

# Oxidation of Zirconium and Zirconium Hydride Powders during Programmed Heating in Air

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**Abstract** The data on oxidation of zirconium and zirconium hydride powders during heating in air to 1373K at a rate of 10K/min were obtained using thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry of reaction products. The specific heat release during oxidation of hydride powder was found to decrease due to the endothermic character of the decomposition reaction and the fact that the hydrogen combustion reaction takes place in the gaseous phase. The phase formation features in the processes of powders oxidation, their connection with the metal and hydride reactivity and the morphology of the reaction products were determined by the X-ray diffraction method.

**Keywords** Powdered Zirconium, Zirconium Hydride, Oxidation, Specific Heat Release, Phase Formation

## 1. Introduction

The scientific foundations of synthesis and application of metal hydrides were developed in fundamental reviews on the structure and properties of these unique materials [1, 2, 3]. Metal hydrides have found wide application as efficient energy carriers [4], they are also used in nuclear power engineering, aerospace and other fields of engineering [5]. The active interest in them is caused by the prospect of using hydrogen sources in mobile and stationary devices [6]. In addition, powders of metals and their hydrides occupy a special place as combustibles in the development of new mixtures of high-density mixed-mode rocket fuels to expand the possibilities for regulating ballistic efficiency [7-8]. In this case, a great interest in transition metal hydrides is due to the fact that during their decomposition, the liberated hydrogen increases the volume of gaseous products in the combustion chamber, positively affecting the value of the specific impulse [9].

This is confirmed by the results of work [10], where the energy capabilities of mixed solid rocket fuels containing

zirconium and Zr hydride powders are calculated. In [10], it is shown that the introduction of metallic zirconium or its hydride into the mixture compositions increases the effective specific impulse and payload of the rocket.

The experimental data on the properties of hydride powders interacting with oxidizing media during heating to temperatures above 1273K are extremely limited. There is available information about the effect of hydrogen on the dynamics of titanium hydride oxidation [11], the effect of the decomposition kinetics on the phase composition of zirconium hydrides [12], the adsorption and desorption kinetics on zirconium hydride [13] and the equilibrium in the Zr-H system [14]. The structure of  $ZrH_2O_{0.11-1.10}$  and  $ZrH_{1.0}O_{0.14-1.90}$  oxyhydrides obtained by oxidation of zirconium hydride was studied in [15]. It is also noted [11] that it is necessary to study the oxidation of hydrogen released during heating of hydrides and its effect on the oxidation of hydrides.

In this paper, we present the experimental results of the study of oxidation of zirconium metal powders and zirconium hydride during programmed heating in air to 1373K carried out to obtain the information about the effect of hydrogen on the interaction of hydride with atmospheric oxygen.

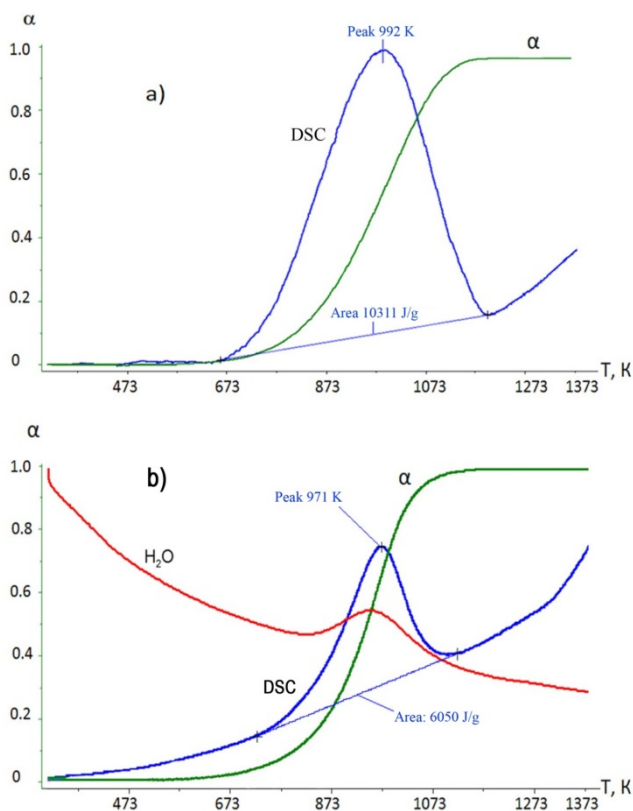
## 2. Synthesis Technique of Hydride and Attesting of Powders Properties

