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DEVELOPMENT OF LABORATORY APPARATUS DEDICATED
TO THE STUDY OF HYDRIDE-DEHYDRIDE REACTIONS*

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ABSTRACT

Hydrogen-compatible laboratory apparatus has been designed and developed to study hydride-dehydride reactions at elevated pressures and temperatures. The system has operated at pressures and temperatures up to 34 MPa and 550°C during experiments conducted on LiAlH_4 and Ni_2Zr . Instrumentation incorporated into the system also allows differential thermal analysis and acoustic emission data to be collected as the chemical reactions progress.

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INTRODUCTION

The need to perform phase equilibria experiments on large (15 g) pure metal or alloy samples during hydriding or dehydriding reactions at elevated pressure and temperatures provided the impetus for this apparatus development. Several previous experimenters¹⁻⁴ have developed instruments limited to the use of a single thermal technique such as differential thermal analysis (DTA), thermogravimetric analysis (TGA) or differential scanning calorimetry (DSC) to detect phase changes. The new apparatus simultaneously employs differential thermal analysis and acoustic emission techniques to confirm phase changes. The ultimate performance goal for the apparatus is 68 MPa hydrogen pressure and 1000°C while monitoring reaction progress with these techniques. Initially, however 500°C and 34 MPa of hydrogen or helium pressure has been utilized.

This apparatus allows a large (15 g) sample to be hydrided in-situ so that initial activation characteristics can be determined. It also offers an advantage over an apparatus which measures only thermal behavior. Thermal measurements (such as DTA) at elevated pressures and temperatures are complicated by conductive heat losses, power supply noise, and temperature differences caused by convective movement of the gases. Simultaneous monitoring of the acoustic and thermal data increases the degree of confidence in the measurements.

EXPERIMENTAL APPARATUS

Pressure Vessel and Closure Assembly

An assembly drawing of the high pressure vessel and closure device is shown in Figure 1 and the details of the pressure vessel and interior components are shown in Figure 2.

The inner pressure vessel component was machined from a billet of hydrogen-resistant A286 stainless steel. A 4340 steel ring forging was heated and shrunk onto the outer diameter of the A286 piece to add strength to the final assembly. The vessel baseplate was also machined from A286 and has 32 holes for electrical feedthroughs, 2 gas ports, and 4 slots milled into the reverse side for wire passage. The primary pressure seal is a Viton O ring installed in the baseplate.

The vessel closure device is a large press that holds the vessel and baseplate together with a force of 4×10^5 Newtons developed hydraulically. The hydraulic system supplies 35 Mpa pressure to a large diameter short-stroke piston under the baseplate. Removable spacer blocks are used to take up the free space in the press frame caused by the need to raise and lower the vessel for access. A low-pressure hydraulic cylinder raises the vessel and the upper cross-member approximately 450 mm. The assembly is then pinned in this position when access to the vessel interior is required.

FIGURE 1. PRESSURE VESSEL AND CLOSURE DEVICE

**FIGURE 2. CROSS SECTION OF PRESSURE VESSEL INTERIOR
SHOWING DTA CONFIGURATION**

Gas Pressure System

The remotely operated gas handling and pumping system for this apparatus consists of pressure transducers, calibrated volumes, hydrogen filters, and a two-stage Aminco diaphragm pump. This part of the system has been described previously.³ The system allows one to closely control pumping speeds, pressures, and flow paths.

Differential Thermal Analysis System

The differential thermal analysis portion of the apparatus consists of two matched furnaces, two matched cylindrical sample containers (235 mm dia. x 30.7 mm high), sample and reference thermocouples, a preamplifier to amplify the temperature difference (ΔT), appropriate temperature monitoring and display modules, and a recorder to allow x-y plotting of ΔT versus reference temperature signals.

The furnaces are formed from 22-gauge Nichrome wire vertically wound on alumina or lava insulating rings supported by a 0.25 mm wall tubular molybdenum form. This heating element is surrounded by five similar concentric molybdenum heat shields. The furnace lid is formed by ten stacked molybdenum discs with spaces and has a 2.3 mm diameter centerline through-hole for thermocouple insertion. A small auxiliary, circumferentially wound heater is located at the bottom of the heat zone and is controlled independently. Each furnace is surrounded by a copper outer sleeve to provide uniform conduction losses to the vessel baseplate.

