

AL-TR-90-031

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AD-A228 150

Final Report
for the period
September 1989 to
March 1990

Hydrogen Storage in Metal Hydrides

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August 1990

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F04611-89-C-0047
ULT/TR-90-7197

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Prepared for the: **Aeronautics Laboratory (AFSC)**
Air Force Space Technology Center
Space Systems Division
Air Force Systems Command
Edwards AFB CA 93523-5000

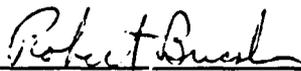
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FOREWORD

This final report was submitted by Ultramet, Pacoima CA on completion of Small Business Innovative Research (SBIR) contract F04611-89-C-0047 with the Astronautics Laboratory (AFSC), Edwards AFB CA. AL Project Manager is Robert Bucsh.

This report has been reviewed and is approved for release and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.



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FOR THE DIRECTOR



ROBERT C. CORLEY
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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for Public Release; Distribution is Unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ULT/TR-90-7197			5. MONITORING ORGANIZATION REPORT NUMBER(S) AL-TR-90-031		
6a. NAME OF PERFORMING ORGANIZATION Ultramet		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Astronautics Laboratory		
6c. ADDRESS (City, State, and ZIP Code) 12173 Montague Street Pacoima CA 91331			7b. ADDRESS (City, State, and ZIP Code) AL/LSSP Edwards AFB CA 93523-5000		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F04611-89-C-0047		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
	PROGRAM ELEMENT NO. 65502F	PROJECT NO. 5730	TASK NO. 004Y	WORK UNIT ACCESSION NO. 345383	
11. TITLE (Include Security Classification) Hydrogen Storage in Metal Hydrides (U)					
12. PERSONAL AUTHOR(S) DelaRosa, Mark J.					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM 8909 TO 9003		14. DATE OF REPORT (Year, Month, Day) 9008	15. PAGE COUNT 34
16. SUPPLEMENTARY NOTATION Additional COSATI: 11/04					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) hydrogen storage, metal hydrides, foam, chemical vapor deposition (CVD); chemical vapor infiltration (CVI)		
FIELD	GROUP	SUB-GROUP			
22	01				
10	03				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The primary objective of this program was to develop an economical process for producing a lightweight hydrogen storage medium by the chemical vapor infiltration (CVI) of a metal hydride former into a reticulated foam substrate. An investigation was conducted to determine the most favorable precursors for forming the candidate hydride-forming materials, along with optimization of their transport and deposition parameters. A substrate optimization study was also performed in order to derive the greatest surface area-to-volume ratio from the resulting metal hydride-forming foam. Thermogravimetric analysis (TGA) was performed on a metal foam sample to determine its hydriding capability. Results were inconclusive, showing only slight if any hydriding.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL ROBERT BUCSH			22b. TELEPHONE (Include Area Code) 805-275-5410	22c. OFFICE SYMBOL LSSP	

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INTRODUCTION

This is the final technical report submitted by Ultramet, Pacoima, CA 91331 to the Astronautics Laboratory (AL/LSSP), Edwards AFB, CA 93523-5000 under SBIR Phase I contract F04611-89-C-0047. The period of this contract was from 21 September 1989 to 31 March 1990. The principal investigator was Mark J. DelaRosa. The AL project manager was Robert Bucsh.

The primary objective of this program was to develop an economical process for producing a lightweight hydrogen storage medium by the chemical vapor infiltration (CVI) of a metal hydride former into a reticulated foam substrate. An investigation was conducted to determine the most favorable precursors for forming the candidate hydride-forming materials, along with optimization of their transport and deposition parameters. A substrate optimization study was also performed in order to derive the greatest surface area-to-volume ratio from the resulting metal hydride-forming foam. Thermogravimetric analysis (TGA) was performed on a metal foam sample to determine its hydriding capability. Results were inconclusive, showing only slight if any hydriding.

BACKGROUND

Current methods of storing hydrogen are suitable for most industrial uses, but they would be highly impractical for applications requiring compact size and light weight.

Storing hydrogen as a compressed gas necessitates a large, heavy vessel. Cryogenic tanks for long-term storage of liquid hydrogen require bulky insulation and elaborate plumbing and valving, which takes up valuable space and weight. Metal hydride formers, in contrast, can store hydrogen compactly with little energy expenditure.

Many elemental metals and alloys will form metal hydrides. While some hydride formers require an "activation" process, most metals will form hydrides simply by being exposed to hydrogen at a temperature and pressure specific to the particular metal hydride.

The advantage afforded by metal hydrides over other storage methods is that hydrogen can be stored at extremely high densities in the metals. For example, the density of hydrogen in a solid block of magnesium is over 40% greater than that of liquid hydrogen [1], and over an order of magnitude more than gaseous hydrogen.

As the rate of absorption/desorption, and therefore the total amount of hydrogen available, are dependent on the diffusion rate of hydrogen, the hydride former ideally should have a large surface area. Reticulated foams offer high surface area per unit volume, and as such were chosen as substrates onto which magnesium would be deposited by chemical vapor infiltration (CVI) to form a lightweight hydride former for hydrogen storage. The void space created by depositing magnesium into a foam lowers the hydrogen density to less than that of liquid hydrogen.

EXPERIMENTAL APPROACH

The primary objective of this Phase I program was to develop an economical process for producing a lightweight hydrogen storage medium using chemical vapor infiltration (CVI), a variation of the chemical vapor deposition (CVD) process, to infiltrate a metal hydride former into a reticulated foam substrate. An investigation was conducted to determine the optimal metal hydride former for use in hydrogen storage. Various infiltration methods and metal precursors were investigated. Once precursors were identified, depositions were performed to optimize plating rates on foams. The porosity of the reticulated foam substrate was also varied from 40 ppi (pores per inch) to 200 ppi in order to obtain a sample having the highest surface area-to-volume ratio without closing off the pores and forming a skin over the foam. Figure 1 shows the process flow diagram for the fabrication of the hydrogen-storing foam.

Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) has been used to produce coatings for more than a century, but only recently has this technique left the laboratory and become a production tool. CVD is a method of plating which relies on the chemical reaction of a vapor at a surface to form solid structural deposits. Since this is done on an atom-by-atom basis, impurity levels are typically less than 0.1% and densities are 99.9%. The CVD process utilizes a gaseous compound of the element to be deposited, which is then flowed over a heated substrate, resulting in thermal decomposition or reduction of the gaseous compound and subsequent deposition of the material onto the substrate. The first layer forms at nucleation sites; after the substrate is fully coated, growth continues on the crystal faces of the deposit.

Successful CVD -- dense, adherent coatings -- depends on experimentally determining the optimal deposition parameters. These parameters include the gaseous compound of the material to be deposited, substrate temperature, gas concentration, flow, pressure and geometry within the reaction chamber, coating thickness, and substrate material. For the coating to have high integrity and adhesion to the substrate, the substrate either must have a similar coefficient of expansion to that of the deposited material, or form a strong chemical or metallurgical bond with it. The thinner the coating, the less similar the coefficients of expansion need be. Where coating and substrate form no intermetallic bond and have widely differing coefficients of expansion, a good bond can often be achieved by using a thin interlayer of a third material.

The essential requirements of a CVD facility are that the substrate be maintained at the correct temperature and the plating gases be supplied in the correct ratio and at the correct pressure. The substrate is typically heated resistively, inductively, or in a hot wall furnace. The composition of the plating gases is determined by the type of reaction to be used. The same materials may be deposited using different compounds and different reactions at different temperatures, with each producing good coatings but different crystal structures. Compounds and alloys can be deposited by simultaneous codeposition of the appropriate elements. Some of the plating gases are volatile liquids or solids which are commercially available. In other cases, the compounds are made in situ as required.

The ability to achieve extraordinary purity in CVD deposits is the result of three stages of purification in the overall process, analogous to triple distillation. First, in the chemical process of preparing the starting compound from bulk metal, impurities tend to be left behind in the unreacted metal or taken off in the other reaction products. Second, in the volatilization of the plating compound, less volatile components are left behind or condense, while more volatile compounds tend to escape. Third, in the decomposition or reaction stage, the pressure and temperatures are optimized for the wanted species; impurities are less likely to deposit and tend to go out the exhaust. The original application of CVD was to purify refractory metals, e.g. the Van Arkel-de Boer iodide process for titanium and zirconium purification.

Chemical Vapor Infiltration (CVI)

The hydrogen-storing foam (metal hydride former) was fabricated using chemical vapor infiltration (CVI), a variation of the CVD process. Magnesium can only be deposited over a specific range of pressures and temperatures. In order to infiltrate material into small pores without closing out the porosity, the CVI process uses the lower end of both ranges. This keeps the number of nucleation sites small and uniform; it causes infiltration, rather than bridging (closing), of the pores, and results in coating of only the surface.

