

TESTS OF CANDIDATE MATERIALS FOR
PARTICLE BED REACTORS

BNL--39508

DE87 008196

F.L. Horn, J.R. Powell, D. Wales

Brookhaven National Laboratory

Upton, New York 11973

ABSTRACT

Rhenium metal hot frits and zirconium carbide-coated fuel particles appear suitable for use in flowing hydrogen to at least 2000 K, based on previous tests. Recent tests on alternate candidate cooled particle and frit materials are described. Silicon carbide-coated particles began to react with rhenium frit material at 1600 K, forming a molten silicide at 2000 K. Silicon carbide was extensively attacked by hydrogen at 2066 K for 30 minutes, losing 3.25% of its weight. Vitreous carbon was also rapidly attacked by hydrogen at 2123 K, losing 10% of its weight in two minutes. Long term material tests on candidate materials for closed cycle helium cooled particle bed fuel elements are also described. Surface imperfections were found on the surface of pyrocarbon-coated fuel particles after ninety days exposure to flowing (~500 ppm) impure helium at 1143 K. The imperfections were superficial and did not affect particle strength.

INTRODUCTION

The materials proposed for use in Particle Bed Reactors (PBR) must withstand reactor operating conditions as well as being neutronically acceptable. Operating conditions vary with PBR application. Generally the uranium fuel is

MASTER

PS

in the form of a bed of small (~0.5 millimeter diameter) particles held between two porous frits. The inner frit is exposed to high temperature coolant gas. The fuel particles have kernels of uranium carbide or uranium oxide, either pure or diluted with some ceramic (e.g. ZrC or ZrO₂). Kernels are coated with one or more layers of chemically vapor-deposited inert ceramic material. The moderator and reflector for the reactor are also required to be compatible with the coolant but they operate at relatively low appropriate temperatures. A list of candidate materials for the reactor parts and their temperature ranges is given in Table 1. ZrC and Re have been successfully tested previously in H₂ at 2000 K, see Ref. 1.

Choice of material depends on the coolant operating temperature and operating lifetime. For example, with helium coolant the commercial High Temperature Graphite Reactor (HTGR) clad fuel particles would be selected for continuous, long life (years) PBR's. With hydrogen coolant at high temperature (e.g. 2000 K) ZrC coated particles would be selected for a short lifetime, open cycle reactor. Tests are required to validate the choices.

FUEL ELEMENT CONSTRUCTION AND THE REACTOR CORE

The fuel element of the PBR contains the spherical particle fuel, about a half millimeter in diameter, packed solidly between two porous cylindrical frits (Figure 1). Particulate fuel has been well developed and tested, Ref. 2, for gas-cooled power reactors. In this application, the particles are held in a graphite matrix shaped into prismatic blocks or balls. The graphite also serves as the neutron moderator.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TABLE 1

Candidate Fuel Element Materials

(Temperatures from ~1100 K to ~3500 K)

<u>Fuel Cladding</u>	<u>Porous Frits</u>	<u>Coolant</u>
Pyro-carbon	C-composites	He
ZrC	ZrC (coated & uncoated)	H ₂
SiC	Re	NH ₃
Re	SiC	D ₂
HfC	Ni	
TaC	HfC	

Candidate Moderator-Reflector Materials

(Temperatures up to ~1000 K)

Be

ZrH_{1.8}⁷LiH

C

D₂O

In the PBR, fuel and moderator are separated in the reactor core. The moderator is kept at a relatively low temperature by incoming coolant, which then flows through the hot particulate fuel between the two cylindrical frits. The only structural portions of the core operating at high temperature are the

outlet frit and the gas outlet plenum, which generally set the limit on outlet temperature. [In electrical power generating systems, the turbine inlet blade temperature may also limit the reactor operating temperature].

For propulsion systems, the highest reactor outlet temperature possible (e.g. ~3000 K) is desired, which restricts the choice of the outlet frit material to high temperature metals, ceramics and zirconium carbide-coated graphite. Rhenium hot frits have been proposed (m.p. = 3453 K) because of its excellent high temperature properties and compatibility with hot hydrogen and helium. A full size, prototype frit has been made by milling small slots in a rhenium tube by Electrical Discharge Machine techniques. A graphite frit has also been made by milling small slots with a cutter wheel. Other candidates for the hot frit include a reticulated vitreous-carbon thick walled tube of open porosity, and an open-weave multilayer carbon filament tube. Both would be coated with zirconium carbide for use with hydrogen propellant.

