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# Effect of Decomposition Kinetics of Titanium Hydride on the Al Alloy Melt Foaming Process

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The gas released from the titanium hydride decomposition is one of the key factors to influence the Al alloy melt foaming process. In this study, a set of decomposition kinetic equations of titanium hydride was acquired by separating its temperature programmed decomposition (TPD) spectrum, which was acquired by a special designed TPD apparatus with argon used as carrier gas and thermal conductivity cell as the detector. According to these equations, the decomposition and hydrogen release characteristics of titanium hydride at a fixed/elevated temperature are described quantitatively, which can be applied to forecast the Al alloy melt foaming process and furnish the theoretical basis for fabrication of three-dimensional complex shaped Al alloy foam.


## 1. Introduction

Metallic foam, in which gas bubbles with millimeter level size are separated by thin metal film, is a class of attractive materials and has promising application potential in the fields of aerospace, transportation, ship engineering and construction due to its unique combinations of physical, mechanical, thermal, electrical and acoustic properties[1–7]. Metal foam can be produced by variety of methods. Among them, melt foaming method[8–11], containing addition of a blowing agent, is especially attractive for commercial purpose because of its relatively low cost, and has been applied successfully to prepare Al alloy foam by using titanium hydride as the blowing agent[12–14]. Apparently, the hydrogen released from titanium hydride decomposition is regarded as the driving force leading to foaming Al alloy melt. So, the decomposition kinetics of titanium hydride directly determines Al alloy melt foaming process and is a key factor for controlling melt pore structure evolution.

So far, thermal gravity analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermal desorption spectroscopy (TDS)[15–18] have been applied to investigate the decomposition behaviors of titanium hydride and to reveal its decomposition kinetics. But, up to now, all the results are semi-quantitative or qualitative. Thus, in order to reveal the decomposition behavior of titanium hydride, in this study, a specially designed temperature programmed decomposition (TPD) apparatus was introduced first. And then, the TPD spectrum of titanium hydride, which was achieved by using the TPD apparatus, was separated and simulated to acquire a set of kinetic equations. According to these kinetic equations, the relationships between the decomposition rate/decomposition quantity of titanium hydride and time under different heating conditions were calculated, which can be used to predict the Al alloy melt foaming process. Moreover, the feasibility of fabricating three-dimension complex shaped Al alloy foam is proven according to these kinetic equations.

## 2. Experimental

### 2.1. TPD method and apparatus

The Arrhenius equation gives a simple but accurate formula, expressing the relations among the reaction rate, activation energy, pre-exponential factor and reaction order, which comes from the summary of a lot of scientific experiments. So, in order to obtain kinetic parameters of a reaction, the reasonable treatments on Arrhenius equations as well as the properly designed experiments are expected. The temperature programmed (usually linear heating rate) technique has been widely used in the thermal analysis, and its obvious advantage is to make acquiring the kinetic parameters

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of a reaction possible. The acquired kinetic parameters will be credible and accurate if the experimental conditions are strictly controlled.

The thermal conductivity of hydrogen, which is the main product of titanium hydride decomposition, differs greatly with that of argon. At 273 K, the thermal conductivity of hydrogen and argon are 173.9 J $cm^{-1}$ $s^{-1}$ $°C^{-1}$ and 16.7 J $cm^{-1}$ $s^{-1}$ $°C^{-1}$, respectively. So, using thermal conductivity cell (TCC) as the detector, a so-called temperature programmed decomposition (TPD) apparatus (as shown in Fig. 1), in which argon used as carrier gas has been established. The hydrogen signal from titanium hydride decomposition can be recorded precisely by the TCC to form the corresponding TPD spectrum. In order to ensure that the detected signal is hydrogen only, the cold trap (Fig. 1(12)) of 123 K was applied, which means that the decomposition products along with argon gas first pass through the cold trap before they enter the TCC.

### 2.2. TPD experiment of titanium hydride

The TPD experiment on titanium hydride has been elaborated in our previous work[8]. Briefly, the as-received titanium hydride powder (74.0 mg) with mean size of 50 μm and chemical formula of $TiH_{1.924}$ was put in a stainless steel tube and at both the top and the bottom of titanium hydride, quartz sand (AR) treated by hydrochloric acid was filled. Then the tube, in which the pure argon (>99.99%) flow rate was 40 mL/min, was put in a furnace. The temperature of titanium hydride was raised from room temperature to 1100 K after the steady base line was reached. The decomposition products were detected by the TCC and the detected signals were collected by the workstation. The ambient temperature of housing (Fig. 1(13)) was kept at 413 K, the bridge current is 81 mA and the heating rate is 10 K/min during the TPD experiment. The temperature should be corrected due to the dead space between the titanium hydride and the detecting arm of the TCC, and the value is −0.5 K.