The substrate for the fabrication of the magnesium foam was a reticulated carbon foam. This material is an open-pore foam composed solely of vitreous carbon. It has an exceptionally high void volume (97%) and a high surface area, combined with self-supporting rigidity. The porous carbon foam does not possess a great deal of strength; rather, it acts as a structural guide for the metal deposit, which possesses good strength and stiffness. The carbon foams are lightweight, with relatively even pore distributions; they are made at Ultramet in a variety of porosities, measured in pores per inch (ppi). Table I lists some of the physical properties of carbon foams.

In order to evenly infiltrate the porous carbon foam with magnesium by CVI, the apparatus shown in Figure 2 is utilized. The porous nature of the foam makes it a poor thermal conductor which, therefore, generally cannot be heated directly by induction (with the exception of small parts and use of a high-frequency generator). Instead, a graphite cylinder (hot wall furnace) is placed around the foam. The graphite is readily heated by induction, and in return heats the substrate by radiation. In this configuration, the substrate contacts a lip on the furnace and the metal-bearing gas is pulled through the entire thickness of the porous sample, evenly depositing metal on the ligaments which form the cells of the foam. The magnesium-infiltrated foam can be fabricated in a wide range of densities, depending on the length of the infiltration run and other deposition parameters, and the resultant amount of material deposited on the ligaments of the foam.

RESULTS AND DISCUSSION

Metal Hydride Former Selection

For this Phase I effort, Ultramet proposed to examine magnesium and its alloys as possible metal hydride formers. Figure 3 shows a comparison of magnesium and the alloys Mg_2Ni and Mg_2Cu in terms of hydrogen desorption [1]. Preliminary investigations indicated that magnesium, and possibly Mg_2Ni , were the best candidates for hydrogen storage via metal hydrides.

The criteria used to select the candidate metal hydrides included hydrogen storage capacity by weight and by volume (see Table II) [1,2], the temperatures necessary to initiate hydrogen desorption, and the resulting hydrogen pressures (Figure 3).

Deposition Investigation

The selection of magnesium as the metal hydride former to be deposited by CVD required extensive investigations into potential precursors, particularly their volatility and stability. This information was required to determine the suitability of a precursor in terms of transport and decomposition. As the chlorides of magnesium, typically used in standard CVD for deposition by hydrogen reduction or thermal decomposition, are extremely stable, they were considered marginal at best for obtaining the optimal transport and decomposition needed for effective foam infiltration.

The obvious alternative was organometallic precursors, and several organometallic compounds containing magnesium do exist. Many of these materials in solid form either sublime or have sufficient vapor pressure that they can be transported, while the liquid organometallics can be boiled to obtain transport. In addition to requiring optimal transport characteristics, the magnesium precursor could not contain oxygen in the ligands lest magnesium oxide (MgO) form. The acetylacetonates ($C_5H_7O_2$) and the fluorinated acetylacetonates ($CF_3COCHCOCH_3$) were thus ruled out. A final, though less binding, consideration was the availability of the compound. The combination of these three criteria narrowed the choice of magnesium precursor to two materials: diethyl magnesium and bis(cyclopentadienyl) magnesium, or magnesiumocene.

Diethyl Magnesium

Diethyl magnesium is a liquid at room temperature and atmospheric pressure. The apparatus used for transporting the material and subsequently depositing magnesium is shown in Figure 4. The diethyl magnesium was placed in a flask connected to the deposition chamber. First, a vacuum was drawn on the flask to a pressure equaling that of the chamber. Next, the material was slowly heated using a heating plate, with temperature measured by a thermocouple. To aid in transporting the material, an argon carrier gas was bubbled through the magnesium compound.

In situ decomposition was noted before and at boiling. It was concluded that while diethyl magnesium is volatile, it is also unstable to the point that it is not suitable for transport. As an additional test, a piece of carbon foam

was placed in the flask containing diethyl magnesium and inductively coupled by a high-frequency generator. This resulted in a coating on the part that contained a considerable amount of organic material. It was therefore concluded that diethyl magnesium could not be used to deposit magnesium on foams.

Bis(cyclopentadienyl) Magnesium

Bis(cyclopentadienyl) magnesium, or magnesiumocene, is a powder, and the deposition setup was therefore modified as shown in Figure 5. Magnesium is used as a dopant in the semiconductor industry, and the volatility of magnesiumocene has been adequately defined at reduced pressures (see Figure 6).

The first factor to be investigated was the optimal deposition pressure for obtaining magnesium. Most of the cyclopentadienyl organometallics do not deposit at reduced pressure, and this was found to be the case with magnesiumocene as deposits made below 300 torr were negligible. The optimal deposition pressure was determined to be approximately 600 torr, and subsequent depositions were made at this pressure.

The second factor to be investigated was the optimal deposition temperature for obtaining magnesium. This can vary, sometimes dramatically, depending on whether hydrogen reduction or thermal decomposition is used. Lower deposition temperatures are usually preferred, particularly when infiltrating a material such as foam, because they generally result in more uniform deposits and minimize reactant depletion. Hydrogen reduction was thus investigated initially, as it was assumed to occur at lower temperatures.

Hydrogen Reduction of Magnesiumocene

That hydrogen reduction occurs at lower temperatures was confirmed by experiment. The hydrogen reduction of magnesiumocene vapor was found to occur between 500 and 650°C. The lower end of this range was used for infiltrating foams. It was anticipated that using hydrogen reduction would also minimize oxide formation, as compared to deposition by thermal decomposition. Energy-dispersive X-ray (EDX) analysis showed that this was not the case, however (see Figures 7A and 7B). As magnesium is known to easily form an oxide passivation layer of MgO on exposure to air, the oxygen in the elemental analysis was likely introduced after deposition. In any event, no benefit in terms of minimizing MgO formation was obtained by using hydrogen reduction. Also, magnesium deposits made by hydrogen reduction were noted to be less adherent to the carbon substrate (see Figures 8A and 8B). As magnesium will hydride at elevated temperatures and at hydrogen pressures below one atmosphere, this "loose" deposit was concluded to be the result of hydriding during deposition.

Thermal Decomposition of Magnesiumocene

As hydrogen reduction did not give satisfactory magnesium deposits, the thermal decomposition of magnesiumocene vapor was investigated, with magnesium found to deposit at 700-775°C. Again, the lower end of the range was used for infiltration. There was no difference in deposition rate between the two processes. A typical deposition would begin with 10 grams of $Mg(C_5H_5)_2$, which contains about 3.1 grams of magnesium. Deposit weight would vary between 0.60 and 0.75 grams, giving an efficiency of 19%-25%, which is good for standard CVD and excellent for organometallic CVD. Without the presence of hydrogen, dense,

adherent coatings were deposited on the carbon foam via thermal decomposition (see Figures 9A and 9B). This seems to confirm that the loose magnesium coatings obtained by the hydrogen reduction process were due to hydriding.

Substrate Selection

Foams ranging from 60 ppi to 200 ppi were examined as possible substrates. The best magnesium deposits were obtained on 100-ppi foam. After refining the heat distribution inside the substrate by modifying the radiating susceptor in order to obtain a hot zone that could be moved throughout the part (see Figure 10), 200-ppi foam could also be infiltrated, although the uniformity was not as precise as for the 100-ppi samples. A "flash coat" of electroless nickel was also deposited on 200-ppi foam to aid in heat transfer, and the resulting magnesium infiltration was more uniform.

Hydride Testing

Hydride testing was performed on one preliminary and two scale-up samples using thermogravimetric analysis (TGA), using the following procedure:

1. Parts were outgassed at 400°C in the presence of an inert gas (helium) until a stable weight was achieved.
2. Parts were activated by heating in the presence of hydrogen to 900°C at a rate of 7.5°C/min, then cooled down in helium. The purpose of activation is to break through the oxide passivation layer and expose fresh magnesium.
3. Parts were hydride tested by heating in the presence of hydrogen to 400°C at a rate of 7.5°C/min, then cooled down in helium.

The preliminary sample was fabricated to 3.67% of theoretical density and tested according to the above procedure. No weight gain was noted during either activation (see Figure 11) or testing (Figure 12). As the magnesium foam has a high surface area, the amount of magnesium that could be contaminated upon exposure to atmosphere was high.

Two scale-up samples were then fabricated, to densities of 12.3% (sample 2) and 20.0% (sample 3). After outgassing, the true densities were measured at 11.3% and 17.3% respectively.

Sample 2 showed typical behavior for the CVD magnesium parts. No weight gain was noted, with a slight weight loss during activation (see Figure 13). The significant weight gain in this sample after activation is an artifact caused by the sample pan in the TGA apparatus sticking against the chamber wall while the wire connecting the pan to the balance was contracting.