The inlet frit is at relatively low temperatures and performs the function of locally controlling the flow of gas coolant to the fuel bed. Generally, the pressure drop through the inlet frit is designed to be a significant fraction of the total reactor pressure drop. By locally varying frit porosity, coolant flow can be adjusted. The inlet frit can be made commercially available porous sintered inconel or high nickel steel.

TESTS OF PBR FUEL ELEMENT FOR CLOSED CYCLE HELIUM COOLED REACTORS

A series of three tests were made on a full size prototype PBR fuel element. The purpose was to determine the effect of impurities in the helium coolant

of a PBR on pyrocarbon-coated fuel. [Additional tests are planned with zirconium-carbide coated fuel].

The PBR fuel element was exposed to flowing helium in which H₂, CO, CO₂ CH₄ and H₂O impurities were continuously monitored and held constant. Three runs at 870°C (1145 K) were performed, each of 720 hours (see Table 2). The local temperature in a particle bed is within a few degrees of the local coolant temperature. For many continuous PBR applications, coolant enters at about 400 K and exits at about 1200 K. The test temperature of 1145 K (872°C) is thus representative of the hottest portion of the PBR element.

METHODS

The fuel particles were contained in a full size fuel element (1 1/2" Dia. x 12" long with 0.078" thick frits) composed of concentric cylindrical stainless steel frits with the fuel filling the annular space between the frits. The element was held and heated to 870°C in a high temperature furnace. Helium circulated through the element. Impurity concentrations in the helium were continuously monitored by an automatic gas chromatograph, and adjusted to the desired preset values (Table 2).

BED RESULTS

The complete bed was removed from the fuel element and weighed after each test. Bed weight loss, after each test of 720 hrs., was 0.052, 0.062, and

TABLE 2

Particle Bed Helium Impurity Runs*

<u>Run</u>	<u>Temperature-1143 K</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Total Hours	720	720	720
PPM H ₂	200	400	400
PPM CH ₄	2	2	2
PPM CO ₂	5	5	10
PPM CO	40	80	80
PPM H ₂ O	5	5	4

*Gas Flow Rate: 6.37 liters per minute.

0.092% respectively. The crush strength of the fuel particles did not change after 90 days of exposure to the impurities. Data were derived from tests on 500 unexposed fuel particles and 500 particles exposed for a total of three runs. On a statistical basis, the 50th percentile crush weight of original pellets was 2000 grams, and the 50th percentile of exposed pellets was 2015 grams, essentially no change.

Photomicrographs of the exposed particles (see Figure 2) showed surface imperfections that did not penetrate the coating of pyrocarbon. The source of these imperfections appears to be small inclusions in the surface coating, probably of iron. Previous studies have shown that iron catalyzes the oxidation of graphite with CO₂ and H₂O impurities in helium (Ref. 3 & 4).

Bed weight data indicate that doubling the CO concentration increases weight loss by 0.010%, while doubling the CO₂ concentration increases weight loss by 0.030%. The iron inclusions in graphite have been shown to cause the oxidative weight loss pitting. These iron inclusions can be removed prior to use by treating the graphite coated fuel with iodine gas at 1173 K (Ref. 4).

TESTS OF FRIT MATERIAL FOR SHORT TERM H₂ COOLED PBR'S

The frits of vitreous carbon and silicon carbide were tested in hydrogen at high temperatures for periods of minutes (see Table 3).

TABLE 3
Frit Tests (H₂-3.8 SCFH)

<u>Run No.</u>	<u>Material</u>	<u>Temp.</u>	<u>Time</u>	<u>Wt. Loss</u>
1	107 mg 3.5% T.D.-V. Carbon	2473 K	1 min.	18.37%
2	233 mg 17% T.D.-V. Carbon	2473 K	1 min.	8.0
3	75 mg 3.5% T.D.-V. Carbon	2123 K	2 min.	10.1%
4	94 mg 3.5% T.D.-V Carbon	2488 K	1 min.	13.0%
5	239 mg 17% T.D.-V. Carbon	2483 K	10 min.	22.6%
6	326 mg 14% T.D.-Si Carbide	2098 K	1 min.	0.4%
7	262 mg 14% T.D.-Si Carbide	2043 K	10 min.	0.61%
8	268 mg 14% T.D.-Si Carbide	2066 K	30 min.	3.25%

% T.D. - % of theoretical density, indicating porosity.