The furnace temperature is controlled by a Data-Trak drum programmer that provides a comparative signal to a Leeds and Northrup Electromax controller which in turn provides a signal to a Leeds and Northrup zero voltage firing power supply. This 220 volt power supply drives the matched furnaces, with temperature feedback to the controller being provided by a chromel-alumel thermocouple on the reference furnace.

The differential temperature signal (ΔT) is developed by connecting the sample and reference thermocouples at the negative leads and taking the output between positive leads. This microvolt signal is then amplified by a factor of 100 using an Omega preamplifier and displayed on the y-axis of the recorder. Direct digital displays of sample and reference temperature are provided by Omega readouts.

The sample containers are cylindrical alumina (Diamonite) liners having a 0.25 mm wall and matching lid. This liner is placed in a 0.75 mm wall platinum crucible that also has a lid. Each of the lids has a 0.64 mm diameter hole for thermocouple access. An outer platinum wall surrounds the crucible to provide a uniform temperature. Pyrex liners have also been used in some experiments.

Acoustic Emission System

The acoustic transducer (Acoustic Emission Technology Model #AC175-1) is attached to the outer diameter of the pressure vessel near the baseplate. Signals received by the transducer are amplified by 50 dB using a preamplifier with a

band-pass of 125 KHz to 2 MHz. The amplified signal is fed to two counters. A Hewlett-Packard Model 5302A counter counts the total number of excursions which exceed an adjustable threshold (V_T) as acoustic ringing from a single event occurs. This is shown schematically in Figure 3(A). The threshold is set at a point just above the background noise of the system.

The second counter, an Acoustic Emission Technology Model 203, records one count for each event. Event rates greater than 1000/sec will lead to an error in counting because of event overlap. The events are sorted according to the amplitude of the first cycle into 50 channels. Each channel is 1.2 dB wide so that an amplitude distribution over a range of 60 dB (10mV to 10V) is obtained for a large number of events. This method is illustrated schematically by V_{max} in Figure 3(B). This represents the only signal counted from a particular acoustic event.

Certain amplitude distributions have been found to be characteristic of specific hydriding processes. Taken over a narrow range of hydride stoichiometry, they can provide a qualitative signature for the process. A typical amplitude distribution is shown in Figure 4. Amplitude distributions can be characterized by $N = AV^{-q}$ where N is the number of events of amplitude V or greater. A and q are constants. Data taken for the Niobium-hydrogen system as a function of hydrogen to metal ratio ($\chi = [H]/[M]$) are shown in Figure 5. A distinct change in the slope of the line is noted as the amount of hydride

FIGURE 3(A). RINGDOWN COUNT MEASUREMENT

FIGURE 3(B). AMPLITUDE DISTRIBUTION MEASUREMENT

FIGURE 4. TYPICAL AMPLITUDE DISTRIBUTION

FIGURE 5. AMPLITUDE DISTRIBUTION FOR NIOBIUM HYDRIDE

formed is varied. Figure 6 shows the result of plotting this experiment q versus the value of χ . A sharp break in the value of q is seen at $\chi = 1.05$. This point coincides with the point on the Nb-H phase diagram where complete conversion to the β niobium-hydride has occurred.

Frequency analysis of selected individual events has also been done by using a high-speed magnetic tape recording of the preamplified events; however, the analysis has not been conclusive and no data are presented in this report.

Total Experimental System

The total system block diagram is shown in Figure 7. The various subsystems are labeled as to the individual pieces of equipment or functions comprising the subsystem.

EXPERIMENTAL PROCEDURE, SAMPLE AND CALIBRATION MATERIALS

Typical experimental procedure consists of weighing a quantity (typically 15 g) of the sample material, weighing a corresponding thermal mass of the reference material (usually Al_2O_3), placing both in their respective crucibles, locating the thermocouples properly, closing the pressure vessel, evacuating the vessel to at least 5 millitorr, pressurizing with hydrogen, and ramp heating (approximately $10^\circ\text{C}/\text{min}$) to the desired temperature. Simultaneous monitoring of the ΔT and acoustic emission outputs reveals whether any hydriding

FIGURE 6. AMPLITUDE DISTRIBUTION SLOPE VS. H/M FOR NIOBIUM HYDRIDE

FIGURE 7. TOTAL EXPERIMENTAL SYSTEM BLOCK DIAGRAM

or dehydriding is occurring at a particular temperature. Controlled cooling to ambient is also used if needed.

