

# A PROSPECTIVE METHOD FOR PRODUCTION OF TiH<sub>2</sub> AND Ti POWDERS FROM TITANIUM WASTES

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## *Abstract*

The increased growth of use of Ti and Ti alloys in industry leads to an accumulation of considerable amounts of Ti wastes. A prospective method for dealing with these wastes is the method described here, based on the hydrogenation of the wastes. The core of the method proposed is as follows: the Ti wastes are hydrogenated at high temperature and pressure in a hydrogen atmosphere; the resulting TiH<sub>2</sub> is very brittle and is easily ground using standard powder mill. The obtained TiH<sub>2</sub> powder is dehydrogenized yielding Ti powder and pure H<sub>2</sub>. The technological path described was studied using Ti wastes from the aviation industry. The waste, in the form of shavings, was subjected to a cyclic hydrogenation. The obtained TiH<sub>2</sub> chips were, optionally, milled to powder in an inert atmosphere using a standard powder mill. The TiH<sub>2</sub> powder was subjected to X-ray and granulometric analyses. The kinetics of dehydrogenation was also studied.

**Keywords:** titanium, titanium dihydride, titanium waste, hydrogenation, kinetics

## INTRODUCTION

In the past two decades the production and application of Ti and its alloys in industry was constantly growing [1]. Simultaneously, this also leads to an accumulation of wastes from Ti products. That is why the development of new methods for utilization of the accumulating Ti wastes and their recycling is one of the permanently outstanding problems for scientists, technologists and environmentalists [2].

Usually the titanium scrap is generated during the melting, forging, casting, and fabrication of titanium components and is primarily used as an alternative to titanium sponge in the production of titanium ingot. Titanium recycling consists in converting titanium scrap into titanium ingot with or without virgin metal by using either vacuum-arc-reduction or cold-hearth melting practices. In addition to that, recycling of titanium involves titanium scrap consumed by the steel and nonferrous alloy industries. Consumption by the steel industry is largely associated with the production of stainless steels and is used for deoxidation, grain-size control, carbon and nitrogen control and stabilization. In the nonferrous metals industry, recycling of titanium involves titanium scrap primary consumed to produce aluminum-titanium master alloys for the aluminum industry.

The aim of the present paper is the study of a new pyrometallurgical method for utilization of titanium waste. The idea of the method studied is to recycle the Ti-waste

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firstly to titanium dihydride,  $\text{TiH}_2$ , and further on to Ti powder. The paper aims to study all processes along the technological path of production of Ti-powders from Ti-waste.

## DESCRIPTION OF THE HYDROGEN DECREPITATION METHOD

The hydrogen decrepitation method studied consists of the following stages; hydrogenation of the Ti waste to  $\text{TiH}_2$ , grinding of the  $\text{TiH}_2$  and dehydrogenation of the  $\text{TiH}_2$  powder to Ti-powder.

The hydrogenation method chosen in the present study is based on the Ti dispergation of the Ti waste in a hydrogen atmosphere. The method of dispergation is based on the experimentally observed fact that the accumulation of hydrogen into the Ti lattice leads to its substantial deformation and at some critical hydrogen concentration to its destruction. Thus, repeating processes of hydrogenation and dehydrogenation would render a very brittle final product,  $\text{TiH}_2$ , which could be easily ground. A typical time-temperature curve of the process of cyclic hydrogenation of Ti-waste (Ti shavings), applied in the present research is shown in Fig.1.

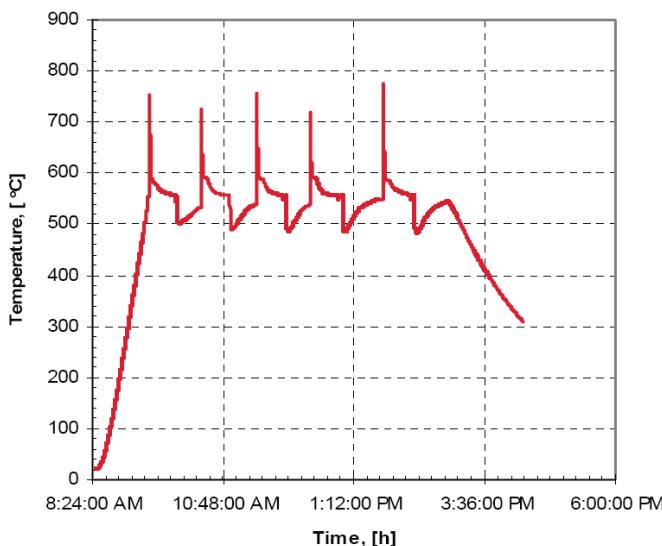


Fig.1. Recorded changes of the temperature vs. time in the reaction chamber of the hydrogenating setup. The exothermal peaks observed are due to hydrogenation reaction at the introduction of hydrogen in the setup' reaction chamber.