FRIT RESULTS

The SiC and vitreous carbon frits were tested in flowing hydrogen at temperatures up to 2500 K. Two densities of vitreous carbon were used, i.e. 3.5% and 17% of theoretical density.

Photomicrographs of the SiC frit in Run #7 are shown in Figure 3. The frit experienced a weight loss of 0.61% after a 10 minute exposure to 2050 K hydrogen. The attack is evident on the surface of the SiC (Figure 4), with holes formed at some locations of the frit structure. Portions of the originally smooth surface show a sharp needlelike structure after exposure to the hydrogen (Figure 5).

DISCUSSION

The vitreous carbon loses weight rapidly, on exposure to hot hydrogen, up to 18% in only one minute. This results from its high reactivity to hydrogen and the large surface area in the frit. In contrast, silicon carbide appears to be a viable frit material; in 10 minutes, it lost only 0.61% in weight. Although there is some surface attack (Figure 5), photomicrographs indicate that it is probably acceptable. The 30-minute test showed continued attack with a 3.25% weight loss.

Based on these tests, SiC appears suitable for the burst power mode of operation up to temperatures of 2150 K. Lower temperatures should result in a slower rate of attack and allow longer operating periods. At higher temperatures, SiC could be coated with an inert material (e.g. ZrC), or methane could be added to the hydrogen to suppress reaction.

SILICON CARBIDE - RHENIUM COMPATIBILITY TEST

The compatibility of fuel particles coating options (e.g. pyrocarbon, silicon carbide or zirconium carbide) with the rhenium hot frit has been investigated. The pyrocarbon and zirconium carbide coatings showed no reaction (Ref. 1); however, silicon carbide began to react with rhenium at 1600 K (Figure 6). At 2000 K, the rhenium formed a silicide which melted around the silicon carbide particles (Figure 7). Accordingly, silicon carbide coated fuel particles with rhenium frits should not be used above 1500 K.

CONCLUSIONS

Material proposed for use in the PBR have been tested under the environmental conditions in which they expect to operate to determine what, if any, deficiencies exist. It has been found that the long term presence of high levels of various impurities in helium, including 400 PPM of hydrogen, has no effect on the strength or integrity of the fuel particles. However, slight surface imperfections have been found in the pyrocarbon after 90 days exposure at 1143 K, due to reaction with small inclusions of iron. Removal of these inclusions is expected to eliminate such imperfections. Based on these preliminary experiments, it appears that long life, direct cooled PBR should operate satisfactorily, even if high levels of impurities are present in the helium coolant. With regard to open cycle operation, it appears possible to use silicon carbide hot frits in hydrogen cooled burst power reactors at temperatures up to ~2100 K. Silicon carbide coated fuel particles should also be suitable for high temperature burst power service. However, silicon carbide particles in contact with rhenium have been found to react at high temperatures. The maximum outlet temperature capability of reactors with rhenium hot frits

and silicon carbide coated particles appears to be limited to ~1500 K. Higher temperature operation thus requires either using zirconium carbide-coated particles, if a rhenium hot frit is used, or using a silicon carbide or other non-reactive frit if silicon carbide coated particles are used.