Sample 3, the most dense sample, should have the lowest ratio of contaminated magnesium to total magnesium. No difference in hydriding characteristics was noted, however, with no weight gain in either the activation or hydriding stages (see Figure 14).

Failure to Hydride

None of the three tested CVD magnesium samples demonstrated any hydriding (as determined by total lack of weight gain). The mechanism by which the CVD magnesium failed to hydride is not known. Analysis of the samples showed no excess contaminants present, or at least no more than in magnesium fabricated by other methods and then exposed to air (albeit for very brief periods). The failure to hydride likely arises due to the high surface area of the magnesium foam. As magnesium is easily poisoned by oxygen, the high surface area does not leave much magnesium available that is not poisoned. If this hypothesis is correct, the problem may not be inherent to CVD magnesium, but rather may be due to the geometry of the parts. As the novelty of the proposed approach was integrally related to the geometry of the sample, there does not appear to be any way around this problem when using elemental magnesium as a foam structure.

Magnesium-Nickel Hydride Formers

In a previous SBIR Phase I program for NASA Goddard Space Flight Center, Ultramet investigated nickel-based hydride-forming foams, LaNi_5 and Mg_2Ni [3]. While the results of this program were extremely promising, follow-on work was not possible due to insufficient NASA funds. Unlike magnesium, the compound Mg_2Ni is not easily poisoned, and still absorbs a high amount of hydrogen by volume (0.081 g/ml, compared to 0.101 g/ml for magnesium). Results from the NASA program would indicate that this figure is actually low, as it assumes a hydrogen storage capacity by weight of 3.84%. The figure for Ultramet's CVD magnesium-nickel compound was 6.02% [3].

Figure 15 shows the TGA data obtained for a CVD Mg_2Ni foam sample from the NASA program, tested under conditions identical to those used for this Air Force program as detailed above. The Mg_2Ni foam sample was fabricated by infiltrating CVD nickel into the carbon foam, followed by CVD magnesium, and then annealing. The weight of the bare carbon foam was 0.140 g; the weight of the nickel deposit was 0.130 g; and the weight of the magnesium deposit was 0.136 g, for a total weight of 0.406 grams. During heatup, the part absorbed 0.016 grams of hydrogen, equivalent to 3.94% of its total weight inclusive of the carbon substrate. Excluding the weight of the carbon, the amount of hydrogen absorbed was 6.02% of the magnesium/nickel weight. A typical value for pure magnesium is about 7%. While not quite as good as pure magnesium, then, Ultramet's magnesium/nickel compound was the second highest practical hydride former ever measured (counting pure magnesium as the highest).

The density of liquid hydrogen is 70 g/liter. To store 70 grams of hydrogen in Ultramet's CVD magnesium-nickel foam would require:

$$\begin{aligned}(1.039)x \text{ grams hydride} &= x \text{ grams metal} + 70 \text{ g hydrogen} \\ 1.039x - x &= 70 \text{ g hydrogen} \\ 0.039 x &= 70 \text{ g} \\ x &= 1794 \text{ g magnesium-nickel foam}\end{aligned}$$

These results would be further enhanced by using a carbon foam substrate with a higher porosity, to give more surface area and lower density (e.g. 100 or 200 ppi rather than 45 ppi), and/or depositing a thicker layer of magnesium or magnesium-nickel.

CONCLUSIONS AND RECOMMENDATIONS

In this Phase I program, Ultramet demonstrated the following:

1. Magnesium can be deposited by CVD by both hydrogen reduction and thermal decomposition over a range of deposition temperatures and pressures, with better quality coatings obtained via thermal decomposition.
2. Reticulated foam substrates between 60-200 ppi can be infiltrated with magnesium using CVI.
3. Magnesium is easily poisoned by oxygen to form an oxide layer (MgO). This appeared to be at least partially responsible for the failure of the magnesium foams to react with hydrogen at elevated temperatures to form magnesium hydride and thereby store hydrogen. This mechanism has previously been demonstrated during hydride testing of magnesium particles [4].

As noted, however, hydriding measurements for magnesium-nickel foams produced in a previous program for NASA showed excellent results. This Air Force program was conducted in hopes of obtaining similar properties from a foam structure of pure magnesium, which in bulk form has shown the best hydriding ability of any material. Magnesium-nickel is evidently a much easier material to hydride in foam form, and the performance of Mg-Ni foam as fabricated at Ultramet showed properties very close to those for pure bulk magnesium. The foam approach to the hydride-forming technique of hydrogen storage is itself fundamentally sound, taking advantage of the desirable properties of foams such as light weight and high strength.

As magnesium-nickel foams demonstrated superior properties that make long-term hydrogen storage in metal hydrides feasible, then, follow-on work is clearly recommended, to be directed at optimization, further characterization, and testing of this material to quantitatively determine its ability to store hydrogen for a given application.

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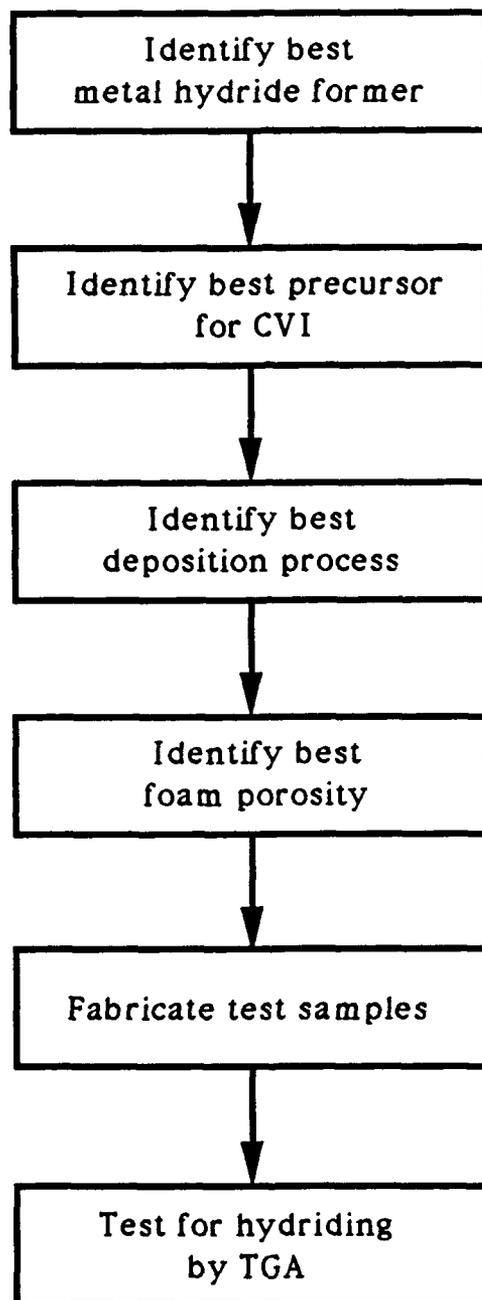