A chemical analysis of metallic zirconium, which was used to synthesize hydride and study the oxidation of powders, was performed using inductively coupled plasma mass spectrometry on an Elan 9000 instrument (Perkin Elmer SCTEX). The zirconium content determined by this method was not less than 99.9%. The metal was saturated with hydrogen from the gas phase and purified by passing through a palladium filter. Before saturation, the metal was annealed for 1 hour at a temperature of at least 973K in a vacuum furnace equipped with a tungsten heater. The saturation was carried out in the same furnace by

decreasing the temperature stepwise from 973K to 600K. When this temperature was reached, an excess hydrogen pressure of 0.5 atm was generated in the furnace volume and the heating ceased. The furnace was cooled to room temperature, while the hydrogen pressure did not drop below 0.2 atm. The hydrogen concentration was determined by the weight method using a Shimadzu AUV 120 analytical balance by weighing the zirconium sample before and after saturation, and it should correspond to a composition close to  $ZrH_{1.95}$ .

The X-ray analysis was performed on a Shimadzu diffractometer ( $CuK_{\alpha}$ -radiation) using the Powder Diffraction File database YCPDSDICDD (PDF2). Oxidation of the powders was studied on a NETZSCH STA 409 PC/PE device at a heating rate of 10 K/min in thin-walled corundum crucibles at 1373K in air on samples of mass 15mg. High-temperature stability of the hydride was studied in pure argon atmosphere with the same analyzer combined with a mass spectrometer, QMS 403 C. The particle morphology was studied with a JEOL JSM-6390LA raster microscope, the specific surface was analyzed on a Gemini VII 2390V1.03 device by thermal desorption of nitrogen.

### 3. Results and Discussion

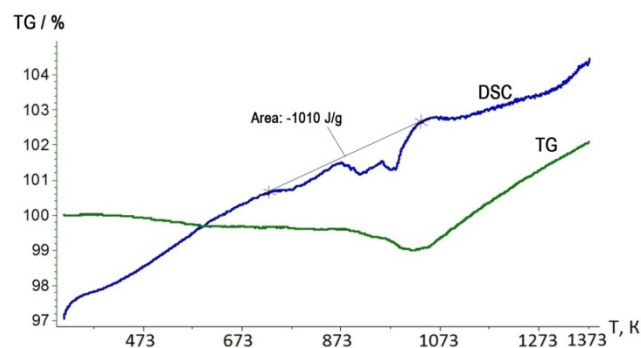


**Figure 1.** Changes in the conversion degree ( $\alpha$ ), DSC curves (specific heat release) and water output ( $H_2O$ ) during the oxidation of (a) zirconium metal and (b) zirconium hydride

Figure 1 shows the conversion degree ( $\alpha$ ) and DSC

curves obtained during oxidation of the powder samples heated to 1373 K. For zirconium hydride, there is also a water output curve plotted during programmed heating in air.

It is seen from Fig. 1a that an increase in the conversion degree (calculated taking into account the oxidation of zirconium to  $ZrO_2$ ) is observed already at temperatures of about 660 K. It should be noted that the increase in the conversion degree of the sample in this case coincides with the onset of heat release (Fig. 1a). In case of hydride powder, the onset of heat release occurs at a higher temperature (723 K). This is due to the endothermic nature of the hydride decomposition process. Figure 2 shows the TG and DSC curves of a hydride sample of the same mass (15 mg) heated in an argon flow to 1373 K at a rate of 10 deg/min. As follows from Fig. 2, in spite of a high degree of Ar purity (99.998%), about 3% of zirconium are oxidized during heating to 1373 K.



**Figure 2.** Changes in the mass (TG) and DSC curve in the process of heating of zirconium hydride powder in an argon flow.