References

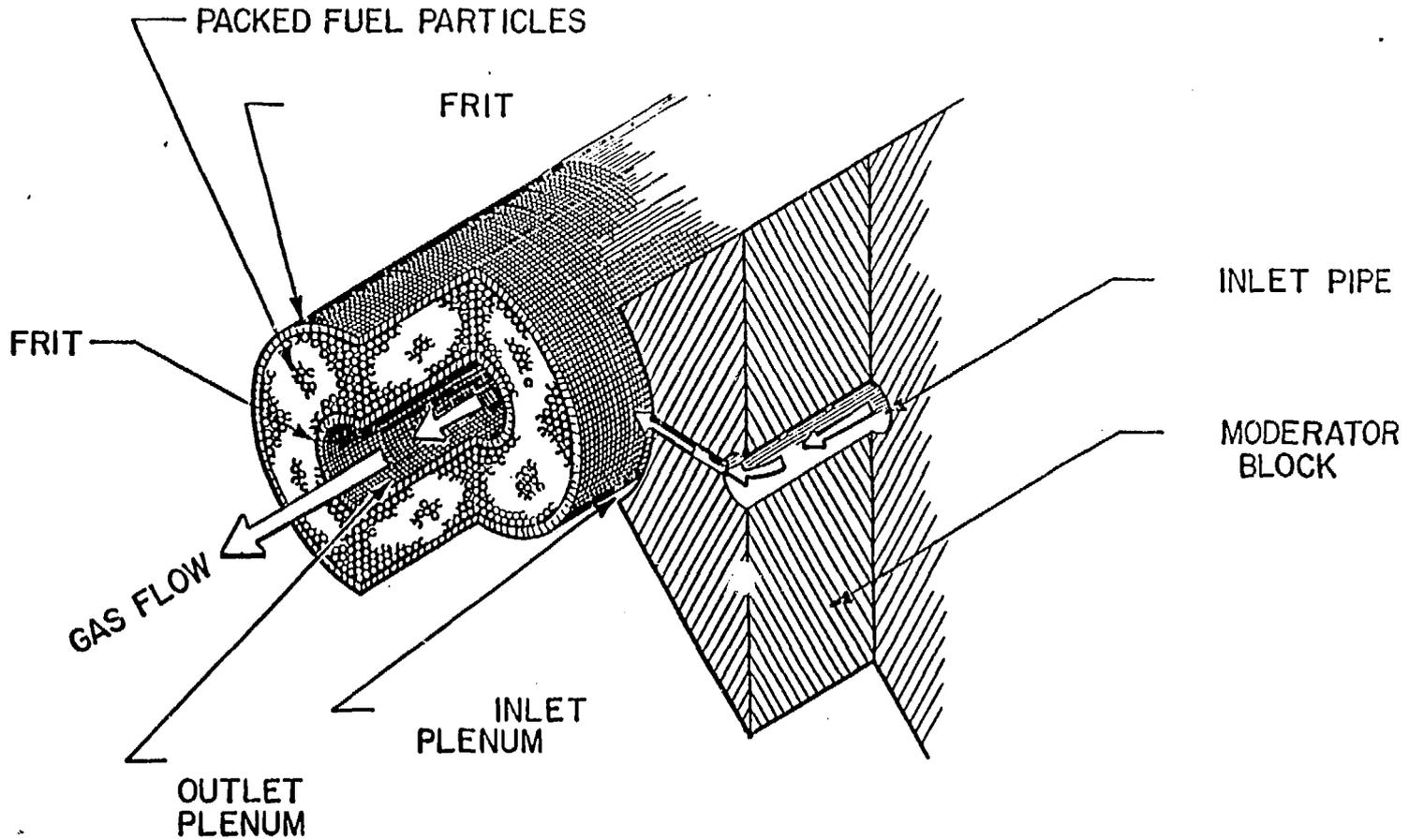
1. Horn, F. L., J. R. Powell, J. M. Savino, "Particulate Fuel Bed Tests," in Trans. 2nd Symposium on Space Nuclear Power Systems, held in Albuquerque, NM, January 1985.
2. Post, R. G., September 1977, "Coated Particle Fuels," Nuc. Tech., Vol. 35, No. 2, entire issue.
3. Growcock, F. B., D. Chandra, J. Heiser, and J. Skalyo, Jr. (1979) "Graphite Oxidation by Moisture," Advanced Reactor Safety Research Division Quarterly Progress Report during January 1979 through March 1979, NUREG/CR-0820, BNL-NUREG-51014, Brookhaven National Laboratory, Upton, NY.
4. Eto, M., and F. B. Growcock, "Effect of Oxidizing Environment on the Strength and Oxidation Kinetics of HTGR Graphites," Part I: Reactivity and Strength Loss of H451, PGX and IG-11 Graphites, NUREG/CR-2480, BNL-NUREG-51493, Brookhaven National Laboratory, Upton, NY.