Figure 1. Process flow diagram

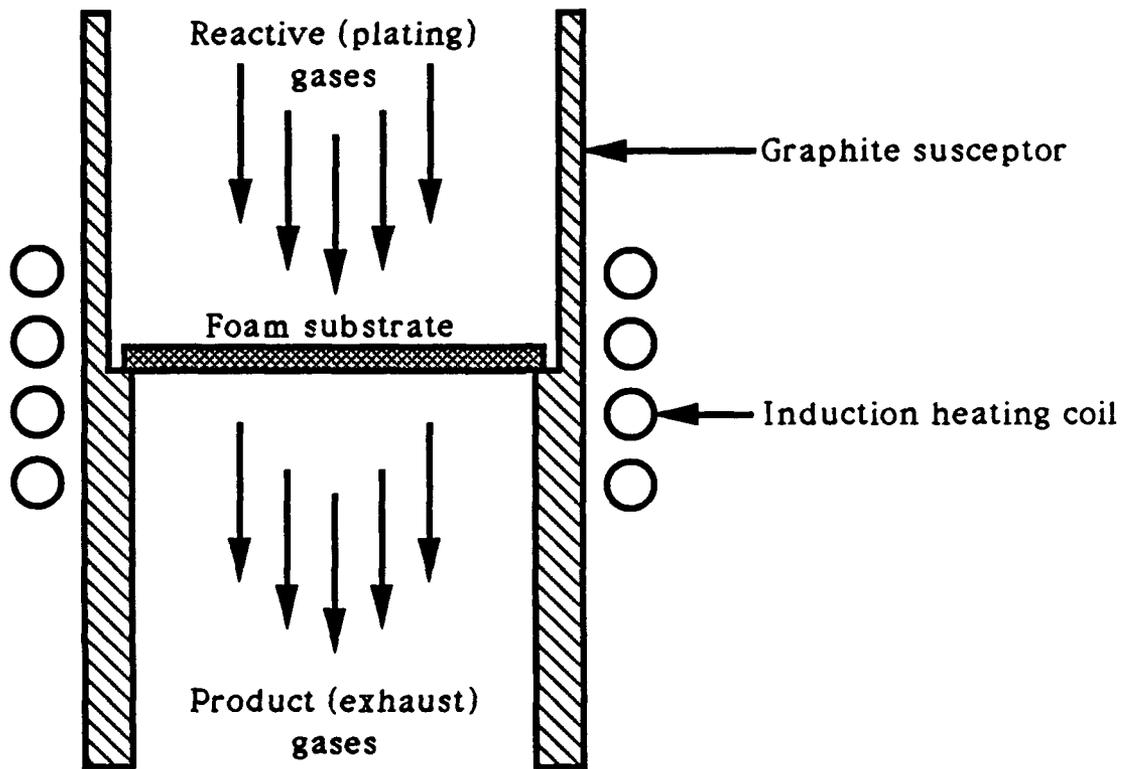


Figure 2. Schematic of CVI apparatus

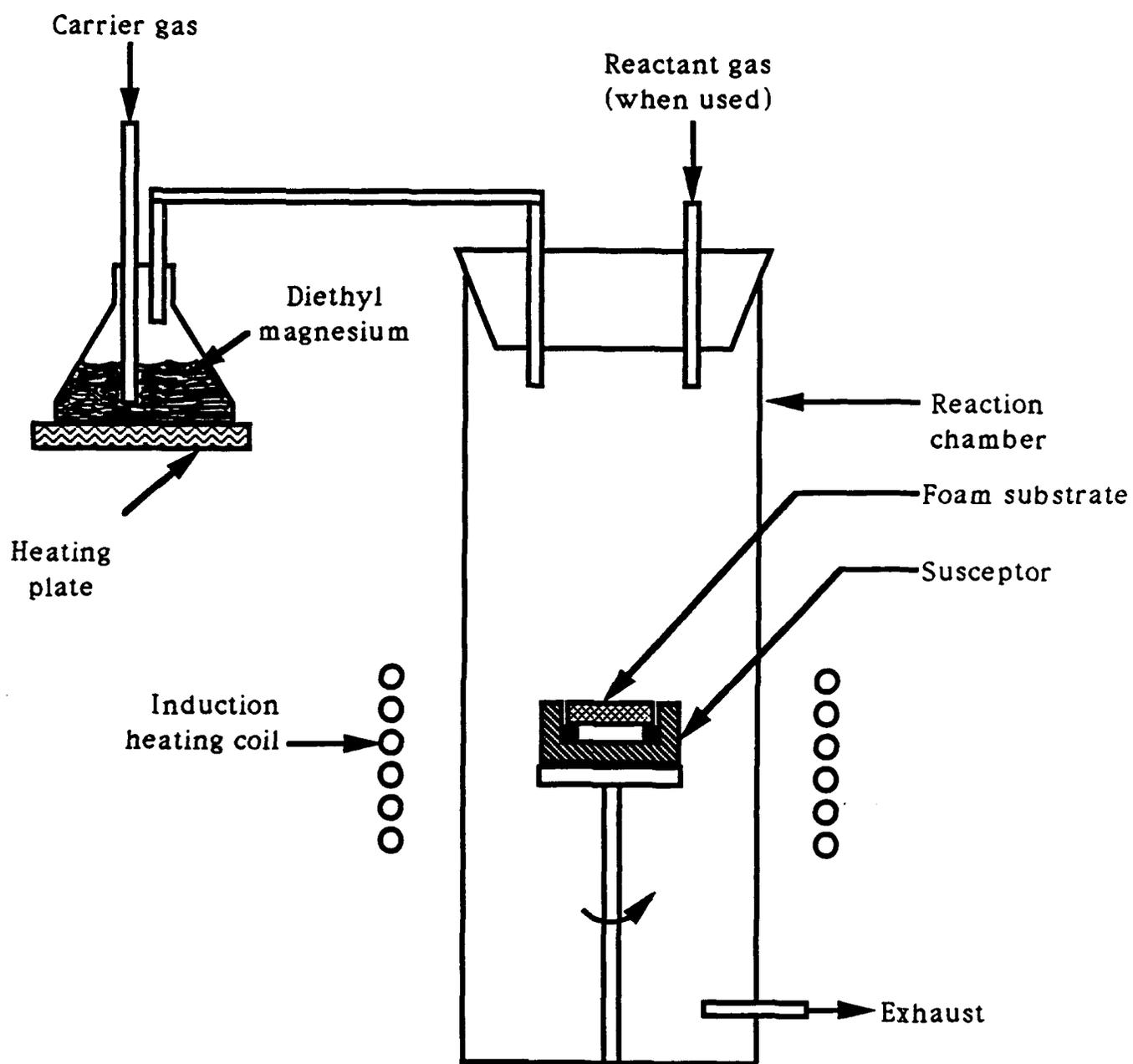


Figure 4. Schematic of diethyl magnesium deposition apparatus

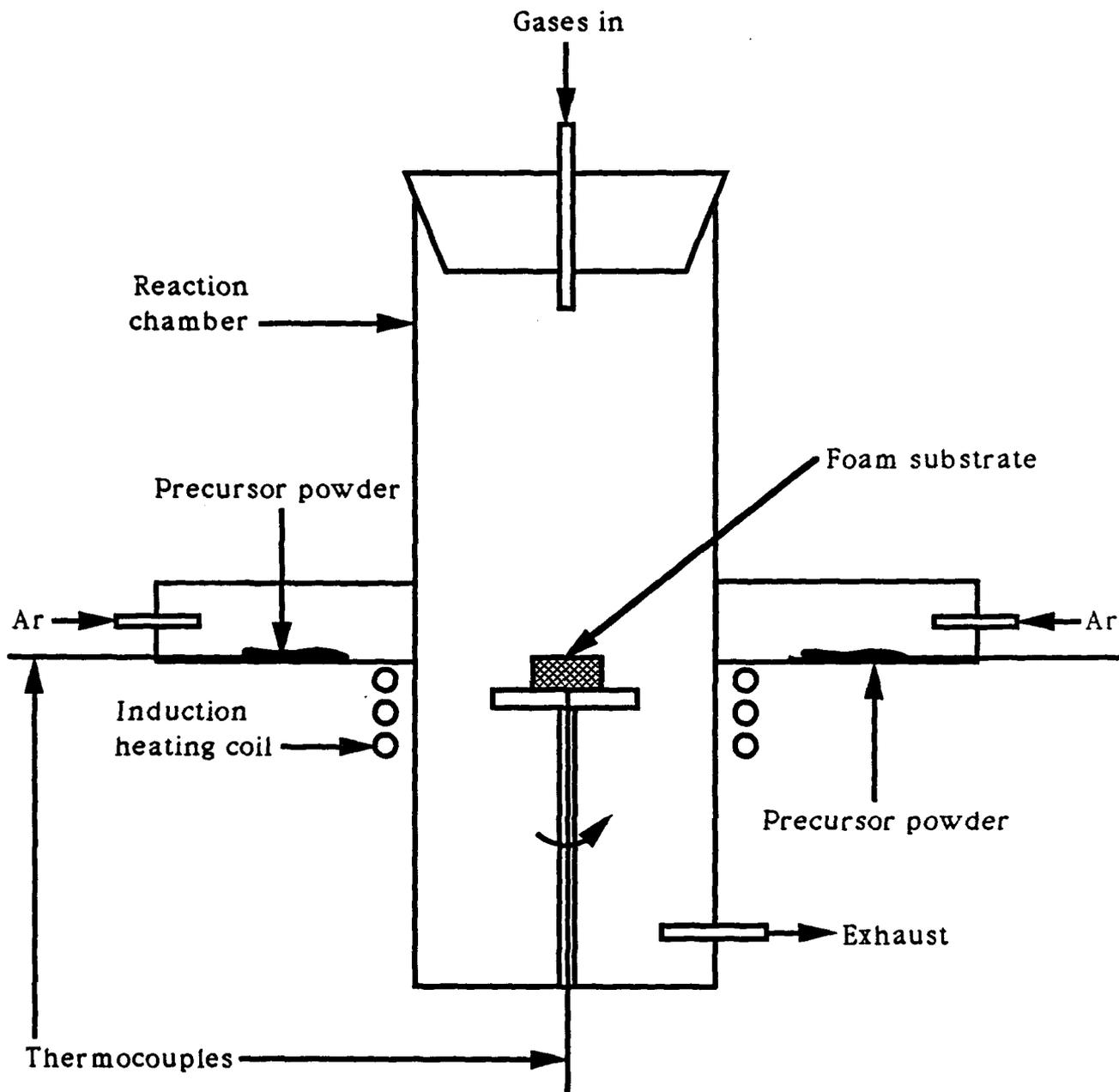


Figure 5. Schematic of magnesiumocene deposition apparatus

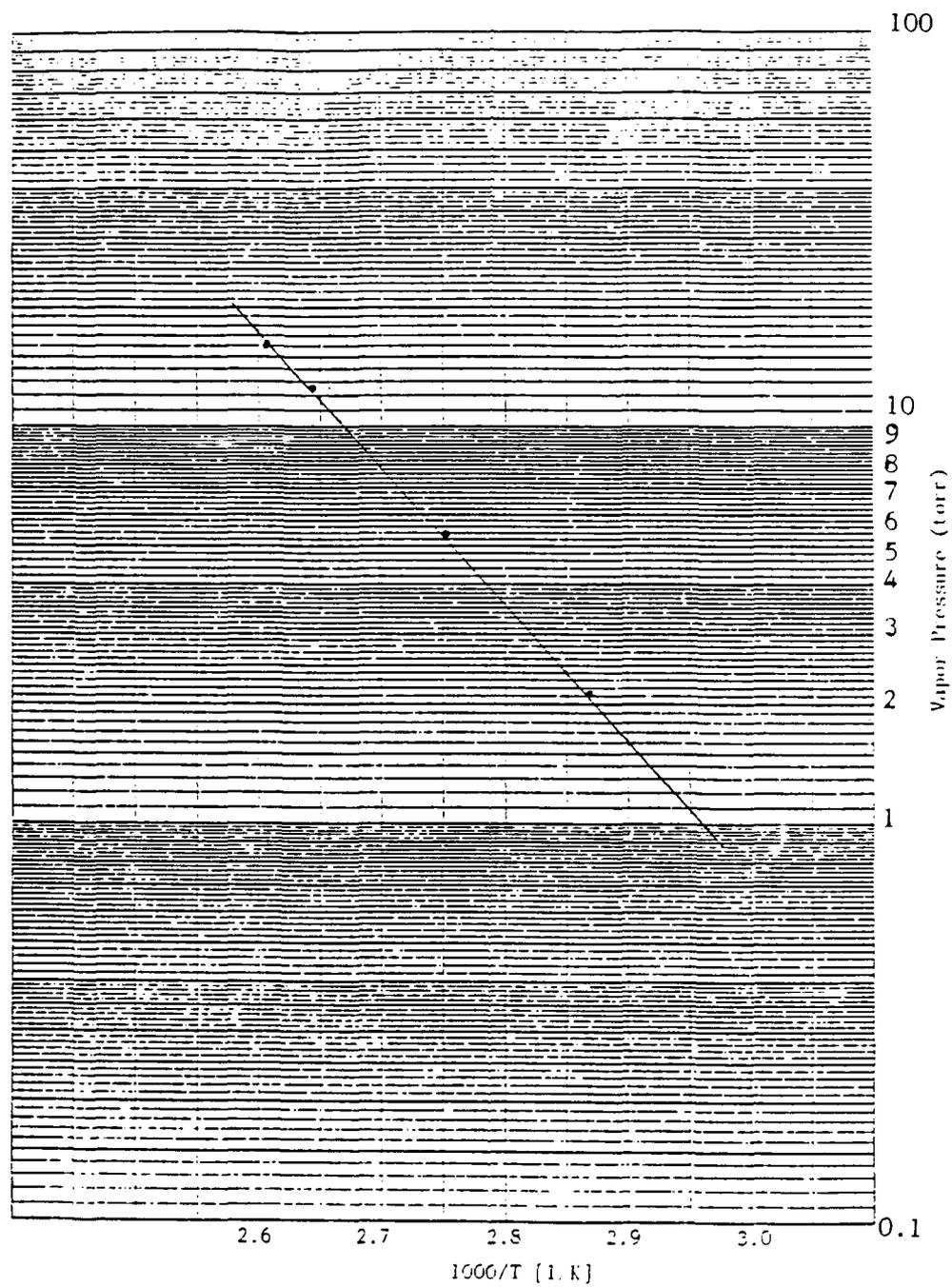