Several initial cycles of hydriding, dehydriding, and rehydriding are sometimes necessary to "activate" a fresh sample so that the thermal and acoustic signals are repeatable. As long as contaminants such as air, water vapor, etc., are not allowed to come in contact with the sample, consistent data will be obtained.

The LiAlH_4 sample material used in the apparatus was commercially available powder having a purity of 95 percent. The NiZr alloy was prepared from the elemental metals.⁶ Commercial purity calibration materials (KNO_3 and KClO_4) with known differential thermal analysis response were used to check the system response.

RESULTS

Figure 8 shows the response of three KNO_3 calibration samples to ramp heating ($10^\circ\text{C}/\text{min}$) at three helium pressures. Also shown is the response at atmospheric pressure as obtained from the literature.⁷ The thermal event shown is the endothermic orthorhombic to trigonal phase transformation which begins at 117°C and peaks at 127°C . Figure 9 shows the identical information for three KClO_4 calibration samples. These calibrations demonstrate the accuracy that can be expected from the apparatus. This accuracy is well within that needed for the experiments anticipated for the apparatus.

FIGURE 8. KNO_3 TEMPERATURE CALIBRATIONS

FIGURE 9. KClO_4 TEMPERATURE CALIBRATIONS

Figure 10 compares the dehydriding of a LiAlH_4 sample with the baseline curve obtained after dehydriding at 21.4 MPa H_2 . Also shown is the acoustic emission detected during the dehydriding. Note the close correspondence of thermal and acoustic activity. Figure 11 shows the dehydriding response of identical LiAlH_4 samples at various H_2 pressures.

The dehydriding of LiAlH_4 was easily detectable and consistent with known decomposition temperatures.⁶ The LiAlH_4 samples were weighed after removal from the apparatus and had lost weight from hydride decomposition as expected. LiAlH_4 could not be rehydrided at H_2 pressures up to 34 MPa.

The hydriding kinetics of NiZr (after several initial activation cycles of hydriding and dehydriding) were rapid but the dehydriding kinetics were extremely slow (2 hours at 450°C and 0.6 MPa). Examination of a NiZr sample cycled only twice revealed that the original solid material had become a fine particulate (10 - 100 μm typical particle size). Figures 12 and 13 show the activation of NiZr samples at various pressures. Also plotted is the accumulated acoustic activity during initial hydriding. An extremely large ΔT indicating a vigorous reaction was detected during initial hydriding in all NiZr samples.

Response of the differential thermal analysis and acoustic emission apparatus to thermal changes of the sample was consistent and repeatable from sample to sample. The gas overpressure had a slight effect on sensitivity showing an apparent shift of the event to higher temperature as the pressure increased.

FIGURE 10. DEHYDRIDING OF LiAlH₄ (SAMPLE 6)

FIGURE 11. DEHYDRIDING OF LiAlH_4 SAMPLES

FIGURE 12. INITIAL HYDRIDING AND ACOUSTIC EMISSION OF NiZrH_x (SAMPLE 1)

FIGURE 13. INITIAL HYDRIDING AND ACOUSTIC EMISSION OF NiZr SAMPLES

The observed amplitude decrease of the event as the pressure increases was probably due to the increased thermal conductivity of the gas at higher pressure.

CONCLUSIONS

This instrument is a qualitative device; however, the combined differential thermal analysis/acoustic emission technique is a reliable method of confirming gas-solid reactions at elevated pressures and temperatures. A large sample is necessary to provide enough signal at the elevated conditions to permit detection of sample heats of reaction and acoustic activity. The apparatus is useful for quick scanning of materials to determine their initial response to hydrogen and determining relative changes due to additional cycling in hydrogen.

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REFERENCES

1. VanVucht, J. H. N., Kuypers, F. A., and Bruning, H. C., Phillips Res. Report, 25 (1970) 133.
2. Williams, J. R., and Wendlandt, W., Thermochemical Acta 7 (1973) 269.
3. Wemple, R. P., and Northrup, D. J., Jr., Thermochemical Acta, 12 (1975) 39-47.
4. Patai, S., Halpern, Y., Esterman, L., and Weinstein, M., Israel J. of Chem., 6 (1968) 445-449.
5. Samples of Ni₂Zr was prepared by F. J. Zanner and R. W. Fisher.
6. Blazeck, A., "Thermal Analysis," Van Nostrand Reinhold, London, 1972.
7. Dilts, J. A., and Ashby, E. C., Inorganic Chemistry, 11 (1972) 1230.

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