



INVESTIGATION OF TITANIUM HYDRIDE PRODUCED FROM TITANIUM WASTE

Yavor LUKARSKI¹, Jordan GEORGIEV¹, Lubomir ANESTIEV¹,
Rositsa GAVRILOVA², and Simona BEJAN³

¹Institute of Metal Science, Bulgarian Academy of Sciences, Sofia, Bulgaria

²University of Chemical Technologies and Metallurgy, Sofia, Bulgaria

³Politechnica University of Bucharest, Romania

e-mail: lukarski@ims.bas.bg

ABSTRACT

The work presents an original method for titanium hydride production by hydrogenation and dehydrogenation of titanium waste in a specially designed for this purpose vacuum chamber. Laboratory quantities of titanium hydride were prepared using LaNi₅ hydrogen accumulator as a source of pure hydrogen. Chemical, X-ray, DTA, TG and granulometric analysis of the obtained hydride were made. The analyses carried out in the temperature range, 680-1070 K, DTA, TG and mass-spectrometry analysis allowed determining the activation energy of decomposition of the obtained TiH₂ which was approximately $E = -135.5$ kJ/mol and the standard enthalpy of formation $\Delta H = -140$ kJ/mol.

KEYWORDS: hydrogen, titanium waste, titanium hydride

1. Introduction

The use of titanium and titanium alloys grows by 8-10% per year [1]. This also leads to increasing the amount of produced titanium wastes. For this reason, the problem of utilizing these wastes comes to the fore. There are different methods for utilization but the recently most widely applied one is hydrogenation of titanium in the presence of hydrogen to titanium hydride (TiH₂) formation. The latter represents grey-black powder with molecular weight of 49.53-49.90 g/mol, specific density of 3.75 g/cm³ and hydrogen content within the range of 3.85-4.02 % (by weight).

The results from the investigation on some characteristics of the titanium hydride produced by the team are given in this work.

2. Methodology of the experiment

The experiments were carried out using specially constructed equipment for this purpose [2]. Fig. 1 shows the photo of this equipment. The main feature is the use of a hydrogen accumulator as a hydrogen source, which solves the problems with hydrogen utilization.

The main elements of the equipment are: heating furnace, programmable thermoregulator, reaction

chamber, vacuum system, hydrogen source, system for hydrogen feeding, system for temperature measurement, system for recording the pressure in the hydrogen accumulator and the reaction chamber, system for charging the hydrogen accumulator.

The initial raw materials subjected to hydrogenation are shavings of pure titanium and titanium alloy. The chemical composition is obtained according to the ACP-AES method and is shown below:

- Pure Ti: 0.081% Al, 0.0014% Mn, 0.0034% V;
- Titanium alloy: 0.504% Al, 0.0065% Mn, 0.0197% V.

The experiments were carried out at three different temperatures of the furnace, adjusted by the thermoregulator—873, 923 and 973 K. The sequence of operation of this installation is as follows:

The titanium crucible wastes in the form of briquettes and a thermocouple is placed in the reactor, which is closed hermetically under vacuum. Another thermocouple is placed in the zone of the crucible, which measures the temperature defined by the thermoregulator.

The vacuum in the reactor is achieved by a vacuum pump with all turn-cocks closed. Then the

intermediate cock to the vacuum pump is closed and the cock to the hydrogen accumulator is opened.



Fig. 1. Installation for producing TiH₂.

Hot water is fed into the accumulator cylinder and the transfer of hydrogen to titanium is started. The furnace heater is switched on, the temperature regime of heating and soaking being preliminarily set by means of the programmable thermoregulator. The heating rate is 10°C/min. When reaching the maximum temperature, the feeding of hydrogen by the accumulator has ceased. The titanium hydrogenation reaction is started at a definite temperature and the pressure of hydrogen in the reactor is decreased. At the moment, when hydrogen pressure stops falling, a new portion of hydrogen is fed to the set pressure.

The procedure is continued until hydrogen pressure remains unchanged after the consecutive feeding of hydrogen. This is an indication that the

hydrogenation process is completed and the furnace is switched off.

