been investigated in [1,2]. It was found that the β_0-cubic phase can absorb up to 2 mass% of hydrogen, and two hydrides (BCC-β and BCT-γ) can form in these aluminides [1]. Ti_3Al has a hexagonal crystal structure and can absorb up to 3.32 mass% of hydrogen. It can form the ordered FCC-, BCC-, and FCT-type hydrides [3–5]. However, the hydrogen desorption temperature of the titanium aluminides is too high to use for practical applications. For example, the desorption temperature of the Ti_3Al alloys is about 1073 K [4]. Reduction of the hydrogen desorption temperature is one of the most important problem to solve for the Ti–Al–H system. Severe plastic deformation can produce the nano-scale materials with unusual physical properties. Recently, the mechanical activation technique has been used to produce the metal hydrides with lowered desorption temperature [6,7]. Severe plastic deformation by the shear under pressure is another way to introduce dislocations into the materials and break grains. In this case we can obtain the nano-scale materials with unusual physical properties.

In the present work, the influence of severe plastic deformations on the hydrogenation processes is investigated for the Ti–Al alloys with the goal of reducing the hydrogen desorption temperature.

2. Experimental

A Ti_3Al alloy was prepared by arc-melting of high purity metals (99.5% Ti, 99.99% Al) in an argon atmosphere. The ingots were homogenized at 1400 °C for 5 h in a helium atmosphere.

An experimental alloy with the composition Ti–25.6 at.% Al–13.9 at.% Nb (Zr,Mo) was prepared by pack rolling. To obtain a single-phase state (β_0), the ingots were annealed in a vacuum at 1200 °C for 1 h and then quenched in icy water. The composition of the alloys was checked by the electron probe microanalysis (EPMA).

The setup for shear deformation under pressure consists of a KM-50-1 standard torsion-testing machine combined with a hydraulic press. The anvils are made of a tungsten carbide VK6 hard alloy. The experiments were performed at room temperature; the applied axial pressure was 10 GPa.

Hydrogenation of the samples was performed in a Sieverts-type apparatus using pure hydrogen obtained by a decomposition of the hydride $LaNi_5H_x$. Immediately before hydrogenation the sample surface was activated by heating in a vacuum at 500 °C. Hydrogen absorption kinetics was recorded by the pressure change in the known volume of the setup and, additionally, the maximum absorption was controlled by weighing the container with the sample before and after the hydrogen treatment. The uncertain in determination of the amount of absorbed hydrogen was ±0.02 mass%.

The mechanical activation in hydrogen atmosphere was performed with a vibration-type mill. As milling bodies, 12 brass or 6 steel balls of 16 mm in diameter were used. The mass ratio of the powder to the balls was equal to 1:179. The mechanical activation was carried out at room temperature; the initial hydrogen gas pressure was 775 mm Hg. The samples, which were preliminarily ground in the mortar, were placed into a cell with the brass (or steel) balls; the cell was evacuated and placed into a unit, which was connected with a tank containing commercial hydrogen. The amount of hydrogen absorbed by the powder during mechanical activation was determined from the drop of the hydrogen pressure in the constant volume experimental unit. The unit was calibrated using the reliably measured amount of hydrogen absorbed by the $ErFe_2H_x$ compound, for which the dependence of the lattice parameter on the hydrogen content was determined quite accurately.

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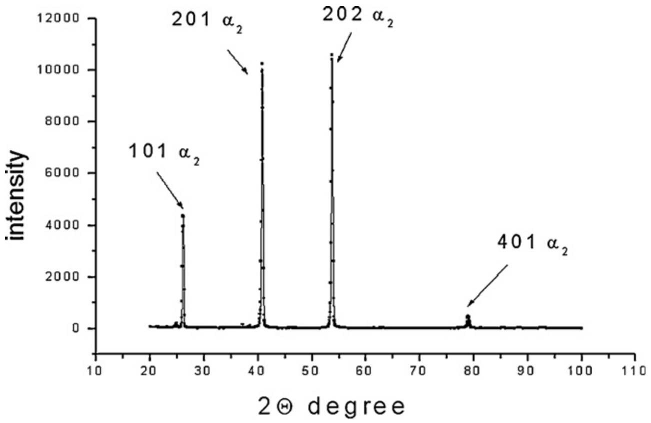

Fig. 1. The XRD pattern of the Ti_3Al alloy at the initial state.

