UCRL-CR--111008

DE92 019570

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for the SP100 Reactor**

Received OSTI

AUG 24 1992

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May 1992

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Alternate Electrode Materials for the SP100 Reactor

Final Report

by

Erik Randich

***Work performed under the auspices of the U.S. Department
of Energy by Lawrence Livermore National Laboratory under
contract number W-7405-ENG-48 and B&R Code AF-65-10-70***

Prepared for

***Astro Space Division
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Philadelphia, PA 19101***

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May 1992

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Introduction and Background

This work was performed in response to a request by the Astro-Space Division of the General Electric Co. to develop alternate electrode materials for the electrodes of the PD2 modules to be used in the SP100 thermoelectric power conversion system. Initially, the project consisted of four tasks: 1) development of a ZrB₂ (C) CVD coating on SiMo substrates, 2) development of a ZrB₂ (C) CVD coating on SiGe substrates, 3) development of CVI W for porous graphite electrodes, and 4) technology transfer of pertinent developed processes. The timing of the milestones for these tasks is shown in Figure 1.

In the early stages of the project, the goals of the overall program (and hence the direction of this project) changed. The project evolved initially into developing only ZrB₂ coatings on SiGe and graphite substrates, and later into developing ZrB₂ coatings only on graphite substrates. Several sizes of graphite and pyrolytic carbon-coated graphite substrates were coated with ZrB₂ during the project. For budgetary reasons, the project was terminated after half the allotted time had passed. Therefore, only certain goals were reached. Apart from the production of coated specimens for evaluation, the major accomplishment of the project was the development of the CVD processing to produce the desired coatings. This report will present the process parameters and the reasons for choosing them in such a fashion that should renewed interest in ZrB₂ occur, experimenters can readily reconstruct the equipment and obtain comparable results in a short period of time.

Experimental Procedure and CVD Equipment

The basic chemical reaction to produce ZrB₂ coatings is¹:

Of course there are many sub-species involved in this reaction, such as ZrCl₃, ZrCl₂, HBCl₂, BCl₂, BCl, H, Cl, and Cl₂, etc. The effect of the presence of these species can be evaluated using free-energy minimization computer programs, such as

FLUEQU² or SOLGASMIX,³ which can handle over 20 such species simultaneously. The value of these programs can be seen when one uses the more common simplistic approach of calculating ΔG° for (1). This result is plotted in Figure 2.⁴ ΔG° becomes negative at temperatures $>1295^\circ\text{C}$, yet satisfactory ZrB_2 coatings are obtained at temperatures as low as 900°C . This is a result of using a large excess of H_2 to "push" the reaction in the desired direction, but more so a result of the many subspecies that are present in the gas-solid system as a whole and which push the free-energy minimization point to lower temperatures. In this study, deposition temperatures between 900°C and 1000°C were used. The lower temperatures allowed a greater control of deposition rate so that very thin coatings could be obtained in reasonable reaction times.

The chemical precursors for ZrB_2 are ZrCl_4 , BCl_3 , and H_2 . The later two precursors are purchased commercially and used directly from pressurized cylinders. ZrCl_4 may be purchased commercially and brought directly into the reaction chamber ($T_{\text{subl}} = 331^\circ\text{C}$) via an inert carrier gas such as Ar; however, controlling the feed rate of ZrCl_4 using this technique is quite difficult. The customary procedure, therefore, is to chlorinate Zr directly by passing Cl_2 over a heated bed of Zr chips. Ar is generally passed through the chlorinator, serving the function of an inert carrier gas to assure efficient transfer of the ZrCl_4 . This was the procedure used in this project to obtain ZrCl_4 .

