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INFRA-RED HEATING SOURCE AND ASSOCIATED APPARATUS FOR THE STUDY OF CONTAMINANTS IN INERT GASES

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ABSTRACT

Vacuum microbalance methods using radiant heating of the sample, a flow type of reaction system and a sensitive monitoring system for water vapor were used to study the reactivity of metal powders with contaminants in inert gases. Kinetic and capacity studies were made on zirconium and aluminum powders in argon atmospheres containing H_2, O_2, H_2O and CO_2 at the 5 to 50 ppm level at 400°C.

INTRODUCTION

Vacuum microbalance methods for the study of gas-metal reactions have been limited by the following: (1) weight changes during the initial period of reaction while heating to temperature and establishing the reaction atmosphere, (2) effects of reactive gases released on heating the furnace tube, (3) water vapor contamination from the gas source, gas preparation system and reaction system, (4) sample temperature measurement and (5) balance disturbances from the gas atmosphere. The difficulties are of importance in the study of gettering reactions of zirconium powders.

To overcome these problems we have developed an apparatus using: (1) an infra-red heating chamber for the sample and container alone, (2) a flow reaction system with sensitive instruments for monitoring water vapor, and (3) a symmetrical bucket for mounting a thermocouple for measuring temperature.

APPARATUS AND METHOD

The flow type of reaction system was used at 1 atm. pressure and was constructed of 304 stainless steel except for the balance housing, furnace tube and oil diffusion pump, a liquid nitrogen cold trap, and a fore pump were used to evacuate the system to a pressure of 10^{-4} torr or lower.

Gulbransen type quartz beam microbalances (ref. 1 and 2) were used having sensitivities of 1.2 and 5 micrograms per 10^{-3} cm deflection.

A high density infra-red radiant heating chamber was used to heat the Pt bucket containing the Zr powder sample without heating the quartz furnace tube. A temperature of 400°C could be reached in 30 seconds. Since rapid heating and cooling were possible all balance readings were made at room temperature to avoid thermal convection. The control thermocouple was mounted inside a second Pt bucket supported symmetrically below the sample bucket.

A gas flow rate of 200 cm^3/s. at 25°C was maintained over the sample by use of a sensitive needle valve and a calibrated flow meter.

Moisture contents of the gases were determined by measuring the dewpoint using an Alnor Dewpointer. Moisture contents of 5 ppm could be measured. Five gas mixtures were used. Three were prepared by Matheson Company from ultra high purity argon (UHP) by the addition of 51 ppm of H_2, 47 ppm of O_2 and 50 ppm of CO_2. Argon containing 5 and 30 ppm of H_2O were prepared by mixing (UHP) argon with (UHP) argon bubbled through degassed high purity H_2O and the H_2O content adjusted by measurements with the Alnor Dewpointer.

A sensitive hydrogen analyses apparatus (ref. 3) using liquid helium cryogenic pumping was used to determine the initial hydrogen contents of the Zr powders.

Foote Mineral Company and Ventron Company Zr powders were used. The Foote Mineral Company powders were nearly spherical in shape, uniform in size and about 3 microns in diameter. The Ventron Company particles were less uniform in shape and had a larger range in particle size. Special care was used in handling the powders to limit oxidation and fires.

THERMOCHEMICAL ANALYSES

Table 1 shows the logarithms of the equilibrium constants for the reactions of Zr with H_2, O_2, H_2 and CO_2 gases at 400°C (ref. 4 and 5).

An equilibrium pressure of 1.3×10^{-7} atm. was calculated for the reaction to form $ZrH_{1.5}(s)$ at 400°C. This corresponds to a residual H_2 content in the gas phase of 0.1 ppm. The terminal solubility of H_2 in α-Zr at 400°C is 208 ppm giving the H/Zr ratio of 0.0189 (ref. 5). $ZrH_{1.98}(s)$ cannot form at 400°C for low concentrations of H_2 in argon.

Zr reacts with $H_2O(g)$ to form oxide and probably hydride following reaction 4. When metallic Zr is no longer available $ZrH_{1.5}(s)$ reacts with $H_2O(g)$ to form more oxide and free H_2. Vacuum microbalance studies do not show a levelling off of the weight gain at the formation of ZrO_2 and $ZrH_{1.5}$.

Zr reacts with O_2 following reaction 2. Extremely rapid reaction occurs unless the reaction was started at a low temperature.

Zr reacts with CO_2 following reactions 6, 7 & 8. This reaction is not well understood. Unless reaction 6 occurs carbon gases are not removed.

TABLE 1

Thermochemical analyses of Zr reactions at 400°C

Gas	Equation	Log K_R (g. atom of Zr)	
H_2	$Zr(s) + 3/4H_2(g) \rightarrow ZrH_{1.5}(s)$	5.13	(1)
O_2	$Zr(s) + O_2(g) \rightarrow ZrO_2(s)$	75.54	(2)
H_2O	$Zr(s) + 2H_2O(g) \rightarrow ZrO_2(s) + 2H_2(g)$	42.74	(3)
H_2O	$3.67Zr(s) + 2H_2O(g) \rightarrow ZrO_2(s) + 2.67ZrH_{1.5}(s)$	17.52	(4)
H_2O	$ZrH_{1.5}(s) + 2H_2O(g) \rightarrow ZrO_2(s) + 2.75H_2(g)$	37.61	(5)
CO_2	$2Zr(s) + CO_2(g) \rightarrow ZrO_2(s) + ZrC(s)$	29.75	(6)
CO_2	$Zr(s) + 2CO_2(g) \rightarrow ZrO_2(s) + 2CO(g)$	40.52	(7)
CO_2	$ZrC(s) + 3CO_2(g) \rightarrow ZrO_2(s) + 4CO(g)$	21.55	(8)

CAPACITY OF ZR POWDERS FOR GETTER REACTIONS

Four factors reduce the capacity of Zr powders: (1) initial oxygen content as dissolved oxygen and as oxide on the surface, (2) initial hydrogen content as dissolved hydrogen and as $ZrH_{1.5}(s)$ in the particle and on the surface, (3) chemisorbed and physically adsorbed water on the surface and (4) other metal and non-metal elements.

