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Effect of hydrogen content on hydrogen desorption kinetics of titanium hydride

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ABSTRACT

Thermal desorption behaviours of titanium hydride powders with different hydrogen contents were studied using simultaneous TG-TDS measurements at a heating rate of 10 °C/min. The as-received TiH_2 powders were pre-heated to different temperatures and subsequently cooled to room temperature in argon. The XPS depth profile analysis demonstrated that after heat treatments, the relative oxygen concentrations decreased slightly compared with that of as-received TiH_2 powder. The changes in the TDS spectra for the pre-heat treated TiH_2 powders were primarily associated with the residual hydrogen contents. The origins of the observed TDS peaks and shoulders were attributed to the equilibrium hydrogen pressures of the phase regions that the decomposition reaction passed through. The hydrogen content was demonstrated to be essential for the phase transformation sequence during titanium hydride decomposition.

1. Introduction

Titanium hydride (TiH_2) is widely employed as foaming agent to produce Al alloy foams [1–6]. The manufacturing process involves the addition of TiH_2 powder into molten Al, generating hydrogen gas to foam the melt. A major drawback in this technique is the temperature mismatch between the Al melting point and decomposition temperature of TiH_2 powder. Premature gas escape from TiH_2 is believed to lead to poor foam expansion and cause a lack of pore uniformity, resulting in non-isotropic and non-reproducible properties of the foams [7,8].

To slow the decomposition kinetics of TiH_2, pre-heat treatment of the hydride in air to temperatures between approximately 400 and 500 °C has been used by many researchers [9–11]. During such thermal treatments, an oxide layer is formed on the surface acting as a diffusion barrier to delay the release of hydrogen. Conversely, pretreatments lead to losses in the hydrogen content in hydride. It was thought that both the thickness of titanium dioxide and residual hydrogen content control the kinetics of hydrogen desorption. Although extensive studies of the decomposition of pre-heat treated TiH_2 and their effect on the formation of Al foams have been performed, the mechanisms interfering with gas evolution are not yet known well [12], especially the influence of the hydrogen content.

In our previous work [13], we examined the effect of the heating rate on the kinetics of hydrogen release from untreated TiH_2 and indicated how the peaks of H_2 release are related to the phase transformation steps. In this work, we study the influence of hydrogen content on hydrogen desorption behaviours. For this purpose, the as-received TiH_2 powders were heated to different temperatures and later cooled to room temperature. The pre-treatments were conducted in argon atmosphere to exclude the influence of oxygen. The decompositions of pre-treated samples were characterized by simultaneous thermogravimetry and thermal desorption spectroscopy (TG-TDS) analysis, which was useful to obtain complete information on the thermodynamic and kinetic properties of metal hydrides [14–19].

2. Experimental

The as-received commercial TiH_2 powder (99% pure), with a particle size ranging from less than 1 μm–20 μm, was characterized using scanning electron microscope (ProX, Phenom, Netherlands) and a laser particle size analyser (1064 L, CILAS, France). The pre-heat treatments and decompositions of TiH_2 were conducted by TG-TDS (IGA-003, Hiden, UK). In IGA-003, an ultra-sensitive microbalance of resolution 0.2 μg was mounted in the thermostated heatsink with high precision temperature control. The sample was

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loaded in a quartz sample container and suspended from the hangdown quartz hook connected to the microbalance. Before the measurements, the quartz reactor tube was vacuumed up to 10^{-5} Pa. The emitted H_2 was measured using a quadrupole mass spectrometer (QMS) connected to IGA-003 through a thin capillary tube. The experimental apparatus and procedures were described in detail in previous publications [13,20,21]. The samples with a weight of nearly 100 mg were heated up at a linear temperature ramp of 10 °C/min to the chosen temperatures, namely, 526, 572, 606, 659, 722 and 800 °C, and then cooled to room temperature at a rate of rough 40 °C/min. The residual H/Ti atom ratios were calculated from the mass losses obtained from TG measurements. The TG-TDS measurements of as-received TiH_2 powder and TiH_2 powders quenched from different temperatures were performed at the heating rate of 10 °C/min from room temperature to 960 °C. All pre-heat treatments and decomposition measurements were performed under pure Ar gas (≥99.999%) flow conditions with a flow rate of 50 ml/min.

The phase structures were identified by XRD (Rigaku D/Max-2400) using Cu-Kα radiation at a scanning rate of 4°/min with a generator voltage of 40 kV and current of 150 mA. All XRD measurements were performed at room temperature and the phase compositions were determined on the basis of JCPDS files provided by the International Center for Diffraction Data. Quantitative phase analysis was performed using the Rietveld refinement method. The experimental patterns were fitted with a linear combination of the theoretical patterns and of the background using optimized values of lattice parameters and parameters of broadening the diffraction maxima of phases [22].