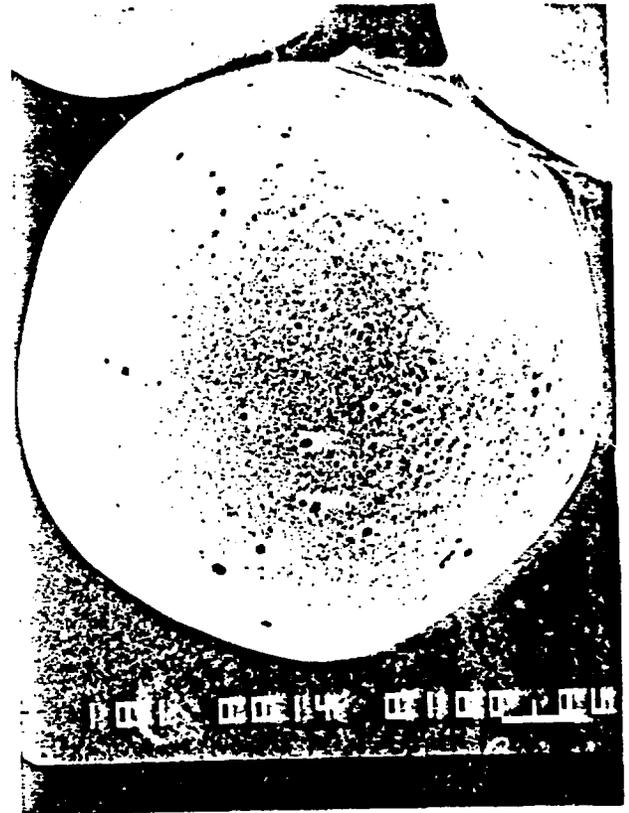
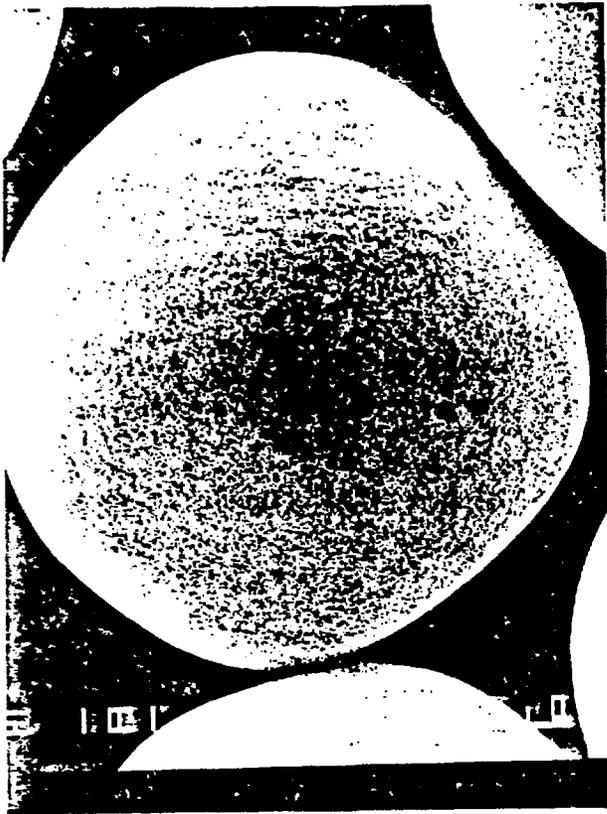
ACKNOWLEDGMENT

Research carried out under the auspices of the U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