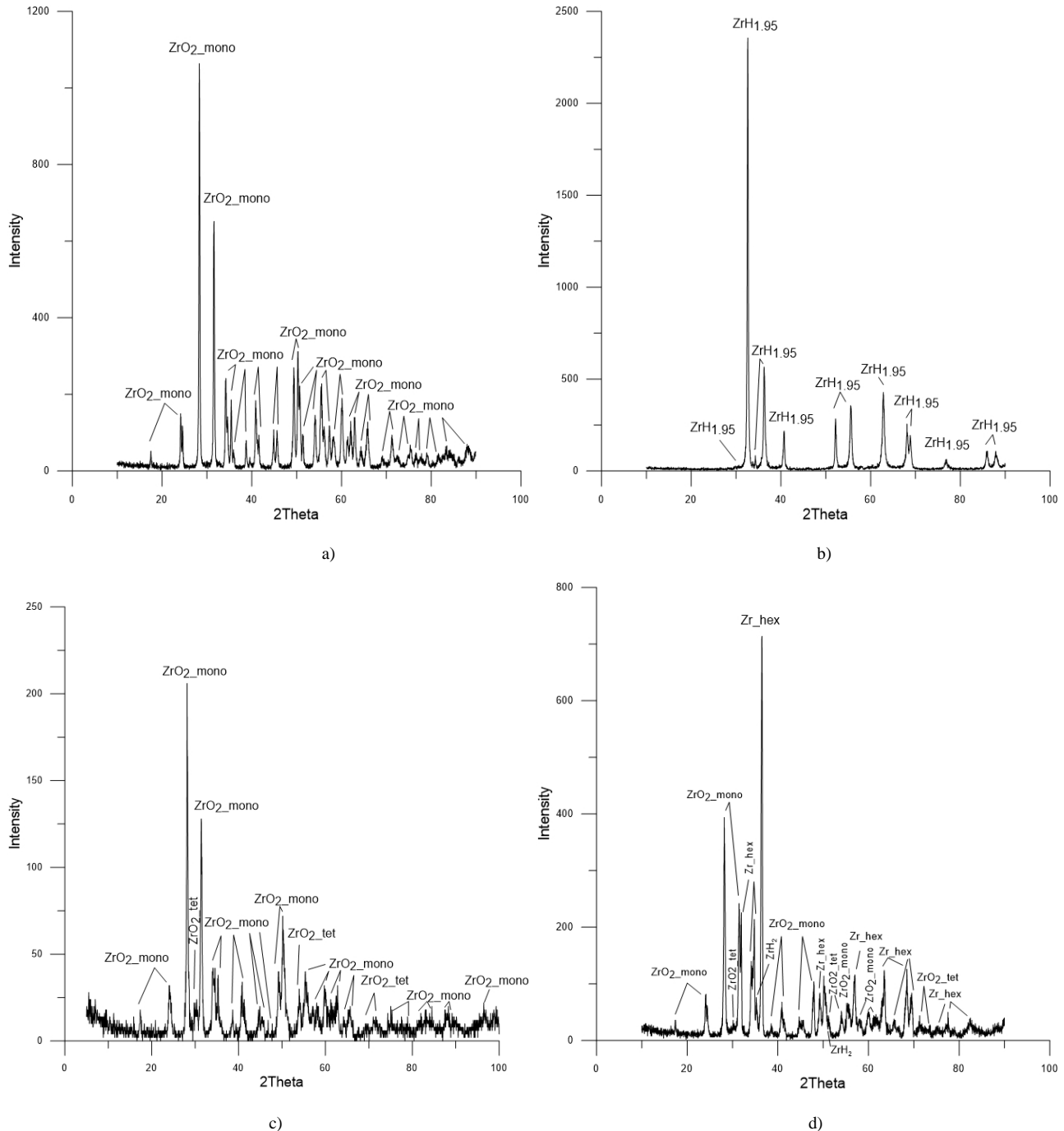
In [16], the decomposition of zirconium hydride was studied during heating in an argon flow at a rate of 20deg/min in the temperature range from room temperature to 1273K. It was found that the decomposition of  $ZrH_2$  is accompanied by three endoeffects at 773, 1003, and 1073 K. However, in this case [16], superposition of partial metal oxidation due to residual oxygen in the carrier gas was observed. For titanium hydride [11], the metal was oxidized during the decomposition of the hydride although He was additionally purified using a standard gas purification device. One of the recent papers [17] showed that the thermal destruction of titanium hydride passes through three stages, with similar activation energies, in the temperature range 673-1073 [17]. It follows from the data presented in [16, 17] that the decomposition intervals for Ti and Zr hydrides are sufficiently close. Comparison of Figure 1b and Figure 2 indicates that the evolution of hydrogen from zirconium hydride coincides with the interval, in which water is formed by interaction with atmospheric oxygen. During heating of zirconium hydride in air, the maximum heat release rate is reached at 971K. This temperature is somewhat lower than the temperature for metallic zirconium powder (992K) (Figure 1a) and it is

probably related to hydride decomposition, which facilitates the oxygen penetration into the metal surface formed on the phase boundaries.