After cooling of the reaction zone to 50°C cold water is fed to the hydrogen accumulator in order to absorb the non-reacted hydrogen.

For this purpose, the turn-cock of the accumulator is opened.

After evacuating the hydrogen the turn-cock of the accumulator is closed, the reaction zone is subjected to vacuum and the reactor is filled with SO₂ or argon to protect titanium hydride against combustion.

The reactor is opened and the ready product is taken out. The change of the actual temperature in the reaction zone is shown in *Fig. 2*.

The exothermal peaks of the titanium hydrogenation process are clearly outlined.

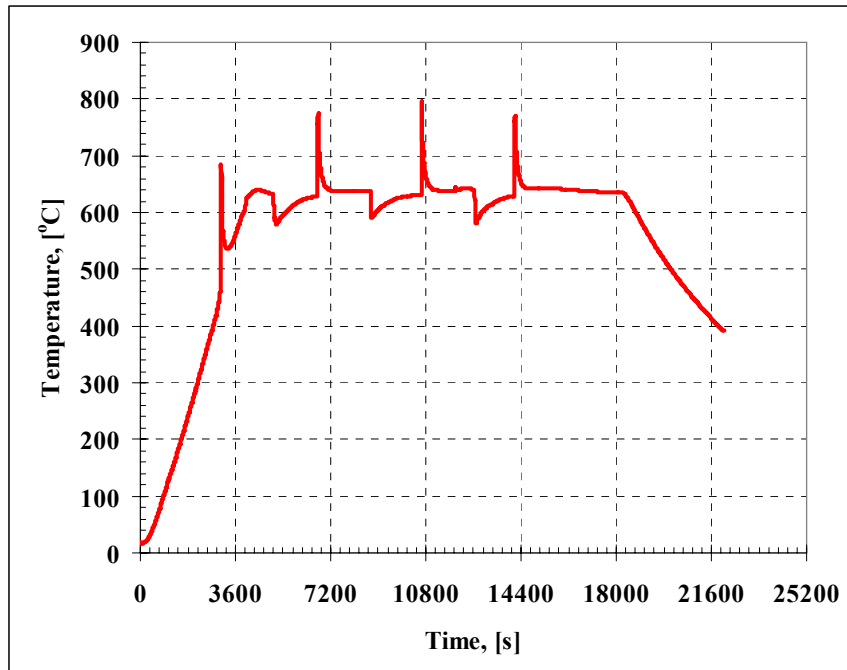


Fig. 2. Temperature change in the reaction zone.

3. Results and analysis

3.1. Granulometric analysis

The performed granulometric analysis of the produced and ground titanium hydride shows that 93.45 % of the product has a grain-size lower than 20 μm .

3.2. X-ray structural analysis

Figure 3 shows the results from the X-ray structural analysis of a titanium hydride sample using a Bruker D8 Advance diffractometer.

The only phase is $\text{TiH}_{1.924}$. No lines of titanium are observed, which shows that practically the whole titanium quantity is bound into titanium hydride.