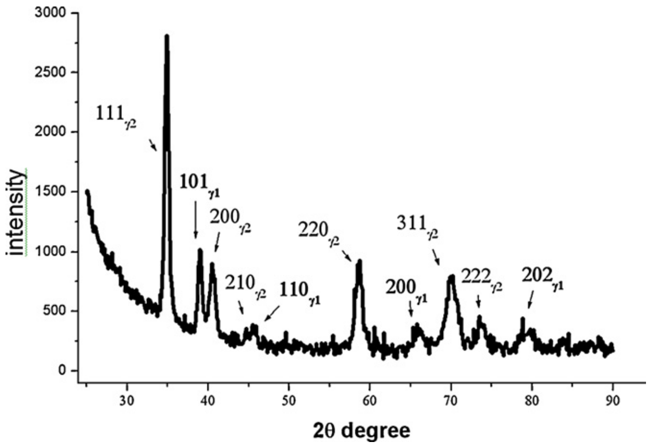

Fig. 2. The XRD pattern of the Ti_3Al alloy after the hydrogenation by the Sieverts-type apparatus.

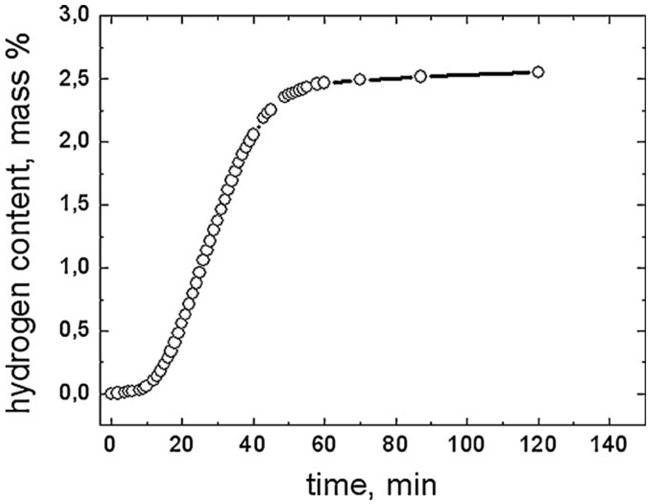

Fig. 3. Variation in hydrogen content in the Ti_3Al sample during the ball milling.

X-ray diffraction studies were carried out using a DRON-3 diffractometer and monochromatized Cu Kα radiations.

3. Results and discussions

3.1. Ti_3Al (hexagonal crystal lattice, $D0_{19}$ superstructure)

For this alloy we performed three different experiments: (1) conventional hydrogenation of the bulk sample in the Sieverts-type apparatus; (2) mechanical activation in a hydrogen atmosphere; (3) preliminary deformation by the shear under pressure followed by hydrogenation in the Sieverts-type apparatus.

The X-ray diffraction pattern of the initial alloy is presented in Fig. 1. It is seen that its structure consists of the single α_2-phase. However, the X-ray diffraction analysis showed that the intensities of the lines did not coincide with the theoretical intensities for the lines of the α_2-phase. Such effect can be explained by a large size of the grains in the initial intermetallic alloy (2–4 mm). It is known that for samples with large grains, it is necessary to choose the mode of operation of the diffractometer without rotation of the sample, and distortions of the lines' intensities can be observed in this case. The lattice parameters of the α_2-phase in the initial state were calculated from the X-ray diffraction data as $a = 0.580$ nm, $c = 0.4766$ nm.

At first we tried to obtain the hydrides of the bulk Ti_3Al samples by the hydrogenation in a Sieverts-type apparatus. We used the temperature 873 K and hydrogen pressure 1.6 MPa. Under these conditions, we prepared the hydride with 2.94 mass% of hydrogen after 5 h of the hydrogenation. The XRD pattern of the hydrogenated alloy is presented in Fig. 2. The diffraction pattern showed the structure composed of the tetragonal γ_1 and cubic γ_2 hydrides. Similar structures of hydrides were found in [4,5]. The lattice parameter of the γ_2 hydride was found to be $a = 0.446$ nm, and the lattice parameters of the γ_1 hydride were calculated as $a = 0.282$ nm, $c = 0.444$ nm. The evacuation of hydrogen from the sample can be completed at 1043 K.