The next stage of the method described is the disintegration of the  $\text{TiH}_2$ . However, due to process of hydrogenation described, a decrepitation of the bulk Ti wastes occurs, yielding  $\text{TiH}_2$  powder with average particles size within 0.03 mm diameter. Note that the method produces  $\text{TiH}_2$  powders with sufficiently small size of the particles, thus, allowing skipping of the grinding stage and moving directly to the last stage, the dehydrogenation. Nevertheless, in case of specific requirements to the Ti-powder grade it could be milled to desired dimensions.

The last stage of the method is the dehydrogenation of the  $\text{TiH}_2$  powder to Ti-powder. The dehydrogenation of the  $\text{TiH}_2$  is carried out at temperatures above 600°C and has two stages, decomposition of  $\text{TiH}_2$  to supersaturated hydrogen solution in Ti and decomposition of this solution to  $\alpha$ -Ti (hexagonal A3 lattice) and/or  $\beta$ -Ti (fcc A1 lattice),

and H<sub>2</sub>. The complexities of the processes taking place at the decomposition of the TiH<sub>2</sub> and their crucial importance to the productivity of the method described make them very interesting, both from a scientific and a practical point of view.

## EXPERIMENTAL PROCEDURE

The experiments on obtaining of Ti powder from Ti-waste, utilizing the method studied, were carried on a specially designed experimental setup described elsewhere [3]. The experiments on hydrogenation of the Ti waste to TiH<sub>2</sub>, were carried at 650°C, with high purity hydrogen, sourced from LaNi<sub>5</sub> hydrogen accumulator. The Ti waste used for hydrogenation were shavings containing 0.018% Al, 0.0014% Mn, 0.0034% V and traces of Fe, Co and Ni (the chemical composition was determined using ACP-AES method). For all experiments carried, the initial hydrogen pressure used was 0.1 MPa and the applied heating rate 10 K/min. Note that pressure in the hydrogenation chamber is not constant, it actually follows the same pattern as the temperature in Fig.1. As seen, several hydrogen inflows into the chamber and average time of four hours per hydrogenation run, are necessary in order to transform the Ti shavings enclosed, into hydrogenated product, TiH<sub>2</sub>. It should be noted that the process of the cyclic hydrogenation is finalized when the pressure of the introduced into the reaction chamber hydrogen does not change with time any more.

The obtained quantities of TiH<sub>2</sub> were in form of powder and were not subjected to milling, but directly used in experiments below and, the leftovers, dehydrogenated to Ti-powder.

The experiments on obtaining of Ti powder from TiH<sub>2</sub>, were carried in the same setup above [3]. The methodology of dehydrogenation is similar to this of hydrogenation, except that the experiments were carried under vacuum, or in atmosphere of flowing inert gas. In order to study the kinetics of decomposition of the TiH<sub>2</sub>, the experiments were carried with different heating rates, from 5 to 15 K/min and at different holding temperatures, between 750°C and 900°C.

It should be noted that the hydrogen used in the first stage, the hydrogen decrepitation, could be recycled after the second stage, the dehydrogenation, thus, making the method described very attractive and cost effective.

## EXPERIMENTAL RESULTS

### X-ray structural analysis

The chemical composition of the obtained, as above, powder of TiH<sub>2</sub> were studied by X-ray structural analysis, on a diffractometer Bruker D8 Advance. The results obtained are shown in Fig.2. It is clearly seen that the only phase present in the studied sample is TiH<sub>1.924</sub>. Thus, the selected by us method of production, temperature and holding time are appropriate for overall transformation of the Ti shavings into TiH<sub>2</sub> powder.

