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Effects of Concentration Titanium on Threshold Character of Deuterium Desorption Temperature Range from Mg-based Composites

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The plasma evaporation-sputtering method was applied to make composite materials of the Mg-Ti system. The ion-implanted deuterium desorption temperature variations as a function of the component concentration were studied. It has been established that, by introducing titanium into magnesium, the deuterium desorption temperature can be appreciably decreased (to 400-450 K) in comparison with the case of deuterium desorption from magnesium (~ 800 K). A step-like shape of the curve of deuterium desorption temperature evidences on the presence of two different structure states of the Mg-Ti system depending on the ratio of components. The deuterium temperature decrease can be caused by filamentary inclusions of insoluble component (titanium) atoms formed in the process of composite making and annealing, providing the deuterium diffusion from the sample at a lower temperature (channels for deuterium diffusion through the surface barrier). The deuterium desorption data obtained on the example of Mg-Ti, Mg-V and Mg-Zr composites provide support for further research into hydrogen storage materials containing low-soluble chemical elements in the alloy component.

Keywords: Nanostructured Composites, Deuterium, Thermal Desorption, Implantation, Hydrogen Storage.

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1. INTRODUCTION

Magnesium-based alloys are promising in the view of present-day requirements to the metal-hydride hydrogen storage systems. Behavior of hydrogen in the magnesium-based alloys is of scientific and applied interest that is confirmed by many publications [1-17]. However, the use of such alloys presents some difficulties because of the high hydrogen desorption temperature (550-600 K).

Particular attention is given to materials in a nanocrystalline state. An exclusive position of nanocrystalline materials as hydrogen storage materials is determined by their unique structural properties that can, probably, provide a high sorption capacitance and potentially high concentrations for hydrogen storage. Therefore it is reasonable that reports about investigations on the hydrogen behavior in the nanocrystalline materials become more and more frequent in the literature [15-17]. One of the methods for obtaining materials in the nanocrystalline state is introduction of nanoformative elements. We believe that they are chemical elements with a low solubility or elements not interacting with components of composites being composed. The literature data confirm that investigations in this direction are promising [5, 6, 15].

The purpose of this work is to make Mg-Ti composites using the method of atom-by-atom mixing of components and to study mechanisms of hydrogen storage and thermoactivated release from the samples obtained depending on the component concentration. Note, that, practically, Mg and Ti are not alloyable, therefore, in the system the liquid-and-solid phase immiscibility is observed [18].

2. MATERIALS AND METHODS

In our work the Mg-Ti composites with a different concentration of magnesium and titanium were made by plasma evaporation-sputtering of composites components (Fig. 1). Using an atom-by-atom deposition of components it is possible to obtain composites with a high concentration of insoluble components.

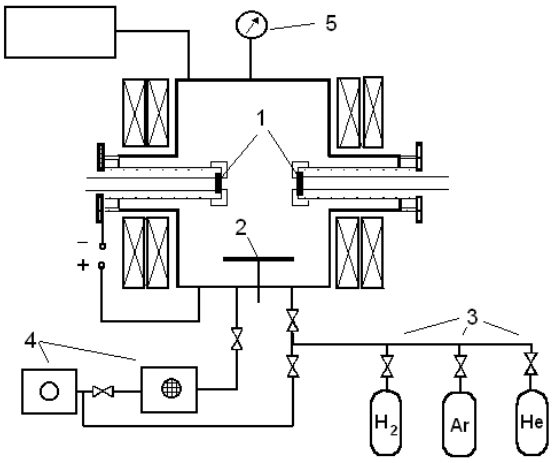

Fig. 1 – Schematic representation of the experimental facility for making the samples by plasma evaporation-sputterings: 1 – cathodes of metals to be sputtered – Mg and Ti; 2 – sample holder; 3 – gas bottles; 4 – pumps; 5 – pressure meters

Thus, the composites with a wide range of the ratios of insoluble components were obtained [16]. A composite was deposited on the molybdenum foils (0.2 mm thickness, 10 mm width, 250 mm length) placed between the cathode assemblies in the facility. In parallel

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with the molybdenum foils there were arranged the copper plates (10×10 mm²) as standards for determining the thickness of obtained samples by the gravimetric method and composite component concentrations – by the X -ray fluorescent method.