The comparison of the DSC curves shows that the specific heat release (the area under the curve) during oxidation of the metal is much higher than that during oxidation of a hydride sample of the same mass (15mg). It might be assumed that they should be close to within 2%, since the amount of zirconium in the hydride is only two weight percent lower than in the sample of metallic

zirconium. However, the specific heat release during zirconium oxidation is  $-10311\text{J/g}$ , and in the case of hydride it is  $-6050\text{J/g}$ .

The X-ray diffraction analysis of the oxidation products of Zr and zirconium hydride powders formed upon heating to 1373 K reveals a monoclinic  $\text{ZrO}_2$  oxide (Figure 3a) [18]. Figure (3b) demonstrates an XRD pattern of the initial zirconium hydride obtained in the present study.



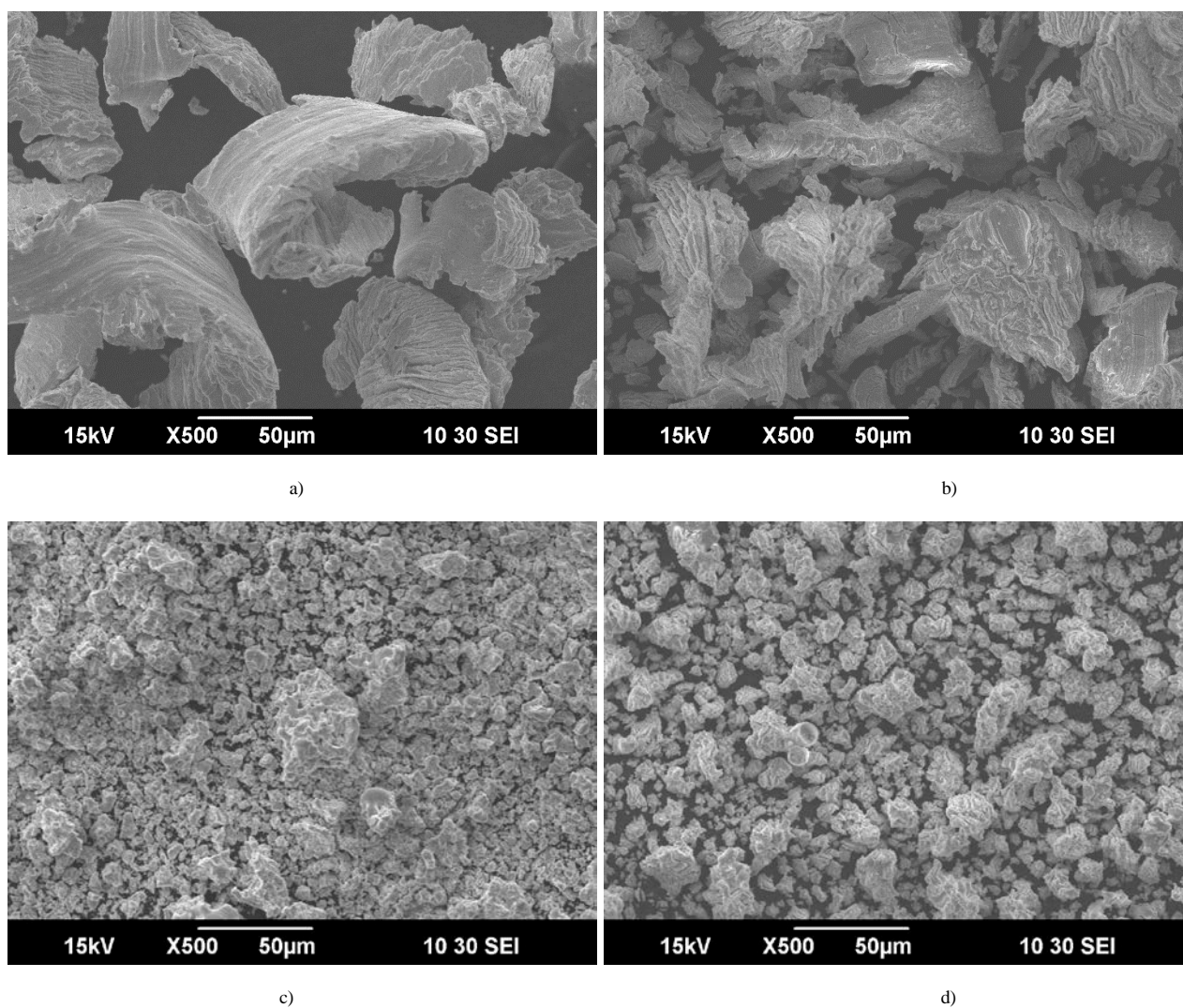
**Figure 3.** The diffraction patterns of powders at different stages of oxidation: a) Zr and Zr-H heated to 1373 K; b) Zr - initial hydride; c) Zr heated to 973; d)  $\text{ZrH}_{1.95}$  heated to 1373 K