Figure 6. Vapor pressure curve for magnesiumocene

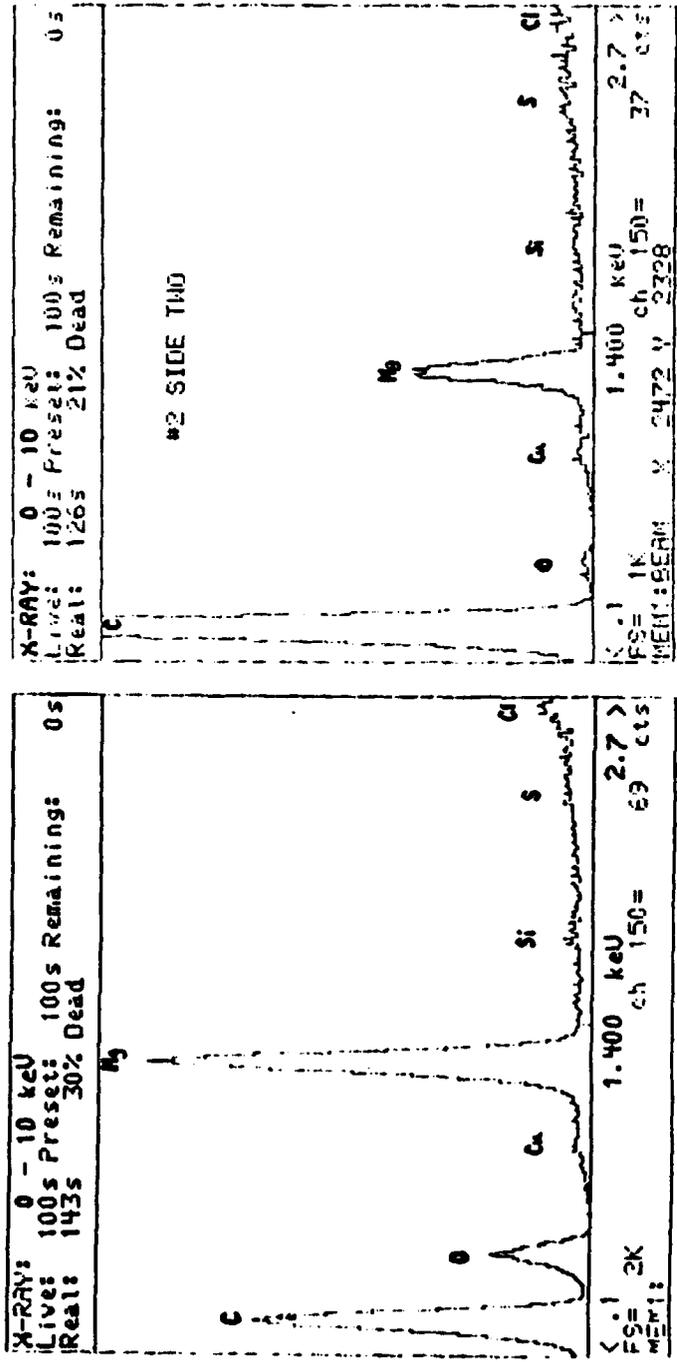


Figure 7. EDX spectra for magnesium deposited from magnesiumocene
 A. Via hydrogen reduction
 B. Via thermal decomposition

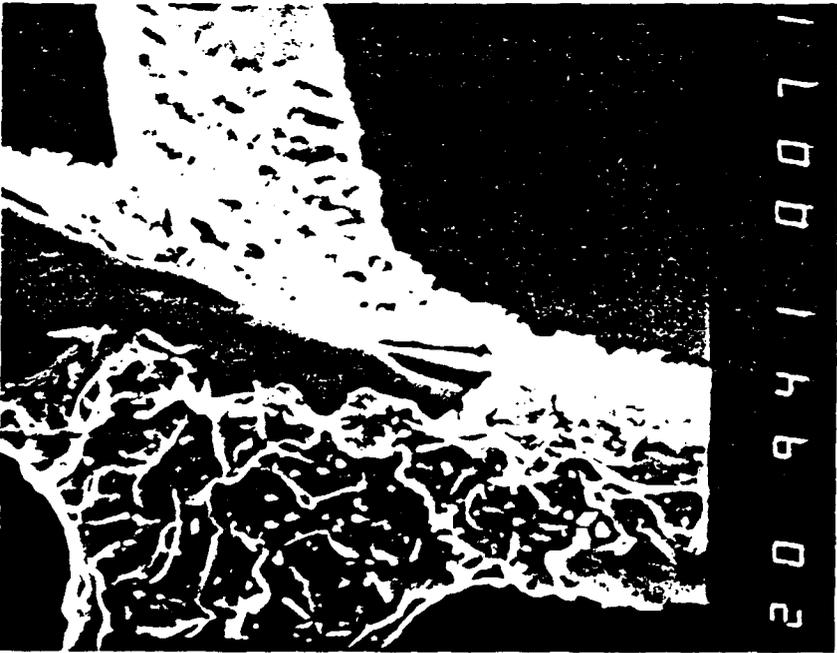


Figure 8. SEM micrographs of magnesium deposited via hydrogen reduction (940x)