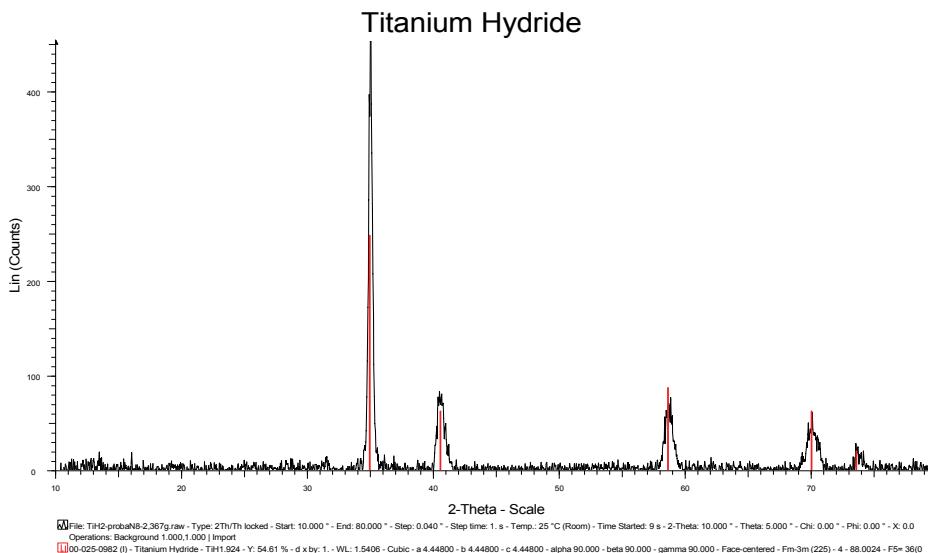


Fig.2. X-ray diffraction pattern of  $\text{TiH}_2$  sample obtained by hydrogenation of Ti.

### Particle size analysis

Since our interest lays in production of Ti- and  $\text{TiH}_2$  powders, samples of the hydrogenated Ti-shavings were subjected to particle size analysis. The experiments were carried on Shimadzu Centrifugal Particle Size Analyzer - SA - lp2, type 20. The results obtained are summarized in Table 1. As seen, the bulk quantity (~93%) of the powder particles diameters is below 30  $\mu\text{m}$ . In other words, the results show that the obtained  $\text{TiH}_2$  powder, respectively the obtained after dehydrogenation Ti-powder could be directly used, without additional milling. As mentioned above, in case of specific requirements of the powder grade, an additional milling stage should be introduced.

Tab.1. Particle size composition of the  $\text{TiH}_2$  powder.

Particle's diameter [ $\mu\text{m}$ ]	Fraction [%]	Particle's diameter [ $\mu\text{m}$ ]	Fraction [%]
> 40	0	5-6	4.8
30-40	7.4	4-5	4.9
20-30	22.0	3-4	5.0
10-20	32.6	2-3	4.6
8-10	7.3	< 2	3.4
6-8	8.0		

### Thermal analysis

The kinetics of the  $\text{TiH}_2$  decomposition to Ti and  $\text{H}_2$  was studied on a DTA, Setaram-LABSYSS-evo, combined with mass spectrometer. The DTA experiments were carried out at five different heating rates, 5, 8, 10, 12 and 15 K/min in argon atmosphere from room temperature to 800°C. Figure 3 shows two DTA-scans of the  $\text{TiH}_2$  decomposition, taken at two different heating rates 5 and 12 K/min. These DTA-scans clearly show that the decomposition passes through two stages i.e. that the resulting outcome of the decomposition are two different products. Taking into account the

equilibrium phase diagram of the Ti-H system [4] one could draw the conclusion that these two reactions should be  $TiH_2 \rightarrow Ti[H] \rightarrow Ti^\alpha + H_2$  and  $TiH_2 \rightarrow Ti[H] \rightarrow Ti^\beta + H_2$ . One should also keep in mind that for hydrogen concentrations below ~10 at.%, and temperatures up to 1100 K the stable Ti lattice is hexagonal A3, which means that during dehydrogenation transition of  $Ti^\alpha \rightarrow Ti^\beta$  is also possible.