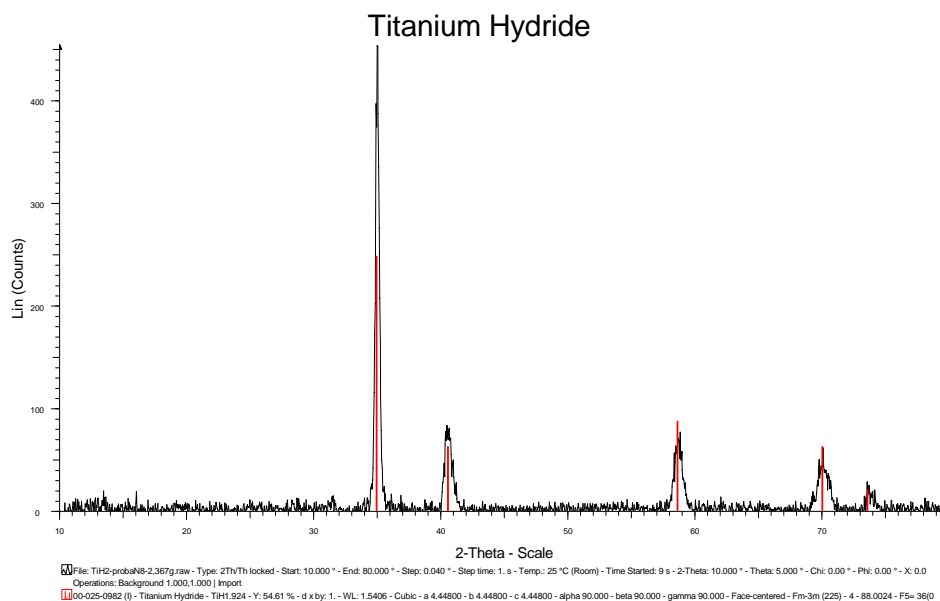


Fig. 3. X-ray diagram of a titanium hydride sample.

3.3. Thermal analysis

Samples of the produced titanium hydride are subjected to thermal and mass-spectrometric analysis. It is performed by a DTA-analyzer LABSYS-evo, combined with a mass-spectrometer of the Setaram Company. The differential thermal analysis (DTA) is carried out for five heating rates of 5, 8, 10, 12 and 15 K/min in argon atmosphere to a maximum temperature of 800°C. Figure 4 presents the obtained DTA-curves for 5 and 12K/min. The temperatures with local extremum – T_{max} , are determined for the five curves.

They are processed according to the method of Kissinger [3] (the equation shown below) and the value of the activation energy of titanium hydride decomposition is determined from the slope of the straight lines in Fig. 5 – $E = -135.5$ kJ/mol. Here β designates the heating rate, E – the activation energy, R – the gas constant.

$$\frac{E}{RT_{max}^2} = \frac{A}{\beta} \exp\left(-\frac{E}{RT_{max}}\right) \left(-\frac{df(\alpha)}{d\alpha}\right)_{T=T_{max}}$$

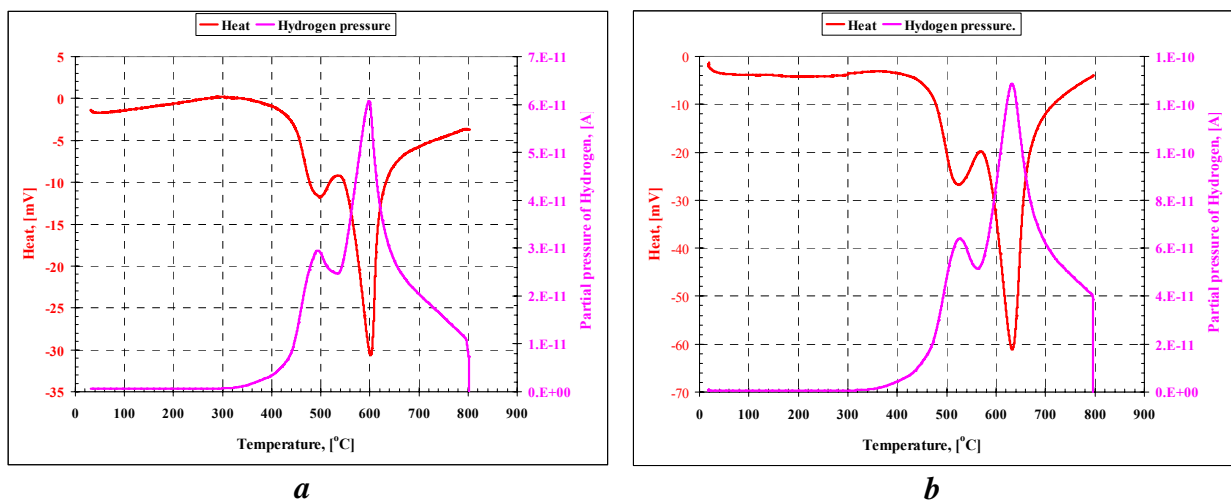


Fig. 4 (a, b). DTA curves of TiH₂ decomposition for different heating rates, (a) -5 K/min, (b) -12 K/min.