The surface characterizations of the as-received and pre-treated TiH_2 powders were analysed using X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos) with a monochromatic Al Kα (1486.6 eV) line of an X-ray source. XPS depth profiles were determined using an argon sputtering gun. A rough sputtering rate was estimated to be 0.07 nm/s on a Ta_2O_5 standard. The photoelectron peaks were fitted using a mix of Gaussian and Lorentzian forms, and the background was determined by the Shirley method.

3. Results and discussion

3.1. Powder characteristics

Fig. 1 shows particle size distribution analysis and the SEM image of the as-received TiH_2 powder. The mean size of the powder is approximately 8 μm. The morphology is represented by irregular polyhedrons with sharp edges and cleavage planes.

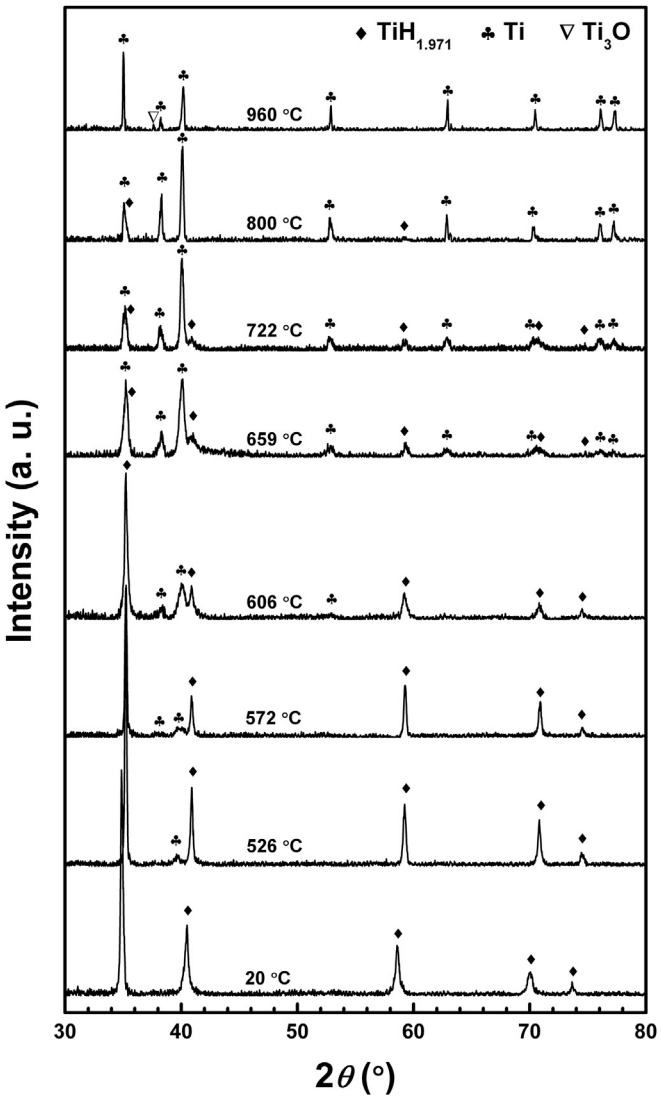

Fig. 2. XRD spectra of as-received TiH_2 powder and TiH_2 powders quenched from different temperatures.

The phase compositions of samples heated to different temperatures were determined by XRD after cooled to room temperature, which are marked in Fig. 2. The corresponding XRD data are

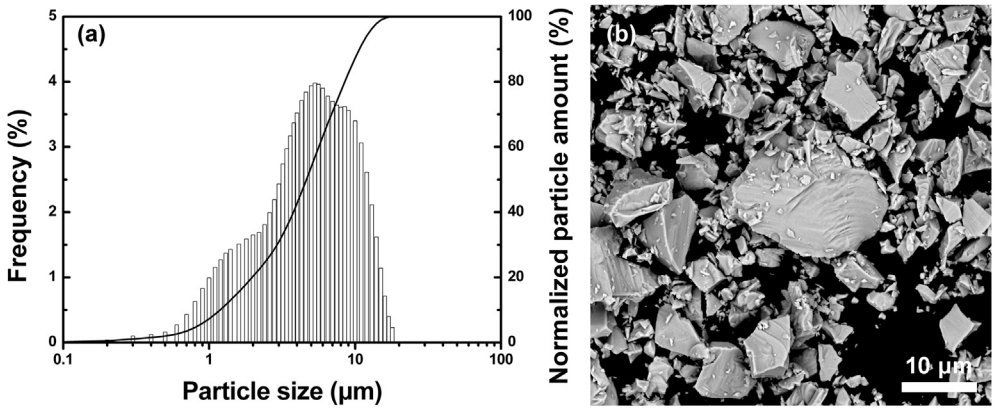

Fig. 1. Particle size distribution of as-received TiH_2 powder (a) and its corresponding SEM image (b). (The histogram in (a) indicates the amount of the particle at the size and read from the left vertical axis. The line indicates the total amount of the particle up to the size and read from the right vertical axis.).