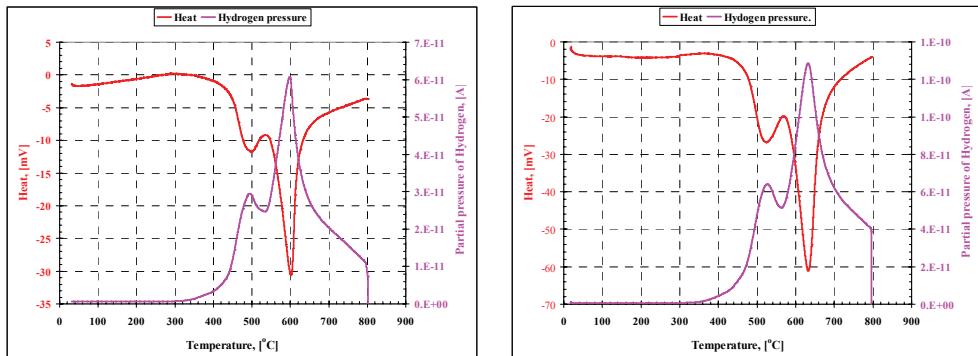


Fig.3. DTA scans of the decomposition of  $TiH_2$  at two different heating rates: (a) - 5 K/min and (b) - 12 K/min.

## MODELING OF THE DEHYDROGENATION KINETICS AND APPLICATION OF THE OBTAINED RESULTS

### Theory

The experiments carried out show that the productivity of the hydrogen decrepitation method studied is directly dependent on the  $TiH_2$  decomposition rate, i.e. on the rates of the reactions  $TiH_2 \rightarrow Ti[H] \rightarrow Ti^\alpha + H_2$  and  $TiH_2 \rightarrow Ti[H] \rightarrow Ti^\beta + H_2$ . Therefore, development of a model, quantifying the rate of these reactions, would be highly desirable. It can be easily shown that the relatively simple rate equation  $\dot{\Psi}_{TiH_2} = -\sum_{k=1}^2 \dot{\Psi}_k = -\sum_{k=1}^2 \frac{aS_k v_k}{V_0}$  could serve this purpose, providing that growth rates,  $v_k$ , of

$\alpha$ -Ti and  $\beta$ -Ti from  $TiH_2$  are known. Here  $\dot{\Psi}_k$  is the volume fraction transformation rate of  $\alpha$ -Ti ( $k=1$ ) and  $\beta$ -Ti ( $k=2$ ),  $a$  is a geometric factor depending on the geometry of the growing phase, taken in the calculations below equal to 2,  $S_k$  is the integral surface of the  $k$ -th precipitating phase and  $V_0$  is the volume of the matrix powder particles. In the research here,  $v_k$ , is accounted for by a set of equations combining the growth rate of the new phases,  $v_k$ , with the chemical compositions of the matrix  $C_H^{TiH_2}$ ,  $C_{Ti}^{TiH_2}$  and the precipitating phases,  $C_{Ti}^{Ti^\alpha}$ ,  $C_H^{Ti^\alpha}$ ,  $C_{Ti}^{Ti^\beta}$ , and  $C_H^{Ti^\beta}$  [5]:

$$\mu_H^{TiH_2} - \mu_H^{Ti^\alpha} = -RT \ln \left( 1 - \frac{v_1}{v_{01}} \right) - \frac{v_1}{v_{01}} (\mu_{Ti}^{TiH_2} - \mu_H^{TiH_2}) C_{Ti}^{Ti^\alpha}$$

$$\begin{aligned}
 \mu_{Ti}^{TiH_2} - \mu_{Ti}^{Ti^\alpha} &= -RT \ln \left( 1 - \frac{v_1}{v_{01}} \right) - \frac{v_1}{v_{01}} (\mu_H^{TiH_2} - \mu_{Ti}^{TiH_2}) C_H^{Ti^\alpha} \\
 C_H^{Ti^\alpha} + C_{Ti}^{Ti^\alpha} &= 1 \\
 \mu_H^{TiH_2} - \mu_H^{Ti^\beta} &= -RT \ln \left( 1 - \frac{v_2}{v_{02}} \right) - \frac{v_2}{v_{02}} (\mu_{Ti}^{TiH_2} - \mu_H^{TiH_2}) C_{Ti}^{Ti^\beta} \\
 \mu_{Ti}^{TiH_2} - \mu_{Ti}^{Ti^\beta} &= -RT \ln \left( 1 - \frac{v_2}{v_{02}} \right) - \frac{v_2}{v_{02}} (\mu_H^{TiH_2} - \mu_{Ti}^{TiH_2}) C_H^{Ti^\beta} \\
 C_H^{Ti^\beta} + C_{Ti}^{Ti^\beta} &= 1
 \end{aligned} \tag{1}$$