Figure 1

BASELINE FUEL ELEMENT & MODERATOR BLOCK





BEFORE

AFTER

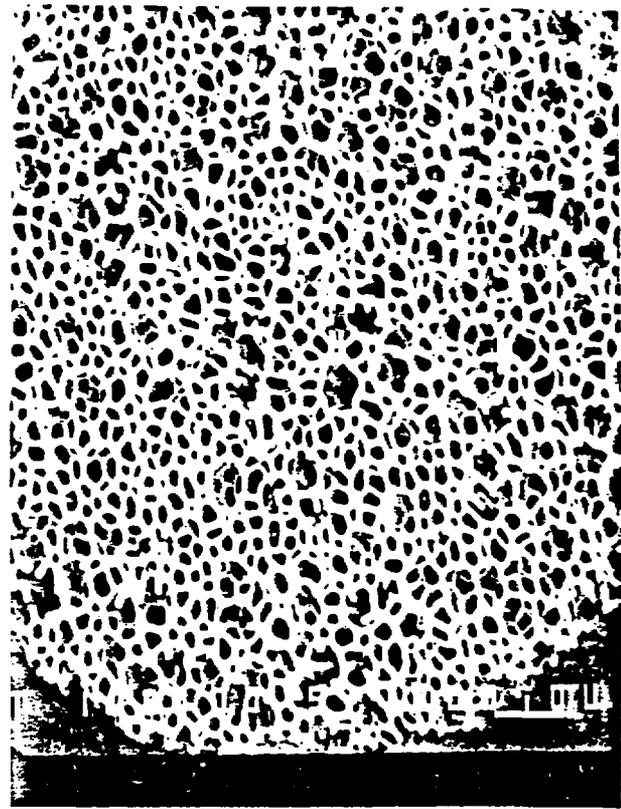
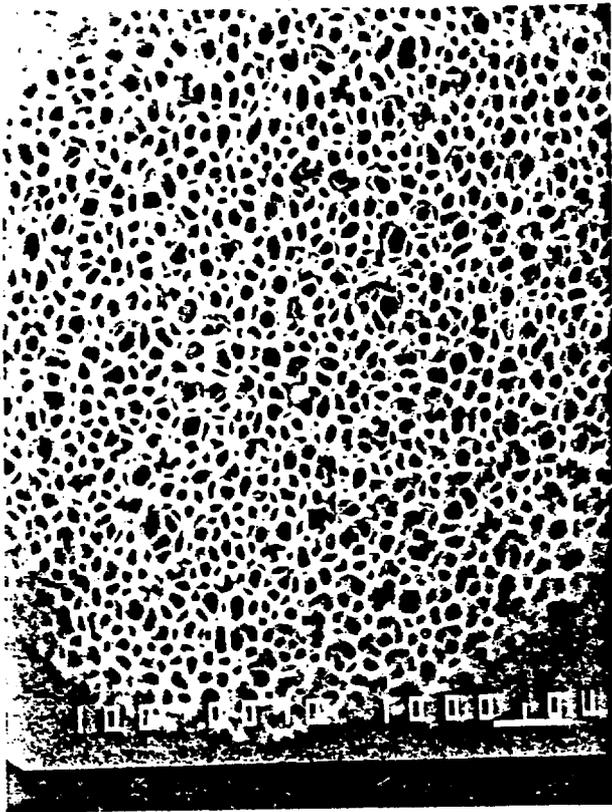
PYROCARBON -- COATED FUEL PARTICLES
(MAGNIFICATION 100X)

