Deuterium desorption temperature of Mg-Ti composites prepared by the method of atom-by-atom component mixing

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Abstract. The plasma evaporation-sputtering method has been applied to obtain composite materials of the Mg-Ti system. Variations in the temperature of the ion-implanted deuterium desorption as a function of the component concentration are studied. It has been established, that introduction of titanium into magnesium leads to the significant decrease of deuterium desorption temperature, namely, to 400-450 K as compared to ~800 K in the case of deuterium release (desorption) from magnesium. The step-like shape of the deuterium desorption temperature curve evidences on the existence of two different structural states of the Mg-Ti composite depending on the ratio of components. The deuterium temperature drop can be caused by filamentary inclusions composed of titanium atoms in magnesium (insoluble component in magnesium) produced in the process of composite formation and providing the deuterium release from the sample at lower temperature (channels for deuterium diffusion and desorption through the surface barrier). The deuterium desorption data obtained on the example of Mg-Ti composites provide a support for further research into hydrogen storage materials containing not readily soluble chemical elements in the alloy components.

1. Introduction
Magnesium-based alloys are promising in view of the present-day requirements to the metal-hydride hydrogen storage systems. Behavior of hydrogen in the magnesium-based alloys arouses intense scientific and applied interest that is confirmed by many publications [1-8]. However, the use of such alloys is accompanied by some difficulties, one of which is a high hydrogen desorption temperature (550-600 K).

Of particular interest are materials in the nanocrystalline state. An exclusive significance of nanocrystalline materials as hydrogen storage materials is due to their unique structural properties which can provide a high sorption capacitance and potentially high concentrations of hydrogen storage. Therefore, naturally, that the reports about investigations of the hydrogen behavior in the nanocrystalline materials are frequent in the literature [7-9].

One of the methods for obtaining materials in the nanocrystalline state is to introduce nanoformative elements. In our opinion among them are not readily soluble chemical elements or elements which can not interact with components of the composites formed. The literature data confirm that investigations in this direction are promising [5-7].
The purpose of this work is to make Mg-Ti composites by the method of atom-by-atom mixing of components and to study the mechanisms of hydrogen storage and its thermoactivated release from the samples obtained. Note, that Mg and Ti are almost not alloyable, therefore, in the above-mentioned system the immiscibility of liquid and solid phases takes place [10].

2. Materials and methods

To make Mg-Ti composites the plasma evaporation-sputtering method was used providing the atom-by-atom growth of components. The composites with a wide range of ratios insoluble components were obtained [8]. A composite was deposited on the molybdenum foils (0.2 mm thickness, 10 mm width, 250 mm length) placed between the cathode assemblies of the facility. In parallel with the molybdenum foils placed were the copper plates (10×10 mm²) which served as standards to measure the sample thickness using the gravimetric method and the composite component concentrations was determined by the X-ray fluorescence method.

To introduce deuterium into the samples the ion implantation method was applied. Deuterium desorption temperature ranges and deuterium storage levels were determined using the thermal desorption spectroscopy. In experiments a hydrogen isotope (deuterium) was used to decrease the influence of the background hydrogen contained in the samples and target chambers. The samples were fixed on the foils-heaters made of stainless steel Cr18Ni10Ti (5×45×0.3 mm³). The temperature was measured with a chromel-alumel thermocouple fastened to the heater.

3. Results

The most characteristic spectra of ion-implanted deuterium thermal desorption from the Mg-Ti composites are presented in Figure 1. One can see the thermal desorption spectrum (TDS) evolution as a function of the composite composition and the implanted deuterium dose. Also the figure shows the plots of corresponding temperatures of maxima of peaks in the deuterium TDS against the magnesium concentration in the samples under study.

![Figure 1. Deuterium desorption temperature as a function of the Mg-Ti composition (■) in the case of a deuterium dose of 1×10⁻¹⁸ D/cm² (T_irr.~100 K) and thermal desorption spectra of deuterium released from composites: (a) Mg₆₆Ti₃₄; (b) Mg₃₀Ti₇₀; (c) Mg₄₁Ti₅₉; (d) Mg₆₆₅Ti₃₃.](image-url)
A low magnesium concentration and, consequently, a high titanium concentration in the composite are demonstrated in the deuterium TDS as a single peak with a maximum temperature at 800-950 K as a function of the implanted deuterium dose and composite composition (Fig. 1a,b). A single-peak character of the deuterium TDS, observed for magnesium concentration values from 1 to 30 at. %, evidences on the homogeneity of composite structural state in this range. As the magnesium concentration in composites increases to the Mg30Ti70 composition, the peak maximum temperature in the deuterium TDS rises to the temperature of 950 K. This is evidence of an increased influence of magnesium on the temperature range of deuterium trapping (see Figure 1b).