Here  $\mu$  is the chemical potential,  $v_{0k}$  is defined as  $v_{0k} = v_{0k}^T \exp\left(-\frac{Q_k}{RT}\right) \exp\left(-\frac{\Delta G^\gamma}{RT}\right)$ ,  $Q_k$  is the growth rate activation energy,  $\Delta G^\gamma$  is the Gibbs energy of the growing phase  $\gamma$  ( $\gamma=a\text{-Ti}, \beta\text{-Ti}$ ),  $v_{0k}^T$  is a kinetic coefficient typical for every growing phase,  $T$  is the temperature and  $R$  is the universal gas constant. Remind that  $\text{TiH}_2$  is not a chemical compound, but phase with limited solubility of one of the components, H, and that its real composition is  $\text{TiH}_x$  (here  $x \approx 1.924$ ).

The equations above are solvable if  $v_{0k}^T$  and  $Q_k$  for every of the reactions studied are known. Usually, the value of  $v_{0k}^T$  is evaluated from the following expression:  $v_{0k}^T = d\nu$  [6], where  $d$  is the interatomic distance in the metal's lattice and  $\nu$  is the vibrational frequency of the atoms in the lattice. A typical values for  $d$  and  $\nu$  in metals are:  $d \sim 2.5\text{\AA}$  and  $\nu \sim 10^{12} \text{ s}^{-1}$ , thus yielding for  $v_{0k}^T \approx 10^2 \text{ m/s}$ . Regrettably, the value of the activation energy  $Q$ , could not be derived from first principles, as above, and is usually determined from experiments using some optimization method [7]. For determination of the activation energy  $Q$ , in the present research the heat fluxes as a function of time  $J_{\exp}(t)$ , measured in the DTA experiments above, are adopted, utilising a non-linear least square method described in [7]. The method minimizes the deviations between experimental quantities  $J_{\exp}(t)$  and their calculated counterparts  $J_{\text{calc}}(t)$ , using the following target function  $\Phi = (J_{\exp}(t) - J_{\text{calc}}(t))^2 \rightarrow \min$ . Thus, our task here is to define  $J_{\text{calc}}(t)$ . Taking into account equations defining the volume fraction transformation rates above, it can be easily shown that  $J_{\text{calc}}(t) = \sum_{k=1}^2 \dot{\Psi}_k \Delta H_k = \sum_{k=1}^2 \frac{aS_k v_k}{V_0} \Delta H_k$ . Here  $\Delta H_k$  is the heat released as

a result of the reactions above.

The regression models, as a rule, vary the values of the parameters, in our case these are  $Q_k$ , until best fit between the calculated  $J_{\text{calc}}(t)$  and experimental  $J_{\exp}(t)$  data is achieved. For the purposes of the present research, determination of  $Q_k$ , a standard minimization procedure, based on the Levenberg-Marquardt method [7], and a computer program were developed and utilized. It should be noted that the model used does not account for the thermal effects resulting from the construction and calibration of the

calorimeter [8], which could lead to some discrepancy between the calculated and the measured fluxes.

### Results from the numerical experiments

Figure 3 shows the dependence of  $v_k / v_0$  as a function of temperature for different concentrations of hydrogen in  $\text{TiH}_x$  obtained after numerical solution of eqn.(1), by the Newton-Raphson method [7]. Thermodynamic data, for the system Ti-H, used in the calculation of the chemical potentials of the involved phases, is taken from Kun Wang et al. [9]. As seen from the figure, an increase of the temperature leads to decrease of the  $v_{\text{Ti}^\alpha} / v_0$  tending to zero at  $T > 800-900$  K and increase of  $v_{\text{Ti}^\beta} / v_0$ . These results explain the existence of two peaks, observed on the DTA scans.