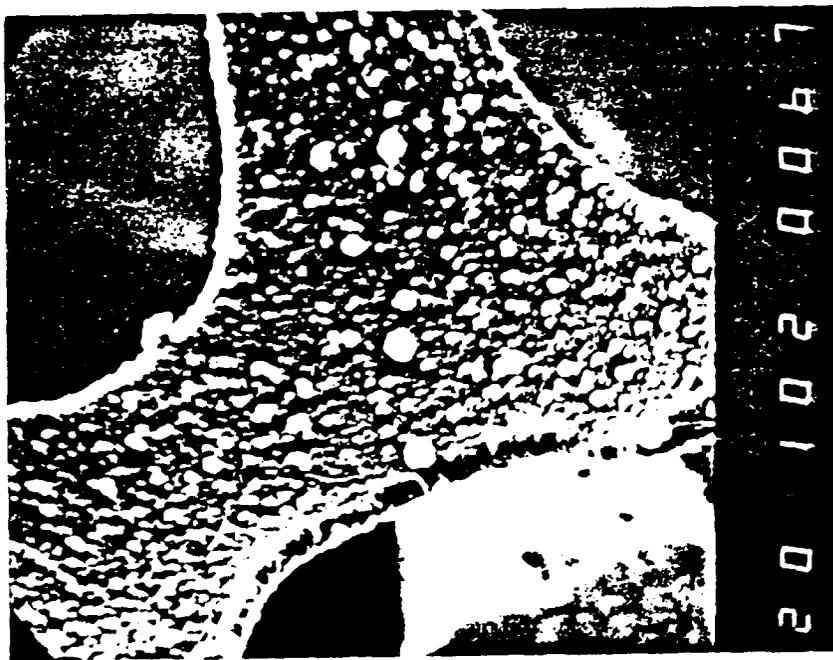
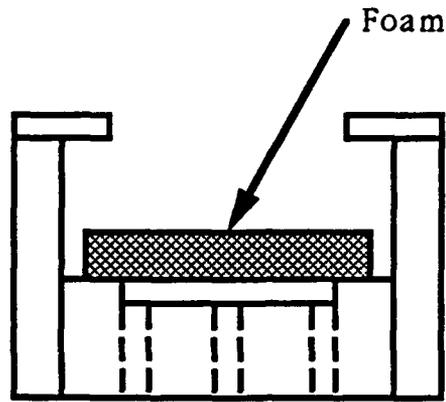
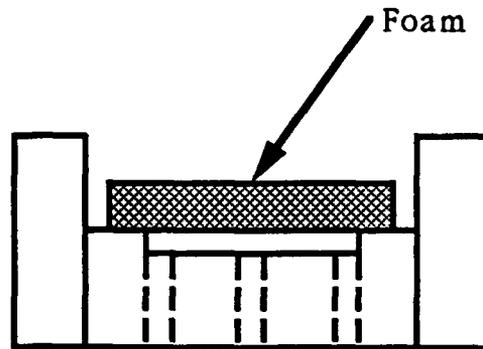


Figure 9. SEM micrographs of magnesium deposited via thermal decomposition (1000x)



Typical susceptor



Modified susceptor

Thicker, shorter walls give thermal gradient
along part to control deposition zone.

Figure 10. Schematics of typical and modified susceptors

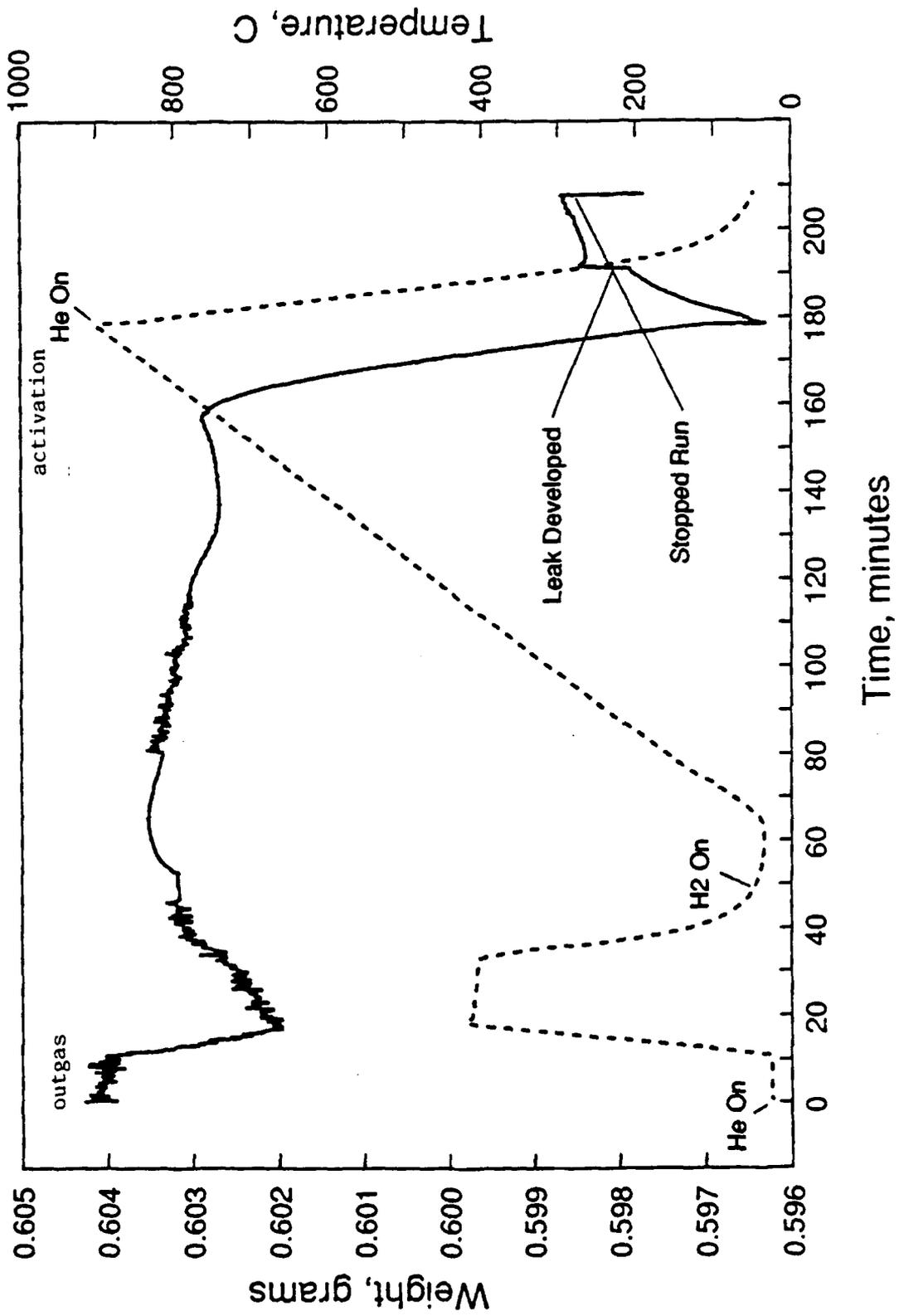


Figure 11. TGA data for sample 1 (activation phase)