Much faster hydrogen absorption by the Ti_3Al alloy is observed during its ball milling in a hydrogen atmosphere. Fig. 3 shows the room-temperature kinetics of hydrogenation of the alloy for these conditions. After 10 min of the latent period, the alloy intensively absorbs hydrogen. Maximum hydrogen absorption (2.6 mass%) in the Ti_3Al sample is reached after 1 h of the ball milling in the hydrogen atmosphere. The XRD pattern of the alloy after the hydrogenation is presented in Fig. 4. The lines' positions on this XRD pattern are similar to a hydride with a cubic crystal lattice, superstructure $E2_1$ (No. 221), ($Pm\bar{3}m$) type, $a = 0.424$ nm. The same structure for the Ti_3Al hydride was suggested in [4]. Dehydrogenation of the samples was done with the Sieverts-type apparatus. Active release of hydrogen in the Ti_3Al powder was observed during its heating in a vacuum up to the temperature of 531 K.

One of the possible reasons of considerable reduction of the dehydrogenation temperature in the Ti_3Al alloy after the ball milling can be a formation of the ultrafine grained structure. On the other side, such a structure can be produced by shear under pressure. Therefore, we studied the effect of shear under pressure on

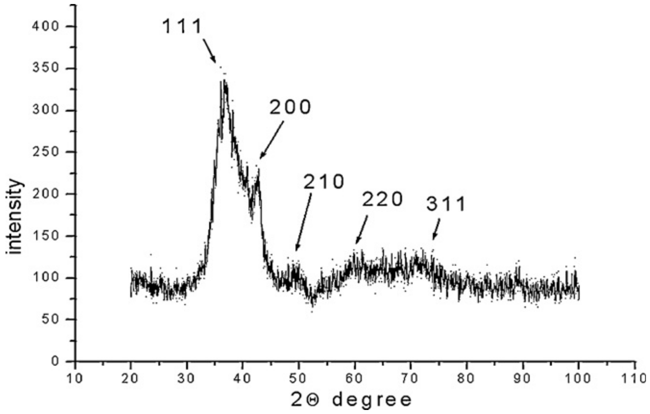

Fig. 4. The XRD pattern the Ti_3Al sample after the ball milling at a hydrogen atmosphere.

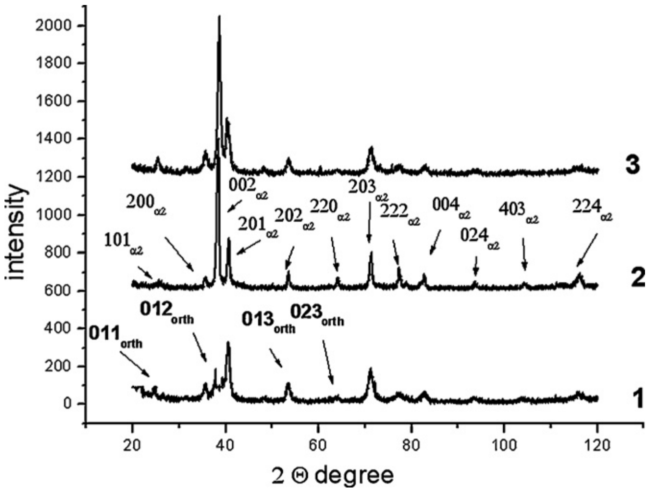

Fig. 5. The XRD pattern of the Ti_3Al sample after the deformation by the shear under pressure: 1 – $e = 4.3$; 2 – dehydrogenated sample; 3 – $e = 3.5$.