Figure 2 represents the magnesium and titanium concentration in the Mg–Ti samples, measured by the method of X-ray fluorescence analysis, as a function of the distance between the magnesium and titanium cathodes.

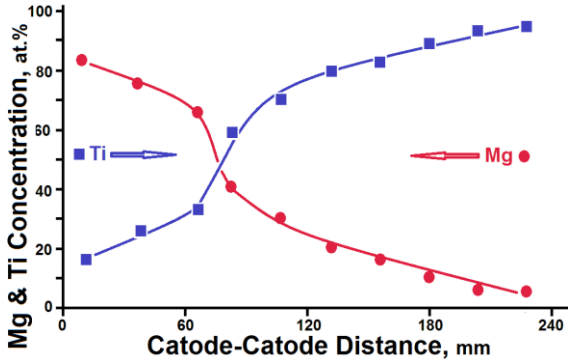

Fig. 2 – Magnesium and titanium concentration in the Mg-Ti composite samples versus the distance between the magnesium and titanium cathodes

Deuterium introduction into the samples was performed by the ion implantation method. Deuterium desorption temperature ranges and deuterium storage levels were determined by the thermal desorption spectroscopy. Deuterium introduction into the samples was performed by the ion implantation method. Deuterium desorption temperature ranges and deuterium storage levels were determined by the thermal desorption spectroscopy.

In experiments a hydrogen isotope (deuterium) was used to decrease the influence of the background hydrogen contained in samples and target chambers. The samples were mounted on foils-heaters made of stainless steel Ch18Ni10Ti (5×45×0.3 mm³). The temperature was measured with a chromel-alumel thermocouple fastened to the heater.

3. RESULTS AND DISCUSSION

The most characteristic spectra of ion-implanted deuterium thermal desorption from the Mg-Ti composites are shown in Fig. 3. The figure demonstrates the thermal desorption spectrum (TDS) evolution from the composite composition and the implanted deuterium dose, as well as, the corresponding temperatures of maximum peaks in the deuterium TDS against the magnesium concentration in the samples under study.

A low magnesium concentration and, consequently, a high titanium concentration in the composite are revealed in the deuterium TDS as a single peak with a maximum temperature at 800-950°K depending on the implanted deuterium dose and composite composition (Fig. 3 a, b). A single-peak character of the deuterium TDS, observed for magnesium concentration values ranging from 1 to 30 at. %, evidences on the homogeneity of composite structural state in this range. As the magnesium concentration in the composites increases to the $Mg_{30}Ti_{70}$ composition, the maximum peak temperature in the deuterium TDS rises to the temperature of 950°K. So, the magnesium influence on the temperature range of deuterium trapping is increasing (see Fig. 3b).

The temperature range of deuterium desorption from the magnesium- titanium composites, having ahigh titanium content, on the temperature scale is within the region of the deuterium solid solution in **α**-titanium. Besides, for $Mg_{30-x}Ti_{70+x}$ composites the peak maximum temperature displaces with implantation dose increasing in the deuterium TDS towards the temperature decrease that has been earlier observed for the titanium samples located at the substrate [19].

With a dose of ~2×10^{18} D/cm² there is in the deuterium TDS of $Mg_{30-x}Ti_{70+x}$ composites an additional low-intensity low-temperature slightly sloped peak with a centre of gravity at ~300-400°K. This indicates on the fact that the process of deuterium solid-solution phase state formation in the composite has finished and the process of hydride formation has started.