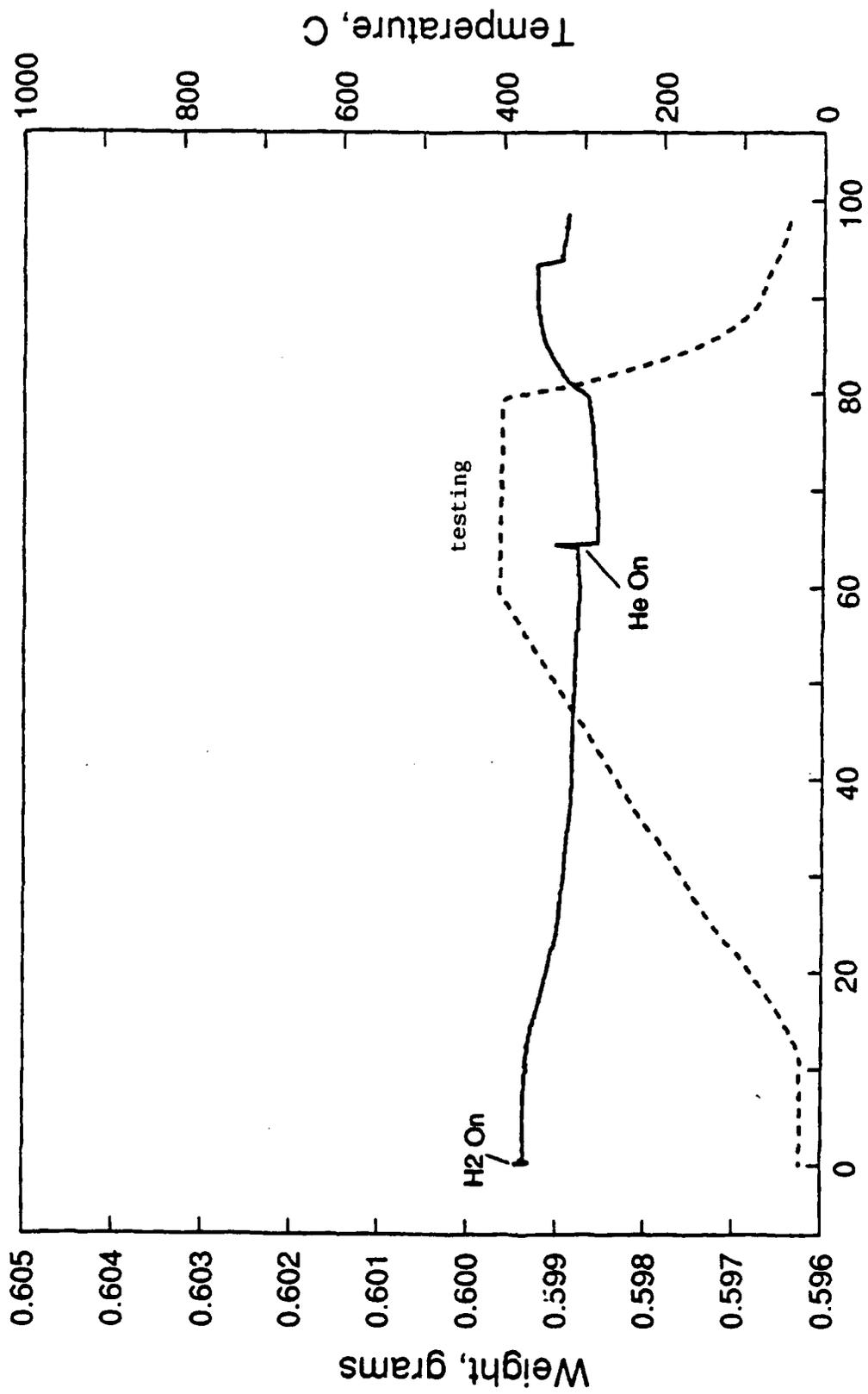


Figure 12. TGA data for sample 1 (testing phase)

