Comparative experiments on hydrogenation of titanium films and foils

D A Karpov, A G Ivanov, E S Chebukov and M I Yurchenkov

JSC “NIIEFA”, Saint-Petersburg, Russia

E-mail: karpov@niiefa.spb.su

Abstract. Comparative experiments have been performed for the gas-diffusion hydrogenation of vacuum-deposited titanium films and commercially produced titanium foils. The sorption and thermodesorption characteristics of obtained hydrogenated materials and the values of hydrogen mass content in these materials have been defined. Differences in the resulting structure of deposited films and foils after hydrogenation are shown.

1. Introduction

The main disadvantages of available powder metal-hydride systems for hydrogen storage are a low thermal conductivity of powder material resulting in a slow kinetics of hydrogen and a non-uniform hydrogen heating. These problems can be solved by using film storages based on metal-hydride films deposited on an ohmically heated foil or a resistive layer deposited on a thin-film carrier from a polymer material [1]. This proposed approach provides a higher occupational safety (no fine powders) and possible reduction of temperatures, which effect the energy efficiency of metal-hydride accumulators [2].

The vacuum-deposited titanium films used as a hydride-forming material hold promise for improving the operating characteristics of metal-hydrogen accumulators [3]. But, the question arises as to whether the like characteristics are provided not by the deposited films but by commercially available foils from the same materials. This would essentially reduce the production costs of the metal-hydride accumulators.

The comparative study has been performed on gas-diffusion hydrogenation of vacuum-deposited titanium films and commercially produced titanium foils. The sorption and thermodesorption characteristics of obtained hydrogenated materials and the values of hydrogen mass content in these materials have been defined. The differences in the resulting structure after hydrogenation are shown.

2. Experiment details

Preparation of film and foil titanium samples:

Ti films were deposited on samples 20x20 mm in size made of 12X18H10T stainless steel (0.9 mm thick) and nichrome foil (50 µm thick) by the vacuum-arc method at the PLAZMATEKH-M facility with the use of a VT1-0 titanium cathode. Samples with a
titanium film 20 µm and 80 µm in thickness were formed under different deposition conditions.

To hydrogenate Ti foils, samples from VT 1-0 titanium foil 20x20 mm in size and 50 µm and 100 µm in thickness and a 2-mm-thick plate were used. Prior to hydrogenation, the sample surfaces were cleaned in a glowing discharge in the argon atmosphere.

Hydrogenation of film and foil titanium samples:

Samples were hydrogenated in the thermal vacuum facility by the gas-diffusion Sieverts’ method (450°C temperature, hydrogen pressure of 3 atm abs., saturation time of 90 min) The same facility was used for desorption of hydrogen-saturated samples. The chamber was evacuated to a pressure of about 1·10⁻⁶ torr and heated to about 500°C. The amount of desorbed hydrogen was defined by the analysis of thermodesorption spectra (TDS) and by a change in the sample weight. To precisely define the pressure, a MKS Instruments 628 membrane-capacitance sensor with an operating pressure range of 0,001 – 10 torr was used.

3. Results

Titanium films:

- Both thick (80 µm) and thinner (20 µm) titanium films deposited without a bias potential at a low temperature controlled by water cooling are hydrogenated to a stoichiometric ratio (~4 wt.%) with a uniform distribution along the entire length of the film and consist completely from ε titanium hydride (close to TiH₂ structure).

- Titanium sublayer deposited with a bias of ~500 V to improve adhesion has a denser structure and is not hydrogenated at a temperature up to 550°C and a hydrogen pressure of 3 atm (figure 1).

- During cyclic tests (5 cycles) the hydrogenated stoichiometric TiH₂ films (20 µm and 80 µm thick) desorb practically the entire hydrogen (3.88 – 3.97 wt.%) without loss of hydrogen-content from cycle to cycle.

Figure 1. Profile of the elemental composition of a hydrogenated Ti film with an unsaturated adhesive Ti sublayer (data obtained by the optical spectrometry of a high-frequency glowing discharge carried out at the GD–Profiler 2 spectrometer).
Titanium foils:
- All Ti foil samples (50 µm and 100 µm thick) were subjected to a complete fracture during hydrogenation (figure 2).
- The mass content of hydrogen in the investigated Ti foils was in the range of 2.6 – 3.7 wt.% (figure 3 shows the TDS samples).
- Decrease in titanium foil saturation time to 20 min and in saturation pressure to 2 atm abs. did not result in a reduction of the mass content of hydrogen in these foils at the same their complete fracture.
- The Ti plate samples retained their geometrical parameters after saturation by hydrogen. The estimated depth of the saturated layer (assuming that it consist of TiH₂ layer with density of $\rho_{\text{TiH}_2} = 3.76 \text{ g/cm}^3$) amounted to about 70 µm.

![Figure 2](image)

**Figure 2.** External view of the Ti foil samples prior to and after hydrogen saturation.

![Figure 3](image)

**Figure 3.** Hydrogen TDS spectra for titanium foils 50 µm and 100 µm in thickness and 2-mm-thick plate obtained by the Extorr Model XT100 residual gas analyzer (all spectra are normalized to a unity element).

4. **Conclusions**
The vacuum-deposited Ti films hold promise for application as a hydride-forming material for metal-hydride film hydrogen accumulators. They can be saturated repeatedly to a practically stoichiometric TiH₂ composition (~4 wt.%) and desorb the entire hydrogen without loss of hydrogen content from cycle to cycle. The Ti layer protected against hydrogen saturation can
be formed by selecting the deposition process condition. Commercially produced Ti foils are saturated by hydrogen in the same way as Ti films. But, the use of these foils as a hydride-forming material for metal-hydride accumulators is problematic, as the hydrogen saturation process results in their complete destruction. Probably, different results of hydrogen saturation of deposited Ti films and foils are attributable to the differences in their structure. The structure of the vacuum-arc deposited films is close to the amorphous porous one, while the foil structure is determined by a crystal lattice.

**References**

[1] Karpov D A and Litunovsky V N 2017 Proceedings of the 13-th international conference "Films and coatings - 2017", 18-20 April 2017, Saint Petersburg, pp. 507–10 (in Russian)

[2] Karpov D A and Litunovsky V N 2017 Accumulator for hydrogen storage in a bound state and cartridge for the accumulator Patent RU 2606301, published Bulletin No.1, 2017 (in Russian)

[3] Lider A, Kudiiarov V, Kashkarov E, Syrtanov M, Murashkina T, Lomygin A, Sakvin I, Karpov D and Ivanov A 2020 *Metals* **10** 880–92