A step-like form of the maximum temperature curve obtained for the thermoactivated deuterium release from composites as a function of the magnesium concentration evidences on the existence of two different structural states of the system depending on the ratio of components. At the same time, in each of the states being observed a main role is performed by one of the components – magnesium or titanium. Analysis of the shapes of curves shown in Fig. 4, illustrating the change in the concentration of deuterium desorbed from $Mg_{30}Ti_{70}$ (part I) and $Mg_{83.5}Ti_{16.5}$ (part II) composites, has shown an appreciable difference in the dependence on the ratio of composite components. In the concentration region where titanium ($Mg_{30-x}Ti_{70+x}$ composites) plays a prevailing role, one can see a linear growth of the amount of deuterium trapped due to the implantation dose increase. The foregoing permits to draw a conclusion about a high mobility of deuterium by diffusion in such composites and deuterium release from the implantation region and propagation throughout the sample volume. A similar effect was observed for palladium at a temperature of deuterium implantation of 100°K [20].

In the case of $Mg_{40+x}Ti_{60-x}$ composites the amount of trapped deuterium is decreasing beginning from the dose of ~1×10^{18} D/cm² with a tendency towards the attainment of saturation when the implantation dose exceeds 2×10^{18} D/cm². It means that in this composite the implanted deuterium has the low diffusion mobility and its accumulation takes place mainly in the implantation volume.

The structure of deuterium TDS in the case of $Mg_{40+x}Ti_x$ composites strongly depends on the implanted deuterium dose. For the low implantation doses (3×10^{15} D/cm²) the spectrum has only one high-temperature peak with the centre of gravity at 850-900 K. The implanted deuterium dose increase is accompanied by the extension of the deuterium desorption temperature range towards the temperature decrease (Fig. 3d, curves 2 and 3). Beginning from the dose of ~1×10^{17} D/cm² there is observed a deuterium desorption region with a centre of gravity at ~400°K. The intensity of this peak continues to grow up to the dose of 9×10^{17} D/cm². As the implanted deuterium dose

goes on, the amount of trapped deuterium decreases (see Fig. 4, curve 2) and an additional low-temperature region of deuterium desorption with a centre of gravity at 300-330°K appears (Fig. 3d, curve 7). The low-temperature intensity increases owing to the implanted deuterium and deuterium trapped before at a higher temperature. The changes observed in the deuterium TDS evidence on the structure transformation in the implantation layer.