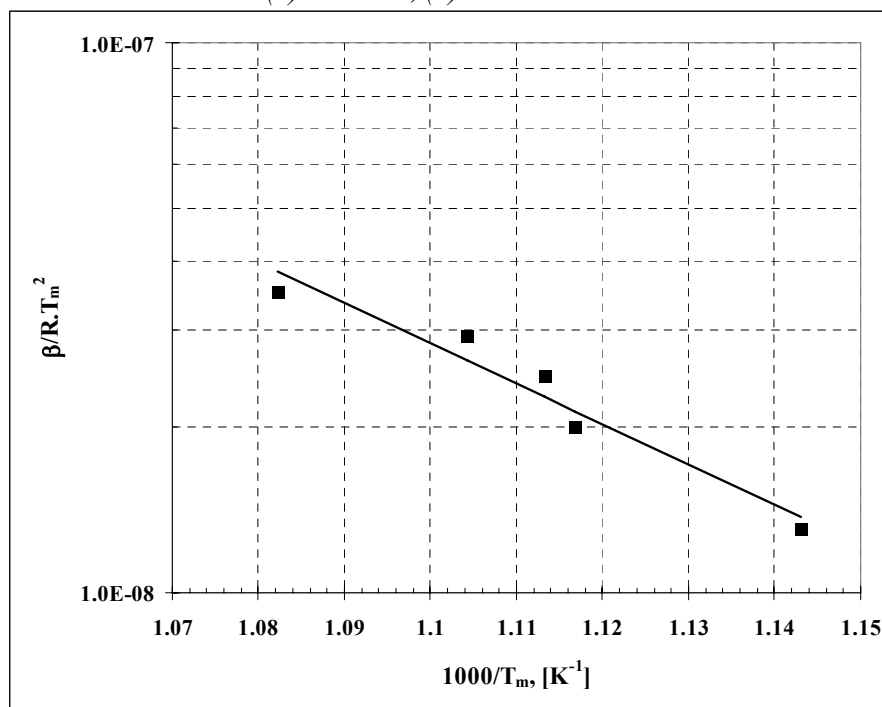


Fig. 5. Kissinger plot of the data for T_{max} obtained for the DTA curves.



4. Conclusion

A laboratory installation has been developed for producing titanium hydride by treatment of titanium wastes with hydrogen and laboratory quantities of the hydride have been obtained. An original method is applied for feeding the hydrogen from a hydrogen accumulator. The granulometric composition of titanium hydride has been determined. The X-ray structural analysis shows the existence of only the $TiH_{1,924}$ phase.

The carried out thermal analysis provided the possibility of determining also the enthalpy of the produced titanium hydride. The value of standard enthalpy of formation obtained by us -140 kJ/mol is in agreement with the value found by other authors [4-6]. On the basis of the results from thermal, thermogravimetric and mass-spectroscopic analysis of titanium hydride samples the activation energy of decomposition of the produced titanium hydride is determined. It is approximately $E = -135.5$ kJ/mol.

Acknowledgment

The present work is supported by Project BRS-11/2007, financed by the National Science Fund of the Ministry of Education, Youth and Science of Republic of Bulgaria.

References

- [1]. www.roskill.com.
- [2]. **Georgiev, J., Y. Lukarski.** *Laboratory Installation for Producing TiH_2 by Hydrogen.* Processing. 5th Congress of the Society of Metallurgists of Macedonia with International Participation, Sept. 17-20, 2008, Ohrid, Macedonia, CD ISBN 978-9989-9571-4-7, M8-02-E.
- [3]. **Kissinger, H. E.,** Reaction kinetics in differential thermal analysis, *Anal. Chem.* **29** (1957) 1702-1706.
- [4]. **Jing-wei Zhao, Hua Ding, Xue-feng Tian, Wen-juan Zhao and Hong-liang Hou** *Chin. J. Chem. Phys.* **21** (2008) 569-574.
- [5]. **E. Koenigsberger, G.Eriksson and W. A. Oates,** *Journal of alloys and Compounds*, **299** (2000) 148-152.
- [6]. **A. San-Martin and F. D. Manchester,** *Bulletin of Alloy Phase Diagrams*, **8**(1) (1987) 30-42.