### 2.3. Preparation of Al alloy foam

An Al alloy containing 4.5–5.3 wt% Cu, 0.6–1.0 wt% Mn, and 0.15–0.35 wt% Ti, whose melting point range is 820.5 K–923 K, was used as the matrix. Calcium particles (purity > 99.9 wt%) was selected as the thickening agent and the as-received titanium hydride powder (purity > 99.2 wt%, Φ50 μm) was chosen as the blowing agent. The melt foaming method was applied to prepare the Al alloy foam and the preparation procedure is as the following:

**Melting:** a definite quantity of Al alloy (~1 kg) was melted in a crucible at a temperature.
**Thickening:** Calcium particles (2.0 wt%) were added into the melt by the impellor with a speed of 450 r/min to raise the viscosity of the melt to a proper value[19].
**Foaming:** Titanium hydride powder (1.0 wt%) was added and dispersed into the melt with the impeller revolution speed of 1000 r/min, leading to the melt being foamed gradually. This time interval is defined as stirring foaming stage whose duration is defined as stirring time, $t_s$. Immediately after the stirring foam stage was finished, the impellor was pulled out of the foaming Al alloy melt promptly, and then the foaming melt was held in the furnace at a proper temperature to keep the blowing agent decomposing. This time interval is defined as the holding foaming stage whose duration is defined as holding foaming time, $t_h$. The summation of $t_s$ and $t_h$ is defined as the total foaming time, $t_f$, and the temperature within the stirring foaming and holding foaming stages is defined as the foaming temperature, $T_f$.
**Cooling:** The crucible was removed from the furnace and the foamed melt was cooled and solidified.

### 2.4. Pore structures of Al alloy foam

The porosity of metallic foams can be classified as bulk porosity, $Pr_b$ and real-time porosity, $Pr$.

(1) Bulk porosity, $Pr_b$, refers to the volume fraction of all the pores in a finished product of Al alloy foam. It can be calculated from the weight $W$ and the volume $V_s$ of a sample using the following expression:

$$Pr_b = \left(\frac{\sum V_i}{V_s}\right) = \frac{V_s - (W/\rho)}{V_s} \tag{1}$$

where $V_i$ is the pore volume, $V_s$ is the volume of a sample, and $\rho$ is the specific weight of the matrix.

(2) Real-time porosity, $Pr$: Al alloy melt foaming process happens in a stainless-steel crucible that has a constant cross-section area in the vertical direction. The upside of a foaming melt can be regarded approximately as a plane, so the height of the foaming melt ($H$) can be measured and the real-time relation curve between the porosity of Al alloy melt ($Pr$) and the foaming time ($t_f$) can be drawn according to the following equation:

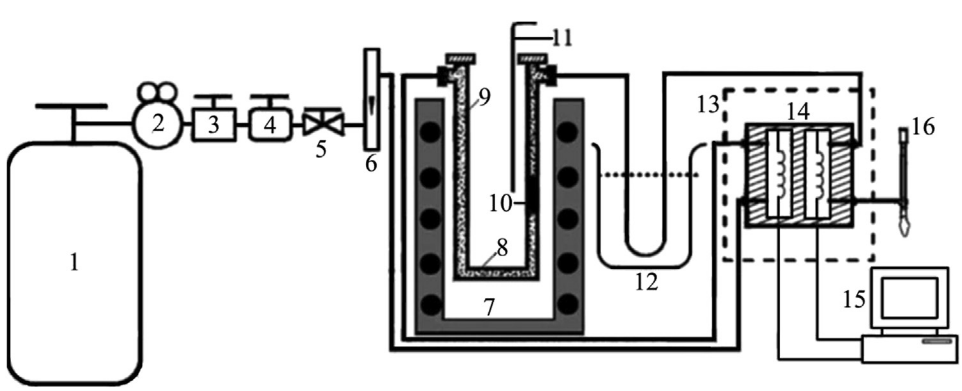


**Fig. 1.** Schematic illustration of temperature programmed decomposition apparatus, where (1) is argon tank, (2) pressure reducing valve, (3) manostat valve, (4) flux controlling valve, (5) needle valve, (6) rotor flowmeter, (7) furnace, (8) stainless steel U shape tube, (9) quartz sand, (10) titanium hydride, (11) thermocouple, (12) cold trap, (13) housing, (14) thermal conductivity cell, (15) workstation-computer station, and (16) soap film flowmeter. The argon flow rate route is 1→2→3→4→5→6→14→8→12→14→16.