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High ramp rate thermogravimetric analysis of zirconium(II) hydride and titanium(II) hydride

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ABSTRACT

Zirconium and titanium hydride are utilized in liquid phase metal foam processing techniques. This application results in immediate exposure to molten metal and almost immediate decomposition at high temperatures. Most decomposition characterization techniques utilize slow heating rates and are unable to capture the decomposition behavior of hydrides under foam processing conditions. In order to address this issue a specialized high ramp rate thermogravimetric analyzer was created from a xenon arc image refiner. In addition to thermogravimetry, complimentary techniques including X-ray diffraction and scanning electron microscopy were used to characterize hydride decomposition and compare the results to literature. Hydrides were partially oxidized and separated into particles size ranges to evaluate the influence of these factors on decomposition. Oxidizing treatments were found to decrease decomposition rate only at temperatures below 933 K (660 °C) while particle size effects appeared to be negligible. Several improvements to the unique TGA apparatus presented in the current work are suggested to allow reliable kinetic modeling and analysis.

1. Introduction

Titanium hydride and zirconium hydride are used in laboratory and industrial scale aluminum foaming processes due to the proximity of their decomposition temperatures to aluminum's melting point [1–3]. The gas evolution rate from these hydrides affects the foam pore morphology [4]; therefore it is important to understand the kinetics of hydrogen evolution from these compounds. There are several routes for utilizing hydrides in foam production, the choice of which determines the thermo-temporal profile governing hydride decomposition. For example, the thermal decomposition metal foam production method, recently studied by Kim [3], and Licavoli [4], involves casting molten aluminum upon titanium hydride placed upon a copper chill plate resulting in hydride heating rates on the order of 18,000 K/min, according to thermocouple data from foaming experiments.

Several studies have been conducted utilizing a spectrum of analytical techniques to characterize the decomposition of hydrides subjected to various treatments [5–8]. These studies examine hydride decomposition kinetics using very slow heating rates (10–40 K/min) due to limitations of the analytical techniques [7–9]. Unfortunately, these low heating rates often prevent the complete characterization of decomposition kinetics since the reaction has proceeded significantly during heating to the foam-processing temperature.

In the current study, both titanium hydride and zirconium hydride were decomposed using a modified xenon arc image apparatus with thermo-gravimetric instrumentation. This allowed for high temperatures to be reached rapidly before the decomposition reaction was complete. In addition to analyzing commercially pure titanium and zirconium hydride, an oxidizing treatment was applied to the titanium hydride and these powders were tested in the same fashion as above to evaluate the influence of oxide barriers on high temperature decomposition. Oxidation of hydride powders has been used to better control pore morphology in metallic foams, but kinetic data for oxidized hydride are also only characterized at low heating rates [5,7]. Since these powders have an additional oxide layer over most of their surface, and hydrogen transport through the oxides of zirconium and titanium is significantly slower than through pure metals [10,11], the overall decomposition rate should be significantly lower than that for the untreated powders.

2. Experimental methods

The as-received titanium hydride powders had nominal sizes of −325 mesh (<43 μm) and 1–5 μm and were purchased from Alfa

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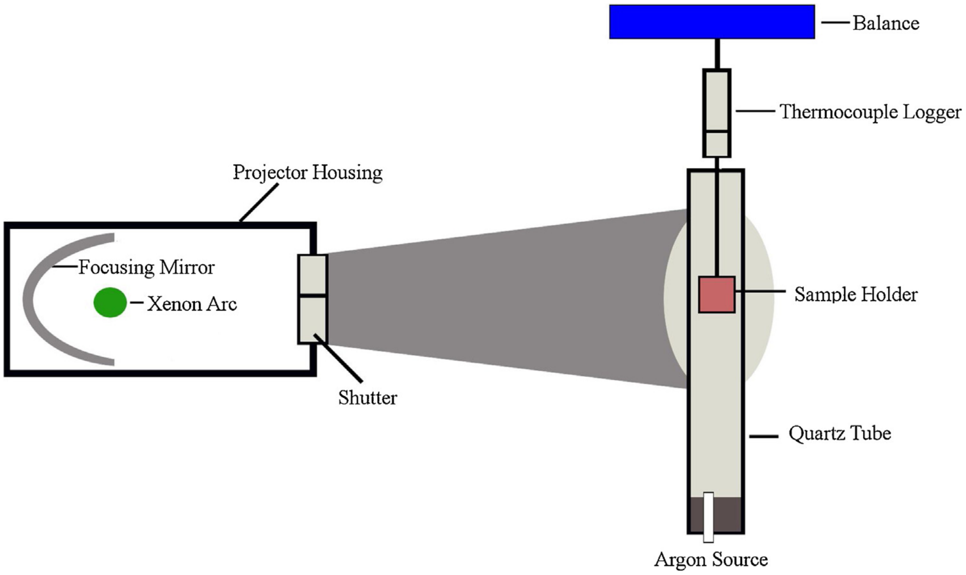

Fig. 1. Schematic of the xenon arc image thermo-gravimetric analyzer. Temperature control for samples was maintained by adjusting the shutter.