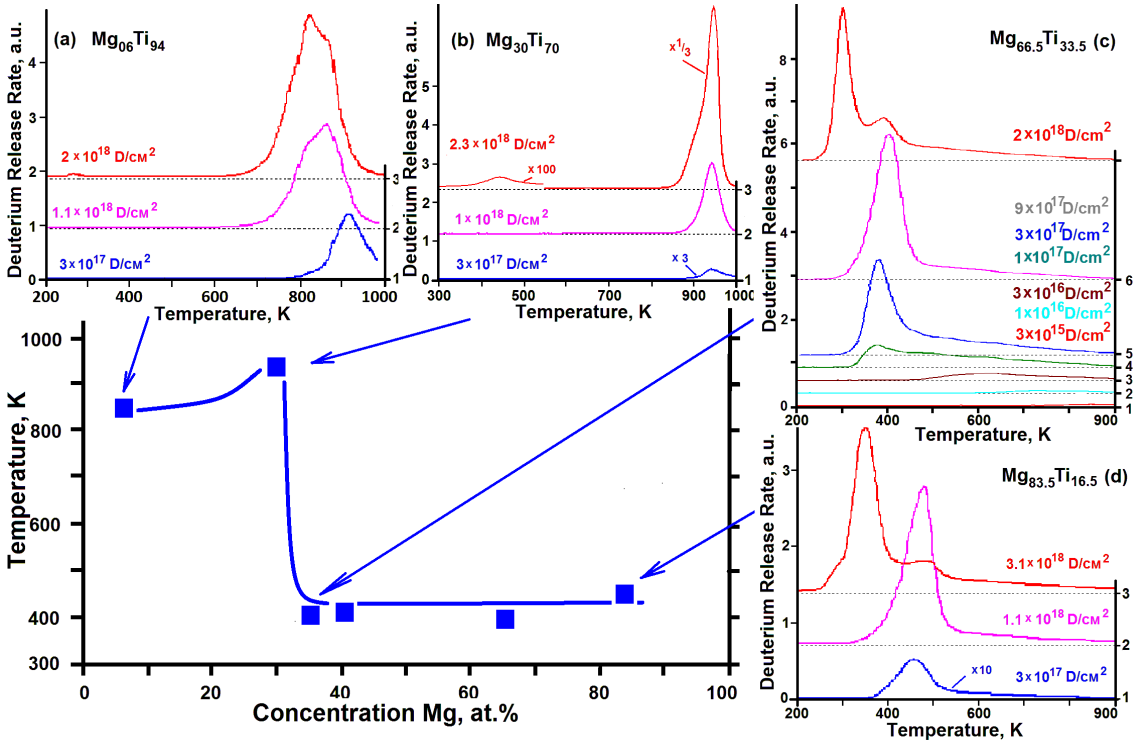

Fig. 3 – Deuterium desorption temperature versus the Mg-Ti composition (■) for a deuterium dose of ~1×10^{18} D/cm^2 ($T_{irr.}$~100°K) and thermal desorption spectra of deuterium released from composites: (a) $Mg_{06}Ti_{94}$; (b) $Mg_{30}Ti_{70}$; (c) $Mg_{41}Ti_{59}$; (d) $Mg_{66.5}Ti_{33.5}$

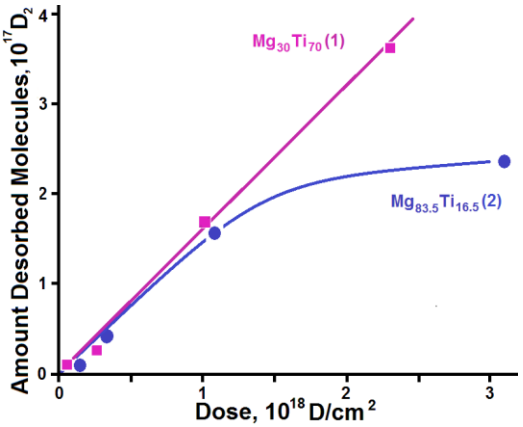

Fig. 4 – Amount of desorbed deuterium versus the implanted dose for the $Mg_{30}Ti_{70}$ (1-■) and $Mg_{83.5}Ti_{16.5}$ (2-●) composites

An additional low-temperature peak in TDS, which becomes prevailing with the implanted deuterium dose increasing and reaches the maximum desorption temperature of the main low-temperature peak ~300°K, arises due to the temperature decreasing during deuterium desorption from the Mg-Ti composites having the titanium concentration less than 60 at.%.The deuterium temperature decrease can be caused by filamentary inclusions of insoluble component atoms (titanium in our case) formed, in the process of composite making and annealing, which provide the deuterium diffusion from the sample at a lower temperature (channels for deuterium diffusion through the surface barrier).

4. CONCLUSIONS

The present paper shows that by introducing titanium into magnesium the deuterium desorption temperature can be significantly decreased (to 400-450°K) compared to desorption from the magnesium samples (~800°K).

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

The deuterium temperature decrease can be caused by filamentary inclusions of insoluble component atoms, formed in the process of making and annealing, which provide the deuterium diffusion from the sample at a lower temperature (channels for deuterium diffusion through the surface barrier).

The deuterium desorption data obtained using Mg-Ti, Mg-V [15] and Mg-Zr [16] composites provide support for further research into the hydrogen storage materials containing low-soluble chemical elements in the alloy components.

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