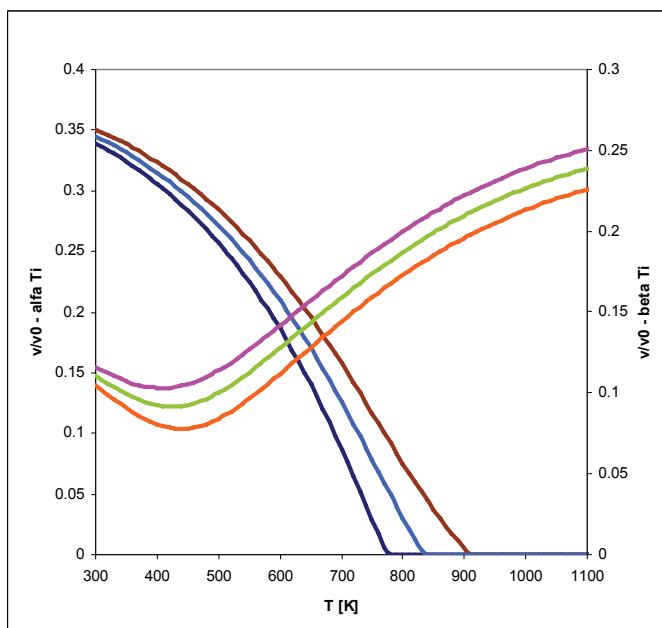


Fig.4. Relative growth rates  $v_k / v_{0k}$  vs. temperature, obtained for different concentrations of hydrogen in  $\text{TiH}_x$ . ( $\alpha$ -Ti: 0.35 - black; 0.375-brown; 0.3625-blue.  $\beta$ -Ti: 0.35-red; 0.375-pink; 0.3625-green).

Figure 4 shows the application of the Levenberg-Marquardt's non-linear least square method to minimization of the  $\Phi = (J_{\text{exp}}(t) - J_{\text{calc}}(t))^2$  target function. The observed discrepancies between the experimental and the calculated heat fluxes result from the simplified model used and because the model does not take into account the thermophysical processes taking place in the calorimeter [8]. The obtained growth rate activation energies of the  $\alpha$ -Ti and  $\beta$ -Ti phases from  $\text{TiH}_2$  are, respectively,  $Q^{\text{TiH}_2 \rightarrow \text{Ti}^\alpha} = 133.75 \text{ kJ/mole}$  and  $Q^{\text{TiH}_2 \rightarrow \text{Ti}^\beta} = 165.75 \text{ kJ/mole}$ .

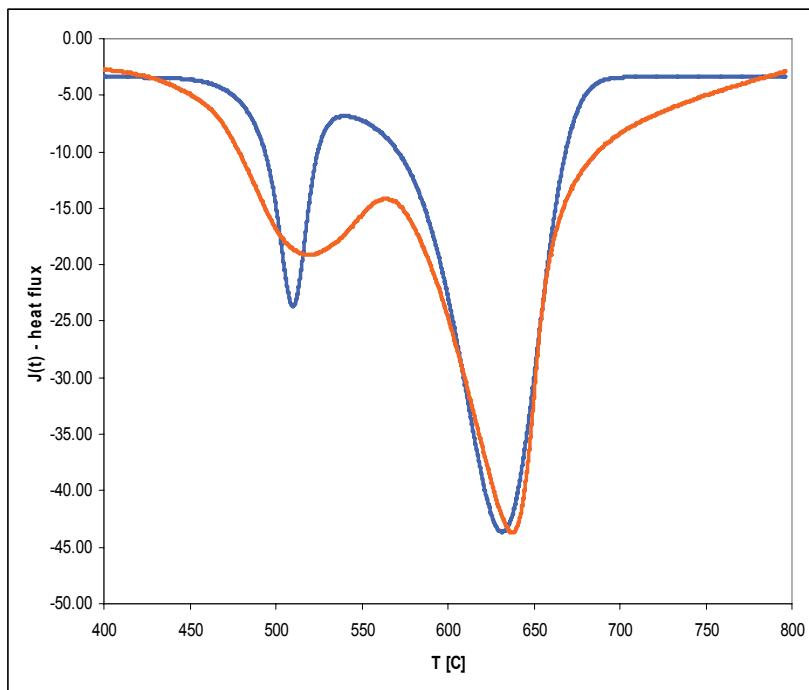


Fig.5. The calculated using the model described, heat flux,  $J_{\text{calc}}(t)$  (blue), (using the optimized values for  $Q^{TiH_2 \rightarrow Ti^\alpha} = 133.25 \text{ kJ/mole}$  and  $Q^{TiH_2 \rightarrow Ti^\beta} = 165.5 \text{ kJ/mole}$ , and heating rate of 12 K/min), compared with the experimental DTA scan taken at the same heating rate,  $J_{\text{exp}}(t)$  (red).