BEFORE - PRIOR TO EXPERIMENT

AFTER - 2160 HRS. IN HELIUM AT 870°C
WITH IMPURITIES AS SHOWN BELOW

TOTAL HOURS	720	720	720
PPM H ₂	200	400	400
PPM CH ₄	2	2	2
PPM CO ₂	5	5	10
PPM CO	40	80	80
PPM H ₂ O	5	5	4

Figure 2



BEFORE

AFTER

SILICON CARBIDE FRIT MATERIAL
BEFORE - PRIOR TO EXPERIMENT
AFTER - 10 MIN. IN HYDROGEN 1770°C
MAGNIFICATION 10X

Figure 3

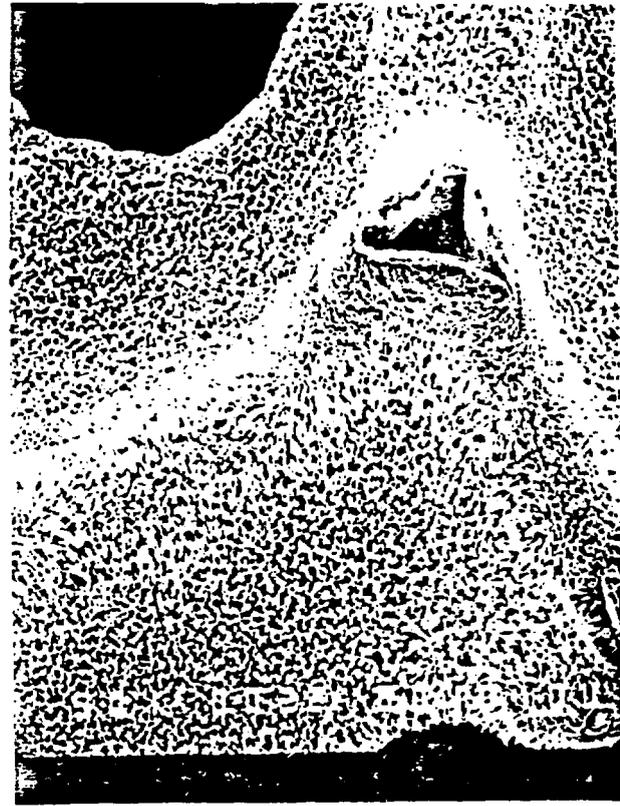


BEFORE

AFTER

SILICON CARBIDE FRIT MATERIAL
BEFORE - PRIOR TO EXPERIMENT