A schematic of the CVD reactor is shown in Figure 3. Cl_2 and Ar enter the top of the chlorinator and pass downward through a bed of Zr chips which is supported by a stainless steel screen. The chlorinator is made from Ni tubing and is 12" long by 1" diameter. The chlorinator is heated to $\sim 400^\circ\text{C}$ by external clamshell heaters. Care must be taken to maintain all parts of the chlorinator and chlorinator/reaction chamber flange at $\geq 350^\circ\text{C}$ to prevent ZrCl_4 powder from forming and plugging flow channels. H_2 and BCl_3 are mixed with the Ar and ZrCl_4 at the base of the chlorinator, and all precursor gases then enter the reaction chamber. A small "top hat" structure was made for the bottom of the chlorinator as a shield to prevent any particulate debris from falling directly on the substrate from the chlorinator. Samples to be coated sit in a graphite susceptor that is RF induction heated. In this study, an ENI 9600B variable frequency RF generator was used as a power source. Typical power needed to heat the susceptor to 900°C - 1000°C was 1.5-2.0 kW at a frequency of ~ 35 kHz. The reaction chamber is 8" long by 4" diameter and

constructed of stainless steel. A side viewport was used for visual observation of the sample and allowed the use of an optical pyrometer for temperature measurement. Typical operating pressures were 10-100 Torr and exhaust gases were pumped by mechanical vacuum pumps fitted with Roots-type blowers. An atomized water spray gas scrubber was used to remove any chlorine containing compounds from the effluent. The scrubbing liquor was an aqueous NaOH solution.

Several test runs were made to determine appropriate temperatures and gas flow conditions. Complete reactor conditions for all experimental runs are listed in Table 1. Standard flow conditions eventually chosen were: 50 sccm Ar, 40 sccm Cl₂, 20 sccm BCl₃, and 1000 sccm H₂. Coating thickness was then varied by changing the time at temperature. The gas ratios were chosen to obtain a smooth adherent coating. The flows used result in a Zr/B ratio of 1:1. Using the stoichiometric ratio of 1:2 results in rough, nodular, very dark-color coatings. Past experience has shown that the Group IV borides like to be sub-stoichiometric in B content and that the 1:1 ratio used here will probably result in a deposit of $\sim\text{ZrB}_{1.95}$.¹ The H/Cl ratio is maintained at $\sim 7:1$ (any ratio of 5:1 to 10:1 is quite acceptable) to assure an adequate availability of H₂ to help push reaction (1) to the right. Large H/Cl ratios also result in a better surface finish, but at some sacrifice in overall chemical conversion efficiency. Linear flow velocity through the reactor is also important to maintain a fresh supply of precursor gases at the substrate surface and an adequate removal rate of HCl. A rate of > 1 cm/s is generally adequate. A typical deposition run consisted of the following steps:

1. Preheat chlorinator to 350°C with or without Ar flow, depending upon chlorinator design.
2. Heat sample to coating temperature in vacuo (~ 10 m Torr). Heating time ~ 4 min.
3. Turn on precursor gases. Allow reactor pressure to rise to desired coating pressure.
4. Maintain flow, pressure, and temperature as necessary to obtain desired thickness.
5. Stop Cl₂ and BCl₃ flows. Maintain Ar and H₂ for 2 min.
6. Turn off RF power. Stop Ar flow. Turn off chlorinator heaters.
7. Cool in H₂ flow at coating pressure.

8. When all temperatures are $<50^{\circ}\text{C}$, evacuate reactor and backfill with Ar or air. Remove sample.
9. Reload Zr chips as needed, usually every 100 min. of run time.

Results and Discussion

Samples were coated on an as-requested basis using substrates supplied by General Electric Co. Minimal characterization of the coatings was done since the major evaluation of coating performance was to be done at General Electric's facilities. X-ray diffraction analysis verified that the coatings were crystalline ZrB_2 (Figure 4). SEM analysis of fracture surfaces demonstrated that the coatings were dense and adherent to the graphite substrates. A typical fracture surface is shown in Figure 5. SEM analysis demonstrated that the weight gains noted in Table 1 were not reliable indicators of thickness. It was found that the graphite substrates absorbed water readily from the surrounding laboratory air, and unless they were baked out in vacuo and handled in inert atmospheres prior to coating, the weight gain provided only a crude estimate of coating thickness. Essentially, the project consisted of process development and supplying coated samples to the requester. Hence, the results are straightforward. The basic reactor design worked satisfactorily and, in a short period of time, an appropriate process was developed which allowed coatings to be made on a routine basis.