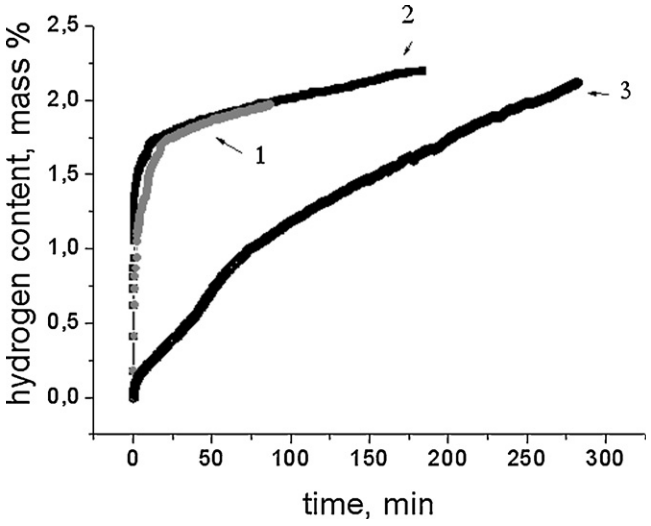

Fig. 6. Variation in hydrogen content in the Ti_3Al sample after the deformation by the shear under pressure: 1 – first cycle ($e = 4.3$); 2 – second cycle ($e = 4.3$); 3 – second cycle ($e = 3.5$).

the hydrogenation and structure of the Ti_3Al alloy. The samples of the Ti_3Al alloy in the form of thin plates (0.3 mm of thickness) were deformed by the anvils at room temperature. We used 5 (degree of deformation $e = 4.3$) and 1.5 (degree of deformation $e = 3.5$) turns of the anvils. In our previous study, we found that the nano-scale fragmented structure had been formed in the titanium aluminides after the degree of deformation $e = 4.3$, while after degree of deformation $e = 3.5$ the structure had the micro-scale fragments [8].

The XRD pattern of the Ti_3Al sample after the deformation by shear under pressure and after the cycle of hydrogenation-dehydrogenation of the deformed sample is shown in Fig. 5. An analysis showed that the positions of all X-ray diffraction lines in the sample after the deformation did not coincide with the lines' positions for the hexagonal lattice. It was confirmed by the calculation of the values $Q_i = \sin_i^2 \Theta_{00L} / \sin_1^2 \Theta_{001}$, as Q_i for the $00L$ planes' systems for the hexagonal crystal should be integers with the following order: 1; 4; 9; 16; 25; ... [9]. In our case, these values are non-integers. Calculation for Q_i showed that only a part of the lines could belong to the hexagonal lattice and the other part of the lines could belong to the orthorhombic structure. Considering the two-phase approximation we could describe all the lines on the XRD pattern. The lattice parameters of the phases were determined as $a = 0.301$ nm, $b = 0.4759$ nm, $c = 0.5495$ nm for the orthorhombic phase, and $a = 0.581$ nm, $c = 0.467$ nm for the hexagonal α_2-phase. After the treatment with a lower degree of deformation ($e = 3.5$) we found only the hexagonal α_2-phase lines on the XRD pattern (Fig. 5).

The XRD pattern of the Ti_3Al deformed sample ($e = 4.3$) after the hydrogenation at 733 K indicates that its structure is composed of two hydrides: the tetragonal γ_1 and cubic γ_2. The lattice parameter of the γ_2 hydride was $a = 0.415$ nm, and the lattice parameters of the γ_1 hydride were calculated as $a = 0.314$ nm, $c = 0.423$ nm. Fig. 6 shows the hydriding behavior of the samples after the deformation by shear under pressure. The sample after $e = 3.5$ is characterized by a slow kinetics of hydrogen absorption. On contrary, the initial absorption rate in the sample after $e = 4.3$ was very high. However, maximum hydrogen content does not reach any plateau even after 1.5 h of hydrogenation, indicating that the sample has a non-uniform structure. The maximum content of hydrogen in the sample was only 2.2 mass% (Fig. 6). The active release of hydrogen was observed during the heating of the samples in a vacuum up to the temperature of 603 K. The dehydrogenated sample had the single-phase structure (α_2-phase) with the lattice parameters $a = 0.579$ nm; $c = 0.467$ nm (Fig. 5). A second cycle of the hydrogenation was performed also at the temperature of 733 K. The hydrogen content in the sample at the second cycle was practically unchanged (Fig. 6). The XRD pattern was similar to the one after the first hydrogenation. We also observed the structure with two hydrides. The lattice parameters were calculated as $a = 0.315$ nm, $c = 0.425$ nm for the γ_1 hydride, and $a = 0.413$ nm for the γ_2 hydride (Fig. 7).

3.2. TiAl-type alloy (cubic B2 superstructure)

We used two different experiments for hydrogenation of this alloy: (1) conventional hydrogenation of the bulk sample using the Sieverts-type apparatus; (2) mechanical activation in a hydrogen atmosphere.