AFTER - 10 MIN. IN HYDROGEN 1770°C
MAGNIFICATION 100X

Figure 4



BEFORE

AFTER

SILICON CARBIDE FRIT MATERIAL
BEFORE - PRIOR TO EXPERIMENT
AFTER - 10 MIN. IN HYDROGEN 1770°C
MAGNIFICATION 500X

Figure 5

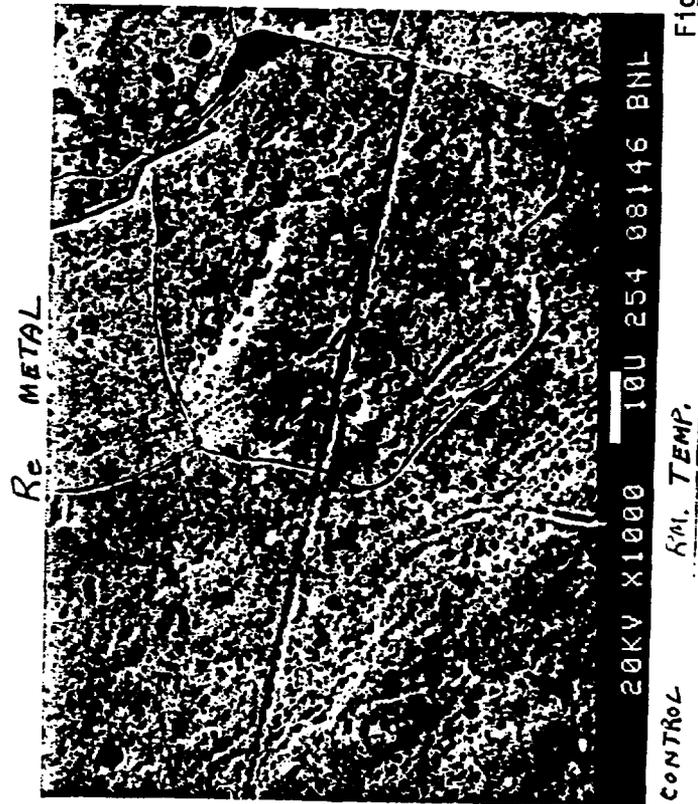
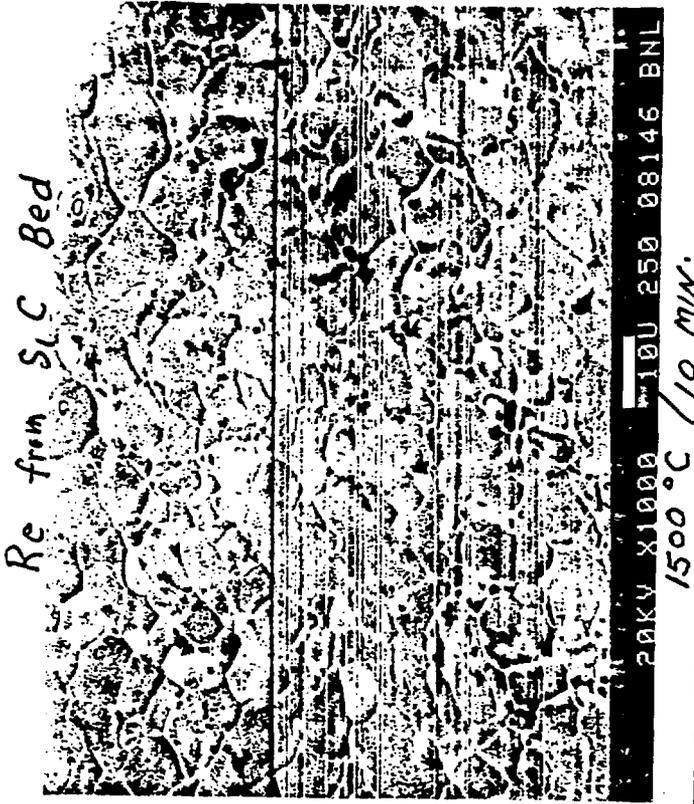
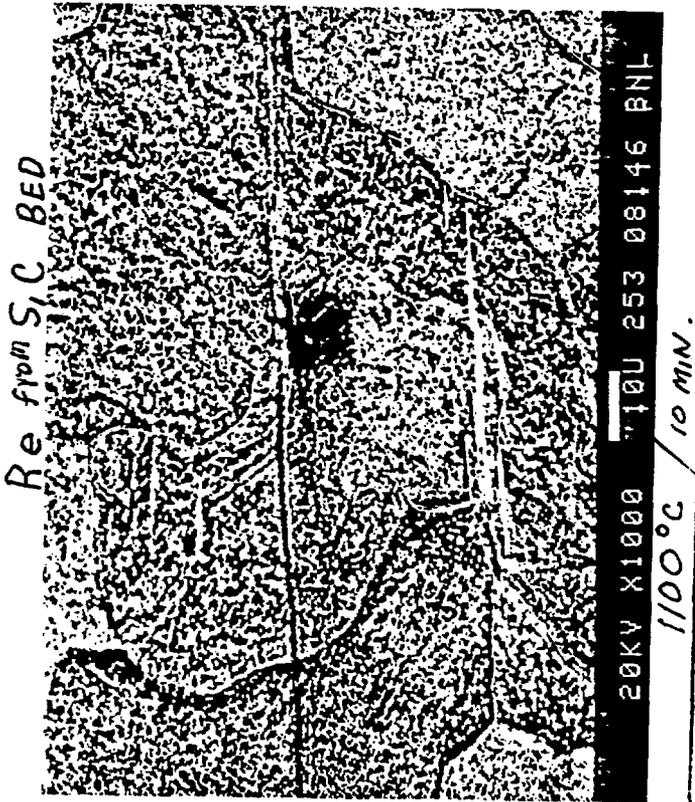
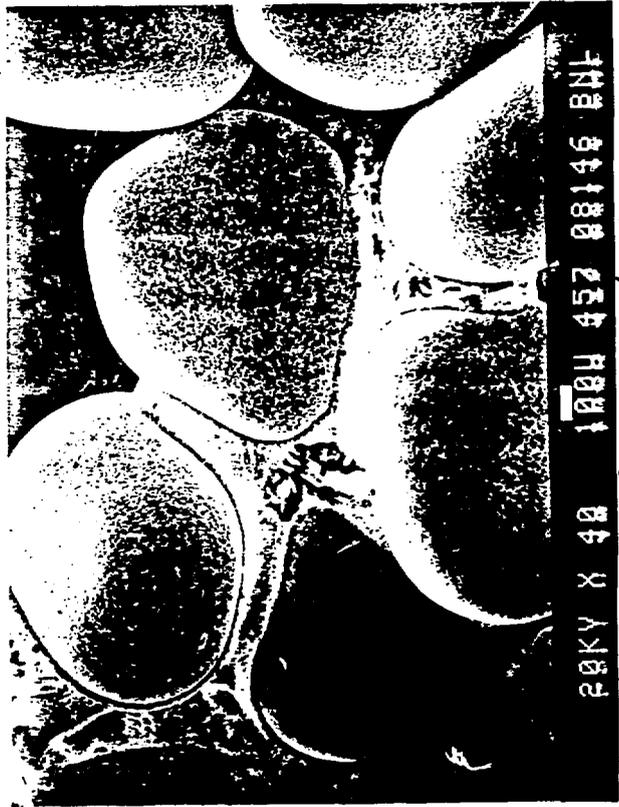


Figure 6



20KV X 40 100µ 457 08146 BNF
Particles in Rhenium Silicide at 200K

Figure 7