According to the weight analysis, the synthesized hydride should correspond to the composition close to  $ZrH_{1.95}$ . The comparison of the obtained X-ray diffraction pattern and literature data gives a complete agreement with the results for the sample synthesized from high-purity metal and hydrogen. This hydride has a composition of  $ZrH_{1.95}$  with a tetragonal structure.

To explain the difference in the specific heat values during the oxidation of powders, the XRD analysis of the phase composition of Zr and zirconium hydride samples heated in air at a rate of 10K/min to 973K (close to the maximum on the DSC curve in Fig. 1b) was carried out. The results of XRD analysis showed a difference in the phase composition of the samples.

In the case of metallic Zr, the sample contains two oxide phases (Fig 3c): monoclinic  $ZrO_2$  - 68 wt.% and tetragonal

$ZrO_2$  - 32 wt.%. The sample  $ZrH_{1.95}$  in this case has four phases (Fig. 3d). Figure 3d shows that in addition to the above-mentioned oxide phases, the products of zirconium hydride oxidation contained hexagonal Zr and zirconium hydride  $ZrH_2$ . Such phase composition is indicative of difficulties in diffusion during hydride oxidation. They are probably related to barrier properties of oxides hampering the decomposition of hydride and hydrogen combustion in the gas phase, which requires more oxygen. For combustion of 1 kg of hydrogen, 8 kg of oxygen are required, while for zirconium the required amount of oxygen is 0.35 kg/kg [19], which is almost 23 times smaller. Combustion of hydrogen slows the oxygen transfer to the surface of metallic zirconium. This reduces the efficiency of oxidation, and the resulting water should be removed from the reaction space, which also leads to heat losses.



**Figure 4.** The morphology of powder particles: a) initial Zr; b) oxidized Zr heated to 1373 K; c)  $ZrH_{1.95}$ ; d)  $ZrH_{1.95}$  heated to 1373 K

The heat release activity during oxidation of Zr and zirconium hydride powders is reflected in the morphology and specific surface area of the particles. From the SEM images of particles (Figure 4) it can be seen that the morphology changes more significantly during zirconium heating (Figure 4a, b). The oxidation products in this case acquire a pronounced lamellar shape (Figure 4b). For the hydride (Figure 4c, d), the changes are not so pronounced. The specific surface area of Zr sample after heating in air to 1373 K increases from  $0.156 \pm 0.02 \text{ m}^2/\text{g}$  to  $0.847 \pm 0.02 \text{ m}^2/\text{g}$  (more than 5 times), while for the hydride powder from  $0.557 \pm 0.01 \text{ m}^2/\text{g}$  to  $1.143 \pm 0.05 \text{ m}^2/\text{g}$  (twice).

Probably, more active heating of metallic sample, due to oxidation, enhances the role of thermal stresses between the interfaces of newly formed phases, which can cause cracking and appearance of new oxygen-accessible surfaces.

## 4. Conclusions

Using DSC it was determined that the specific heat release during oxidation of zirconium metal powder in air with a heating rate of 10 K/min to 1373 K is -10311 Joules/gram, and for zirconium hydride it is -6050 Joules/gram.

The formation of water in the process of zirconium hydride oxidation (hydrogen combustion) impedes the reaction of oxygen with the metal surface, because it occurs in the gas phase and requires more oxidant.

The intervals of water formation and hydride decomposition coincide with the active metal oxidation interval, which affects the character of heat release during the reaction.

A correlation was found between the oxidation activity (heat release), the morphology and the specific surface of the initial particles and their oxidation products.

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