According to the X-ray diffraction analysis (Fig. 8), after conventional hydrogenation the γ hydride of composition $Ti(Al,Nb)H_2$ with a tetragonal lattice was formed. The lattice parameters of this hydride were determined as $a = 0.3194$ nm and $c = 0.382$ nm. Fig. 9 displays the hydrogen-absorption curve of sample at 773 K and a hydrogen pressure of 1.2 MPa. Maximum hydrogen content in the sample was 1.76 mass%. The dehydrogenation was successfully performed in a vacuum also at 773 K.

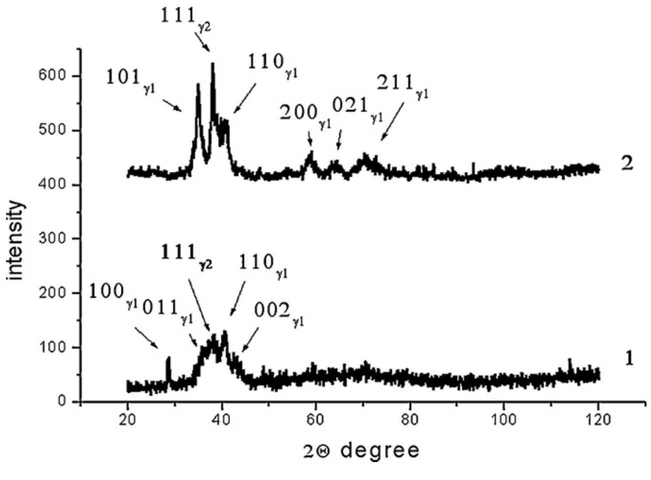

Fig. 7. The XRD pattern of the hydriding sample after the deformation by the shear under pressure ($e = 4.3$): 1 – first cycle; 2 – second cycle.

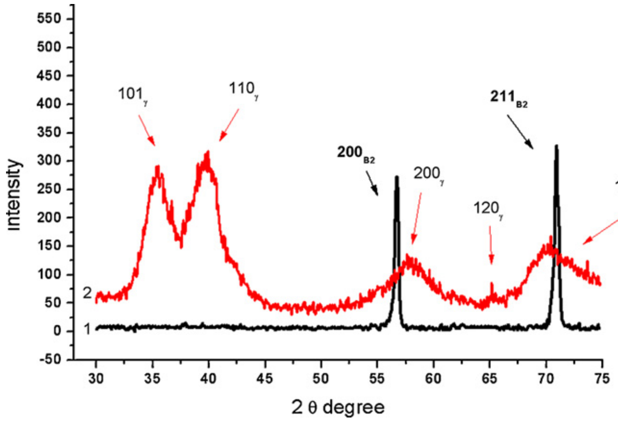

Fig. 8. The XRD pattern of TiAl sample: 1 – the initial state; 2 – the hydrogenation by the Sieverts-type apparatus.

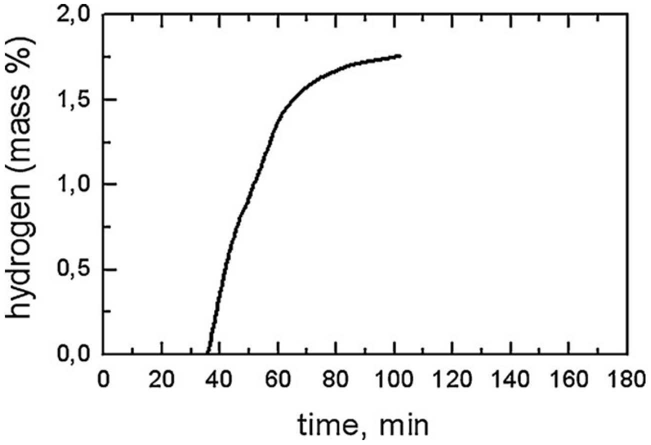

Fig. 9. Variation in hydrogen content in the TiAl sample during the hydrogenation by the Sieverts-type apparatus.

The rate of the hydrogenation of this intermetallic compound during the ball milling in hydrogen atmosphere was found to be very high (Fig. 10). According to the XRD results, a hydride with a cubic crystal lattice was formed upon mechanical activation of this alloy in a hydrogen atmosphere. In comparison with the literature data for the cubic hydride (0.8 mass% H_2 and $a = 0.334$ nm [4]), the hydride we obtained had increased both the lattice parameter $a = 0.3358$ nm and the content of hydrogen 1.96 mass% (Fig. 11). We performed dehydrogenation of the TiAl-type samples and found that a small part of hydrogen had escaped from the sample in vacuum already at room temperature. With heating in a vacuum, an active release of hydrogen began at a temperature of 453 K.