References

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Table 1.

Run	Cl ₂ (sccm)	BCl ₃ (sccm)	H ₂ (sccm)	Power (kW)	Temp (°C)	Pressure (mT)	Time (m)	Δw (g)
1	40	40	500	3.0		100	15	
2	40	40	500	2.6	945	100	20	
3	40	40	500	2.5	1015	100		
4	40	40	1000	2.6	960	350	15	
5	40	40	1000	2.0		300	5	
6	40	40	1000	2.0		300	10	
7	40	40	1000		965	300	5	.0066
8	40	40	1000	2.0	950	240	5	.0113
9	40	40	1000	2.0	945	240	5	
10	40	40	1000	2.0	945	240	5	.0037
11	40	40	1000	2.0	980	100	10	.0282
12	40	40	1000	2.0	995	200	10	.0231
13	40	40	1000	2.0	990	300	10	.0154
14	40	20	1000	2.0		100	10	.0132
15	40	20	1000	2.0		200	10	.0197
16	40	20	1000	2.0		50	10	.0204
17	40	20	1000	1.6	995	100	10	.0137
18	40	20	1000	1.6		50	10	.0098
19	40	20	1000	1.6		20	10	.0045
20	40	20	1000	1.6	985	5	10	.0032
21	40	20	1000	1.6	980	20	10	.0065
22	40	20	1000	1.6	985		10	.0054
23	40	20	1000	1.6		10	10	.0047
24	40	20	1000	1.6		10	10	.0059
25	40	20	1000	1.6		10	8	.0041
26	40	20	1000	1.6		10	10	.0026
27*	40	20	1000	2.6*	915	10	8	***
28	40	20	1000	2.6	910	20	10	.0801
29**	40	20	1000	2.8	935	10	10	***
30	40	20	1000	2.8	915	20	5	.0311
31	40	20	1000	2.6		20	5	***
32	40	20	1000	2.6		20	8	***
33	40	20	1000	2.6		30	8	.0348
34	40	20	1000	2.6		60	8	.0827
35	40	20	1000	2.6		30	4	.0280
36	40	20	1000	2.4		30	4	.0300
37**	40	20	1000	2.0	935	30	5	***
38	40	20	1000	1.8	905	30	5	.0275
39	40	20	1000	1.8		20	5	.0213
40	40	20	1000	1.8		20	5	.0232
41	40	20	1000	1.8	900	20	5	.0161
42	40	20	1000	1.8		20	10	.0044
43	40	20	1000	1.6	880	20	10	
44	40	20	1000	1.6		20	5	
45	40	20	1000	1.6		20	5	.0030
46	40	20	1000	2.0	915	20	100	

Table 1.

Run	Cl ₂ (sccm)	BCl ₃ (sccm)	H ₂ (sccm)	Power (kW)	Temp (°C)	Pressure (mT)	Time (m)	Δw (g)
47	40	20	1000	1.6	915	20	10	.0357
48	40	20	1000	1.6		20	5	
49	40	20	1000	1.6		20	5	
50	40	20	1000	1.6		20	5	
51	40	20	1000	1.6		20	5	
52	40	20	1000	1.6		20	5	
53	40	20	1000	1.6		20	5	
54	40	20	1000	1.6		20	5	
55	40	20	1000	1.6		20	5	
56	40	20	1000	1.6		20	5	

*coil design changed

**susceptor design changed

***samples acid-etched and reused

Tuesday, September 10, 1991

Figure 1. Milestone summary of project as initially outlined.

Figure 2. ΔG° versus temperature for reaction (1).

Figure 3. CVD Reactor

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Figure 4. X-ray diffraction analysis of ZrB_2 coating on 8826 graphite, $\text{Cu K}\alpha$ radiation.

Figure 5. Fracture surface of typical ZrB₂ coating on graphite.