Initial oxygen can be measured using the apparatus here described by slow oxidation at relatively low temperatures to avoid rapid reaction and comparing oxygen pick up to theoretical. Initial hydrogen, can be determined by heating to 1200°C, condensing the hydrogen by liquid helium and volatilizing the hydrogen into a known volume and measuring the pressure (ref. 3). Initial H_2O can be measured using the apparatus described by evacuation at 25°C and heating to 400°C in high purity argon flowing over the sample. Other metals and non-metals can be evaluated from the chemical analyses of the powder.

Initial hydrogen and water contents

Two Zr powders were tested. The Foote sample showed 1728 ppm of H_2 and the Ventron sample showed 1875 ppm of H_2.

The initial water on the particle surface was determined by the method described. Both samples showed a total weight loss of 1.00 µg/mg.

Measurement of capacity-oxidation and hydrogen method

In the oxidation method a 4 mg Zr sample was heated in O_2 at 1 atm. pressure from 250° to 600°C over a 125 min. time period. The Foote sample showed 84% of the Zr was available for gettering and the Ventron sample 91.5%.

In the hydrogen method H_2 is reacted with Zr at 25°C and 1 atm. pressure to form $ZrH_{1.98}(s)$. To achieve rapid reaction we react at 400°C and 1 atm. pressure and cool in H_2 to 25°C. Capacity values of 84.5 and 85.5 percent were found for the Foote Zr powder. The reaction was very rapid with 95% completion in 1 min. and 100% in 10 min. The oxide film on the Zr particle was readily penetrated by hydrogen at 1 atm. pressure.

KINETIC STUDIES

91 mg of 84% Zr – 16% Al powders were reacted at 400°C, 1 atm. pressure and a flow rate of 200 cm^3/min. The powder mix was placed in the platinum bucket weighing 0.5 gm and having a sample surface of 0.5 cm^2. The Al powder was inert in the gas atmospheres and acts as a diluent for the reactive Zr particles. The apparatus was evacuated to 10^{-4} torr pressure, flushed with the reactive gas mixture before filling to 1 atm. pressure and imposing gas flow on the system. Initial microbalance readings were taken and the infra-red heating chamber activated. Readings were then taken at 25°C after 0.5, 1.5, 3.5 and 5.5 h. of reaction.

H_2O reaction at 5 and 30 ppm in argon

Initially a weight loss was observed due to moisture loss from the Zr + Al powders. For the time period of 0.5 to 5.5 h. a 3.8 μg/mg weight gain was observed for the argon + 30 ppm of H_2O gas mixture and a 1.5 μg/mg weight gain for the argon containing 5 ppm or less of $H_2O(g)$. Linear weight gain curves were found. For the reaction in argon + 30 ppm of H_2O 25% of the $H_2O(g)$ passed over the specimen was reacted. Hydrogen analyses of the powder mixture before and after reaction showed an increase in hydrogen content from 1256 to 1543 ppm H_2 which suggests some H_2 was absorbed from the H_2O + Zr reaction.

H_2 reaction at 51 ppm in argon

A weight change of 5.3 μg/mg for the time period between 0.5 and 5.5 h. was observed. Since up to 5 ppm of $H_2O(g)$ was also present the $H_2O(g)$ reaction must be included in the total reaction. For the 91.5 mg sample a total weight change of 4.84×10^{-4}g was observed. Based on the flow rate and H_2 content 2.4×10^{-4}g of H_2 were passed over the sample. Therefore, 2.44×10^{-4}g of H_2O was reacted in addition by the getter. This is about the $H_2O(g)$ content of the gas mixture at the 5 ppm level. We conclude the Zr + Al powder mixture reacts readily with both H_2 and H_2O in this gas mixture with nearly 100 percent efficiency.

CO_2 reaction at 50 ppm in argon

A weight gain of 5.7 µg/mg for the time period of 0.5 to 5.5 h. was observed. Based on the flow rate and gas analyses we calculate that 9.8% of the total contaminants were reacted. The Zr + Al powder mixture was not too effective for removal of CO_2 from pure argon at the 50 ppm level. It was also not possible to state which of the Zr + CO_2 reactions, 6, 7 or 8 of Table 1 were occurring.

O_2 reaction at 47 ppm in argon

A weight gain of 7 µg/mg was found for the time period of 0.5 to 5.5 h. Based on the flow rate and gas analyses we calculate 16.7% of the contaminants were reacted. O_2 contaminants in argon react with the Zr + Al powder mixture but only with moderate efficiency. This may be due to the formation of a compact oxide film which limits oxidation. However, the weight gain versus time curve was nearly linear which suggests that access of O_2 to the specimen was the limiting factor.

SUMMARY

An infra-red heating chamber and a flow type of reaction was used successfully for the study of the capacity of reactive metal powders and the kinetics of reaction with H_2, O_2, H_2O and CO_2 contaminants in the 5 to 50 ppm level in high purity argon.

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