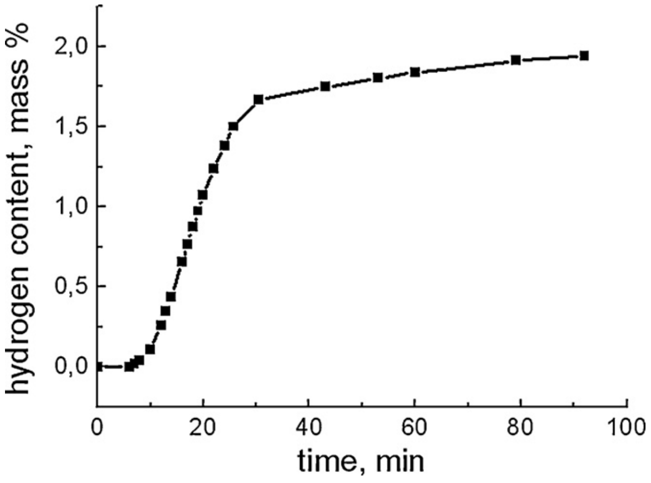

Fig. 10. Variation in hydrogen content in the TiAl sample during the ball milling.

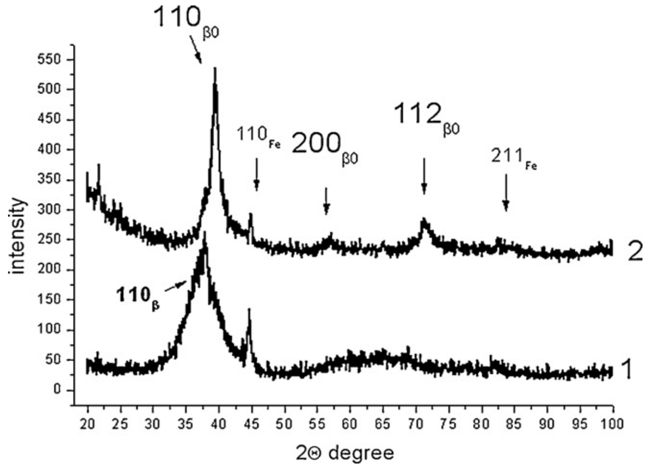

Fig. 11. The XRD pattern of TiAl sample: 1 – after the ball milling under a hydrogen atmosphere; 2 – dehydrogenated sample.

Thus we observed that the ball milling in a hydrogen atmosphere and shear under pressure promoted the rapid hydrogen absorption and desorption. We suppose that there are several factors responsible for this behavior: (1) milling breaks grains, exposing fresh surfaces through which hydrogen can be absorbed before oxidation occurs; (2) reduction of grain size increases the surface to volume ratio of the grains; and (3) severe plastic deformation introduces defects, such as dislocations, along which hydrogen may diffuse into the grains.

4. Summary

The influence of severe plastic deformations on the hydrogenation of two titanium aluminides (Ti_3Al and TiAl-type alloy (B2)) has been studied. The results obtained can be summarized as follows.

(1) It is shown that a conventional hydrogenation of the bulk samples of the TiAl (B2) and Ti_3Al alloys leads to the formation the hydrides with high hydrogen content and high desorption temperature: TiAl (773 K, 1.76 mass%); Ti_3Al (1043 K, 2.94 mass%).
(2) The mechanical activation in a hydrogen atmosphere at room temperature allows one to obtain the hydrides of the TiAl (B2) and Ti_3Al alloys with high hydrogen content and reduced desorption temperature: TiAl (453 K, 1.96 mass%); Ti_3Al (531 K, 2.6 mass%).
(3) The severe plastic deformation by the shear under pressure produces the phase transformation in the Ti_3Al intermetallic compounds. As the results of hydrogen treatment of the deformed samples, the hydrides with the orthorhombic structure and 2.2 mass% of hydrogen can be formed. The active release of hydrogen was observed during heating of such samples in a vacuum at the temperature of 603 K.

Acknowledgments

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