The temperature range of deuterium desorption from magnesium-titanium composites, with high titanium content, on the temperature scale is within the region of the deuterium solid solution in α-titanium. Besides, for Mg30-xTi70+x when the implantation dose increases the peak maximum temperature in the deuterium TDS displaces towards the temperature decrease, that has been earlier observed for the titanium samples fixed at the substrate [11].

For dose of ~2×10^18 D/cm^2 in the deuterium TDS of Mg30-xTi70+x an additional, not intense, low-temperature slightly-sloped peak with a centre of gravity at ~300-400 K is observed. Thus, in the composite the process of deuterium solid-solution phase formation is finished and the process of hydride formation is started.

As the magnesium concentration in composites increases the deuterium TDS is significantly changing and, as a result, the deuterium desorption temperature for Mg40-xTi60+x composites sharply decreases (see Fig. 1c,d).

A step-like shape of the maximum temperature curve of thermoactivated deuterium desorption, as a function of the component concentration change, evidences on the existence of two different structural states of the Mg-Ti system depending on the ratio of components.

At the same time, in each of the states only one of components plays a main role – magnesium or titanium. Analysis of curve shapes (Fig. 2), which are changing with concentration of deuterium desorbed from Mg30Ti70 (part I) and Mg83.5Ti16.5 (part II), shows that they are strongly dependent on the ratio of composite components. In the concentration range, where titanium (Mg30-xTi70+x) is dominant, the amount of trapped deuterium linearly increases with implantation dose increasing. The foregoing shows that in this composite the deuterium diffuses with a high mobility, releases from the implantation region and propagates throughout the sample volume. A similar effect was observed for palladium at a temperature of deuterium implantation of 100 K [12].

In the case of Mg40-xTi60+x the amount of trapped deuterium begins the decrease when the dose is ~1×10^18 D/cm^2 and reaches the saturation when the implantation dose exceeds 2×10^18 D/cm^2. It is evident, that in this composite the implanted deuterium has low diffusion mobility and its accumulation occurs, for the most part, in the implantation volume.

The structure of deuterium TDS in the case of Mg40-xTi60+x strongly depends on the implanted deuterium dose. For low implantation doses (3×10^15 D/cm^2) the spectrum has only one high-temperature peak with the centre of gravity at 850-900 K. As the implanted deuterium dose increases
the deuterium desorption temperature range enlarges towards the temperature decrease (Fig. 1d, curves 2 and 3). Beginning from the dose of $\sim1\times10^{17}$ D/cm$^2$ a deuterium desorption region with a centre of gravity at $\sim400$ K arises. The peak intensity is growing up to the dose of $9\times10^{17}$ D/cm$^2$. As the dose of implanted deuterium increases, the amount of trapped deuterium decreases (see Fig.2, curve 2) and an additional low-temperature region of deuterium desorption with the centre of gravity at 300-330 K takes place (Fig. 1d, curve 7). The low-temperature intensity of the low-temperature peak increases owing to the implanted deuterium and deuterium trapped before at a higher temperature. The changes in the deuterium TDS evidence on the implantation layer structure transformation.

An additional low-temperature peak in TDS, becomes dominant with implanted deuterium dose increasing and reaches the maximum value of $\sim300$ K. This peak arises due to the temperature decreasing in the process of deuterium desorption from the Mg-Ti composites with titanium concentration less than 60 at.%. The deuterium temperature decrease can be caused by filamentary inclusions of insoluble components (here titanium atoms) formed in the process of composite formation that provides the deuterium desorption from the sample at lower temperatures (channels for deuterium diffusion through the surface barrier).

3. Conclusions

The present paper shows that by introducing titanium into magnesium it is possible to decrease significantly the deuterium desorption temperature (namely, to 400-450 K as compared to $\sim800$ K in the case of deuterium desorption from magnesium). A step-like shape of the maximum temperature curve of thermoactivated deuterium desorption, changing as a function of the component concentration, evidences on the existence of two different structural states of the Mg-Ti system depending on the ratio of components.

The deuterium temperature drop can be caused by filamentary inclusions composed of titanium atoms in magnesium (insoluble component in magnesium) produced in the process of composite formation and providing the deuterium release from the sample at lower temperature (channels for deuterium diffusion and desorption through the surface barrier).

The deuterium desorption data obtained using Mg-Ti, Mg-V [7] and Mg-Zr [8] composites provide a support for further research into the hydrogen storage materials containing not readily soluble chemical elements in the alloy components.

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