Aesar in purities of 98% on a metals basis. The zirconium hydride powder had a nominal particle size of −325 mesh (<43 μm) and was also from Alfa Aesar at a purity of 98% on a metals basis. The size distribution of the −325 mesh powders of titanium hydride and zirconium hydride was narrowed to 20–30 μm using dry micro-sieves. A portion of the two size ranges of titanium hydride were heat treated in air at 663 K (390 °C) for 30 min to form an oxide layer. All powders were stored in a desiccator until just before they were loaded into the TGA apparatus to reduce moisture absorption.

A high ramp-rate TGA apparatus was constructed utilizing a xenon arc-image projector as a heat source (Fig. 1). A 10 μg resolution balance was used to measure hydrogen mass loss of samples suspended from the bottom attachment hook. The balance was equipped with a fully automated traceable calibration function and had a repeatability of 100 μg. Mass readings were output using a HyperTerminal connection at a sampling frequency of 7.14 Hz. A battery-operated thermocouple logger was hung from the balance and sample holders were suspended by plugging into the thermocouple logger. The logger had a resolution of 0.5 K and an accuracy of ±1 K. High conductivity alloy 101 copper sample holders were fabricated from 25 mm tubing crimped at the bottom. A hole was drilled through the tubing diameter and thermocouple wire was threaded through the holes and welded so that the thermocouple junction was within the tube and in direct contact with the hydride powders.

The handmade thermocouple probes were dynamically calibrated against Omega brand KTIN-116G-24 type K thermocouples by attaching each thermocouple to a large slab of steel and allowing the slab to cool from 1073 K to 873 K (800–600 °C). The cooling curves were analyzed for divergence from one another and throughout the cooling process maximum differences were found to be no more than 5 K. The Omega brand thermocouples had a nominal read error of 0.75% of the signal output or 4.5–6 K error over the calibration range. A dynamic calibration was used due to the fact that no convenient calibration media was available for the 1073–873 K (800–600 °C) range used in thermal decomposition experiments.

Argon cover gas was flowed through a rubber stopper at the bottom of the fused quartz protective tube in order displace the ambient atmosphere and minimize both powder and sample holder oxidation. To calibrate for any weight change due to contaminant burn off from within the sample holder and cover gas convection, each empty sample holder was held at the test temperature for a period of 100 s prior to every test. The weight change was recorded and used as a correction factor when analyzing the hydride decomposition curves. After each calibration, the holder was cooled to a temperature of 298–323 K (25–50 °C) and powder was added to the sample holder. Titanium hydride samples were 1 ± 0.01 g while the zirconium hydride samples were 2 ± 0.01 g. These sample sizes are large compared to standard test specimens [12], but due to the resolution of the balance and maximum estimated hydrogen mass losses, this large mass was necessary. Such large sample sizes can introduce some inhomogeneity.

Table 1
Experimental test matrix for target hold temperatures.

Material	873 K (600 °C)	933 K (660 °C)	1003 K (730 °C)	1073 K (800 °C)
1–5 μm $TiH_{1.98}$	X	X	X	X
20–30 μm $TiH_{1.98}$	*1	X	*1	*1
Oxidized 1–5 μm $TiH_{1.98}$	X	X	X	*2
Oxidized 20–30 μm $TiH_{1.98}$	*1	X	*1	*1
$\mathbf{ZrH_2}$	*3	**X**	**X**	**X**

*1 – Preliminary results indicated identical behavior therefore no further tests were conducted.
*2 – Not tested due to potential sintering.
*3 – Slow kinetics limited the ability to test.

The manual shutter on the xenon arc image heat source was completely opened to rapidly heat the powder to target temperatures. The powder test temperature was maintained by partially closing the shutter to deflect part of the xenon arc image allowing the temperature control within 5 K of the target.

Test temperatures and times were chosen to match the processing temperature range and times for gasarite foam processing. A summary of the powders and various target hold temperatures is included in Table 1. Sintering of the 1–5 μm titanium powders and destruction of two sample holders occurred at 1073 K (800 °C), so this temperature was not used for further tests of titanium hydride. During preliminary testing, the oxidized and un-oxidized 20–30 μm powder showed nearly identical