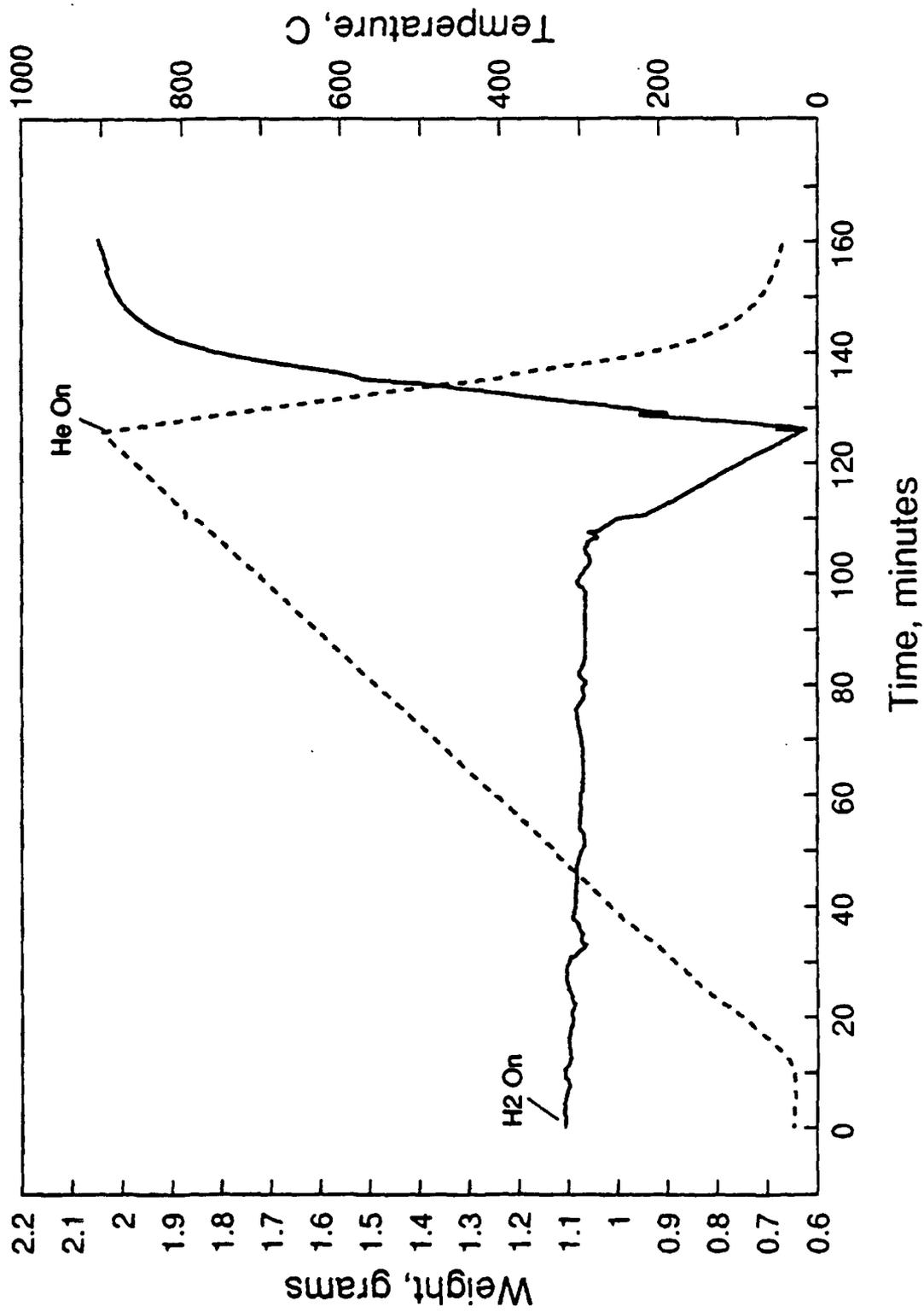


Figure 13. TGA data for sample 2

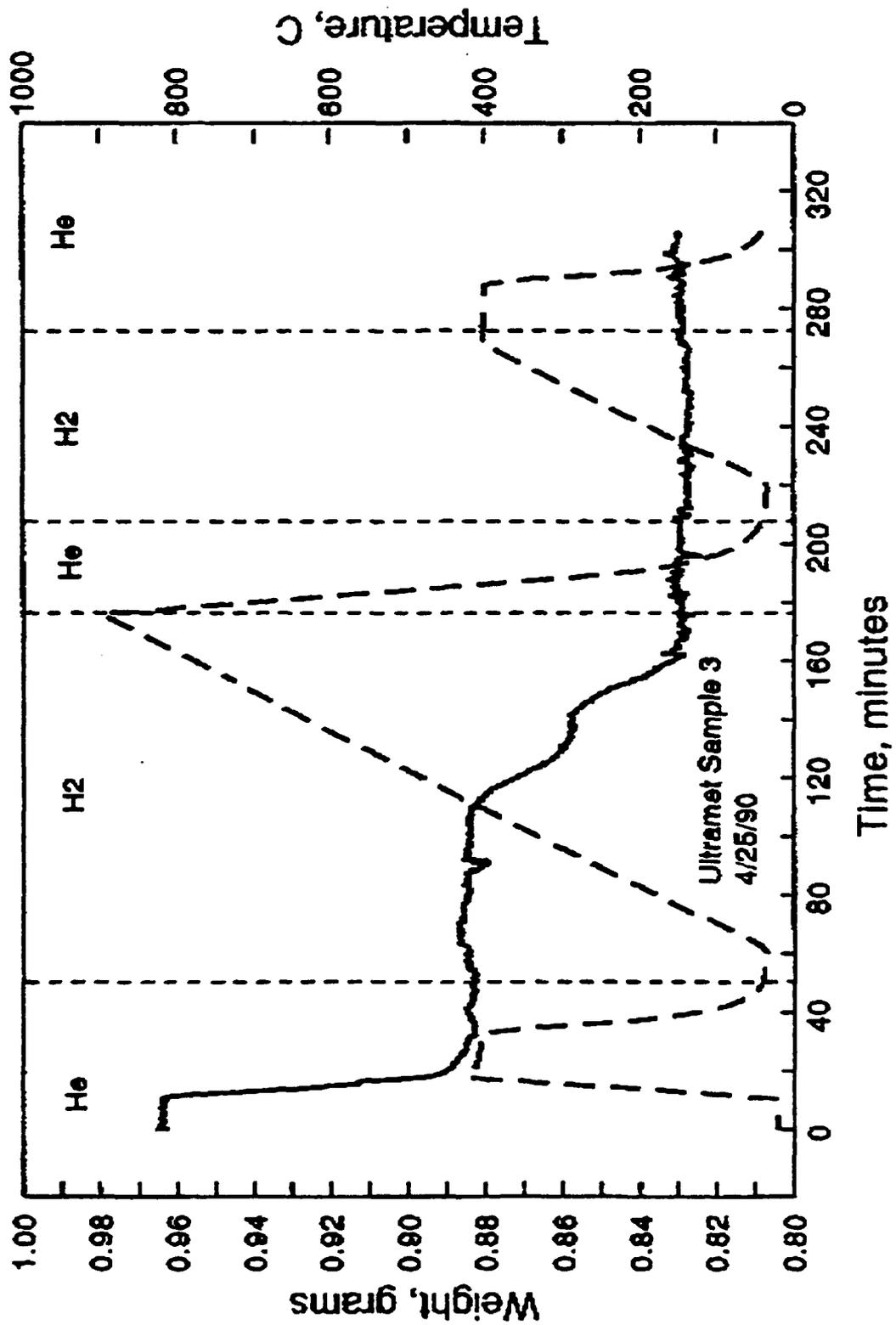


Figure 14. TGA data for sample 3

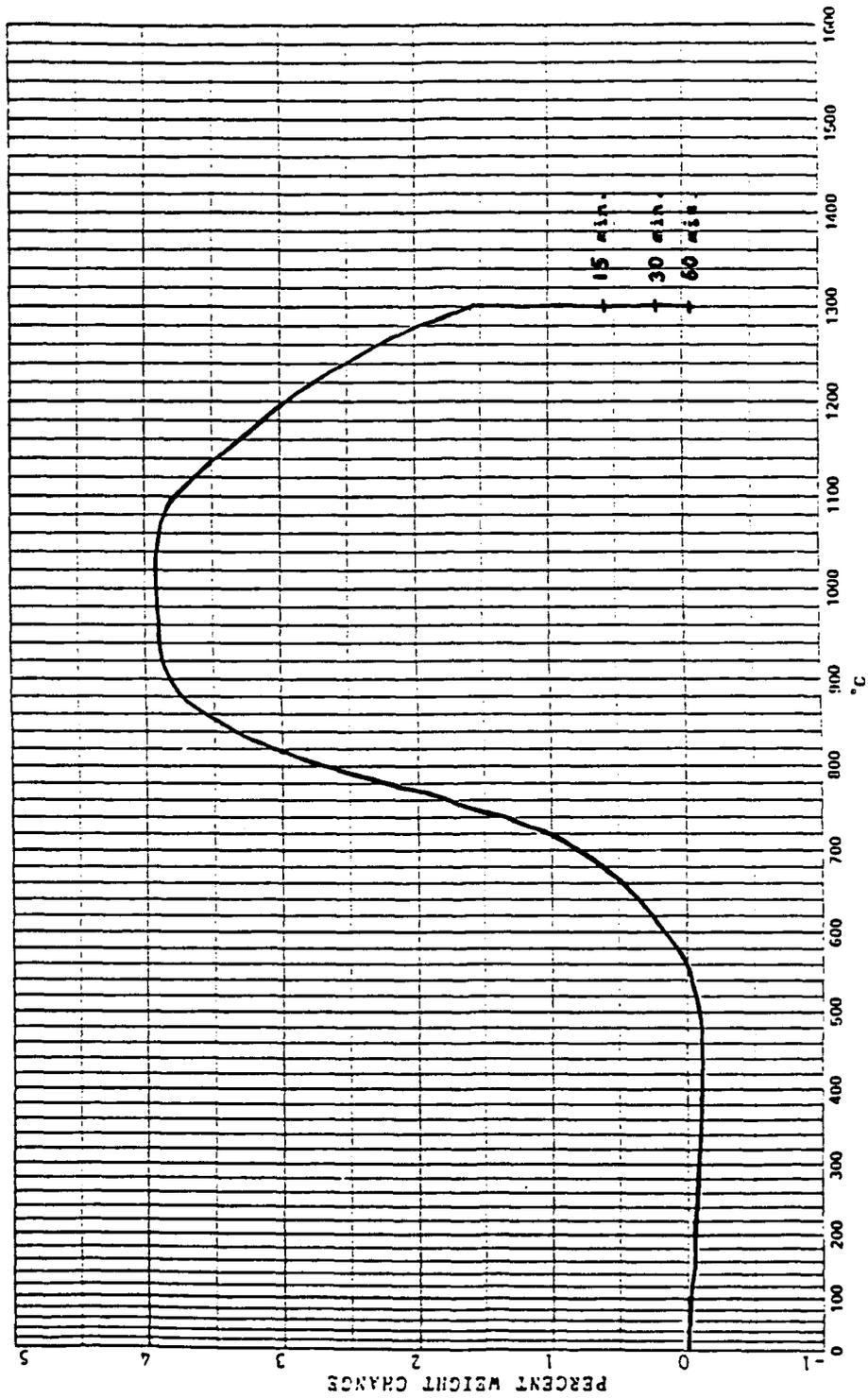


Figure 15. TGA data for Mg₂Ni sample from NASA program [3]
 15, 30, 60 min.: test duration at given points

Table 1. Physical Properties of Reticulated Carbon Foam

PHYSICAL PROPERTIES

NOMINAL VALUES, ALL PORE SIZES, STANDARD GRADE:			
Bulk Void Volume, %.....	97	Thermal Shock Resistance	Excellent
Bulk Density, lbs/ft ³	3.1	Shrinkage to 2000°F	Nil
Strut Density, lbs/ft ³	93	Volatiles to 2000°F	Nil
Strut Resistivity, 10 ⁻⁴ ohm cm	50	Melting Point (sublimes)	6330°F
Crushing Strength		Temperature Limitation: in air	600°F
@ 70°F, lbs/in ²	Varies with pore size—10 to 50	In non-oxidizing atmosphere	6330°F

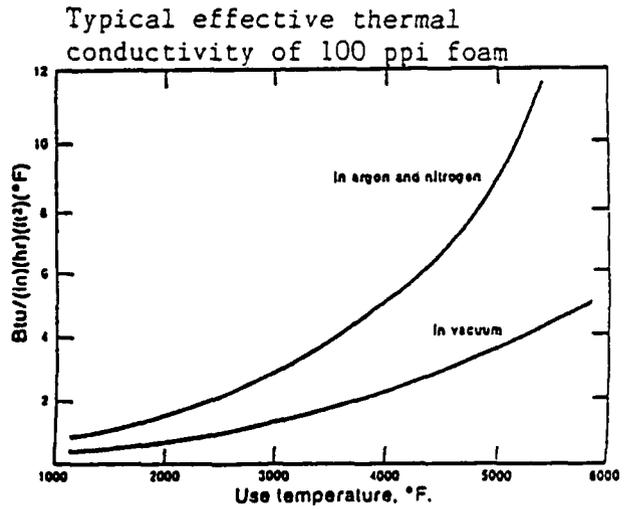
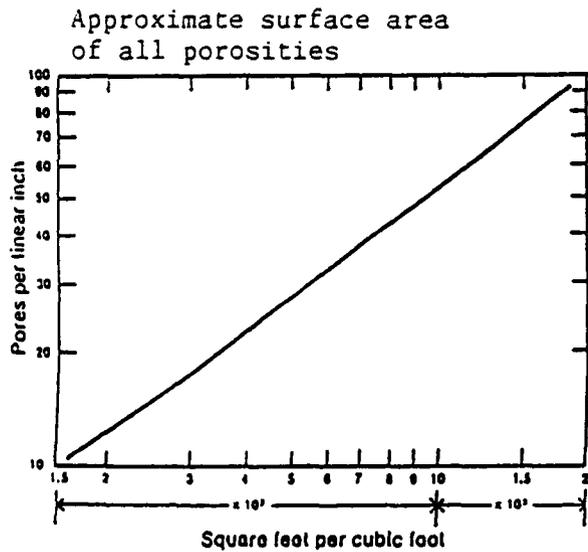


Table 2. Hydrogen Storage Capacity for Various Hydrides

Hydride	Hydrogen Storage Capacity	
	by weight (%) [1]	by volume (g/ml) [2]
MgH ₂	7.00	0.101
Mg ₂ NiH ₄	3.84	0.081
Mg ₂ CuH ₄	2.04	--