The values of the growth rate activation energies of  $\alpha$ -Ti and  $\beta$ -Ti phases from  $TiH_2$  obtained were used to study the dehydrogenation process, simulating different technological conditions, e.g. different heating rates, holding temperatures etc. and their influence on the dehydrogenation time. Some results from these simulations are shown in Fig.6. Obviously the temperature regime: heating with 1 K/min up to 600°C and holding at this temperature for about 1500 s (25 min) is the most favourable for complete decomposition of  $TiH_2$  and is preferable to the other two regimes shown.

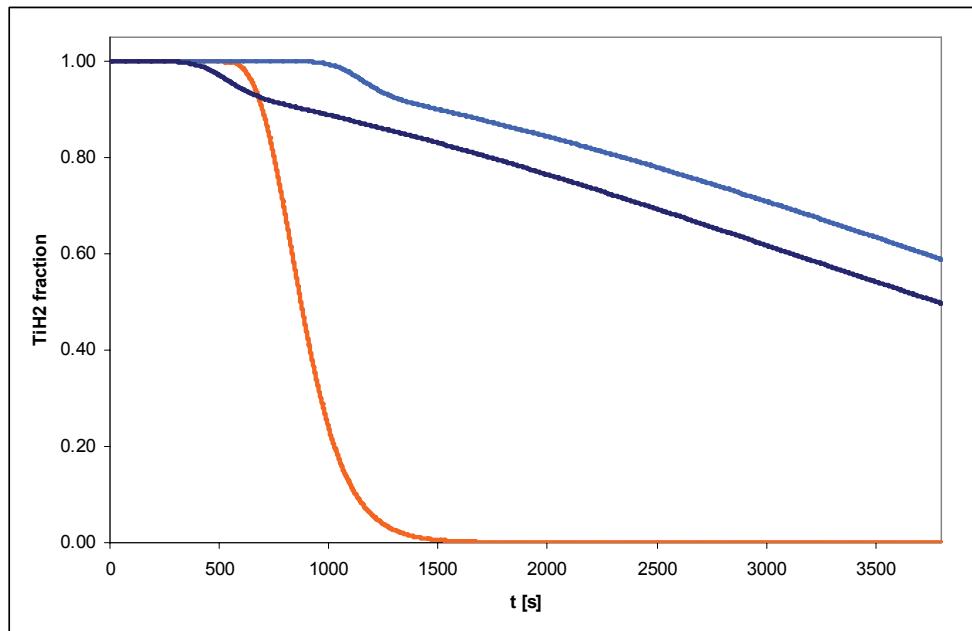


Fig.6. Influence of the applied temperature regime: heating rate 1 K/s, holding at 600°C (red); heating rate 0.75 K/s holding at 500°C (blue) heating rate 2 K/s, holding at 500°C (black), on the time for complete decomposition of TiH<sub>2</sub>.

## CONCLUSIONS

A prospective method for utilization of the Ti-wastes, turning them, through a cyclic hydrogenation-dehydrogenation process, firstly into TiH<sub>2</sub> and subsequently into Ti-powder, is described and the processes along the technological path studied.

The analyses of the intermediate product, TiH<sub>2</sub>-powder, carried after hydrogenation, show that the intermediate product, the TiH<sub>2</sub> powder, is ready for application as produced: The particle size analysis, show that 93% of the powder particles sizes are below 30 µm and the X-ray analysis confirmed that the method of hydrogenation chosen, based on the Ti decrepitation of the Ti waste in hydrogen atmosphere, is reliable and leads to complete transformation of the Ti waste into TiH<sub>2</sub>.

Using a simplified model of the TiH<sub>2</sub> decomposition to α-Ti and β-Ti, combined with Levenberg-Marquardt's non-linear least square method of minimization, the valuable for the practical application of the method growth rate activation energies of the reactions:  $TiH_2 \rightarrow Ti[H] \rightarrow Ti^\alpha + H_2$  and  $TiH_2 \rightarrow Ti[H] \rightarrow Ti^\beta + H_2$ , were obtained from the DTA experiments, yielding:  $Q^{TiH_2 \rightarrow Ti^\alpha} = 133.25 \text{ kJ/mole}$  and  $Q^{TiH_2 \rightarrow Ti^\beta} = 165.5 \text{ kJ/mole}$ .

The obtained growth rate activation energies were used to simulate the last stage of the method, the process of dehydrogenation of TiH<sub>2</sub> powder to Ti-powder, and the optimization of the dehydrogenation technology.

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