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FINAL REPORT

DEVELOPMENT AND FABRICATION OF INSULATOR SEALS FOR THERMIONIC DIODES

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ACKNOWLEDGEMENT

This report was prepared by Thermo Electron Corporation for the Jet Propulsion Laboratory. Responsibility at Thermo Electron belonged to the Direct Conversion and Electronics Group under the direction of Arvin H. Smith; the Nuclear Thermionics Department, under the direction of John B. Dunlay, carried out the program. Dr. Seigo Matsuda provided metallurgical support and H. Hardister and B. Nowokunski provided assistance in the area of specimen fabrication.

1. INTRODUCTION AND SUMMARY

1.1 PROGRAM DESCRIPTION

This program was carried out to develop and deliver fabricated cermet seals for thermionic diodes. Eight different types of cermet seals were investigated:

Type 1 - 1 micron Al_2O_3 with Nb spheres.
Type 2 - 200 Å Al_2O_3 with Nb spheres.
Type 3 - 1 micron Al_2O_3 with Nb 1% Zr spheres.
Type 4 - 200 Å Al_2O_3 with Nb 1% Zr spheres.
Type 5 - Pure Y_2O_3 with Nb 1% Zr spheres.
Type 6 - Y_2O_3 3% ZrO_2 with Nb 1% Zr spheres.
Type 7 - Y_2O_3 10% ZrO_2 with Nb 1% Zr spheres.
Type 8 - ZrO_2 12% Y_2O_3 with Nb 1% Zr spheres.

Investigations were made to determine the most favorable fabrication techniques and the effect of the bonding cycle, (length of bonding time and shutdown sequences). The analysis of the seals included tensile test, vacuum test, electrical test and metallurgical examination.

At the conclusion of the development phase, 36 seals were fabricated for delivery to and evaluation by the Jet Propulsion Laboratories.

1.2 SPECIMEN PREPARATION

The powder metallurgy process was used to form a cermet insulator body and to join the cermet to metallic flanges. Development work was concentrated on assemblies in a cylindrical geometry. The cermet insulator body consists of niobium or niobium 1% zirconium spheres dispersed in a continuous matrix of ceramic. A sphere diameter of

.001 inch to .002 inch was chosen to insure a multiple sphere structure for typical wall thicknesses of .010 inch to .020 inch.

The metallic spheres, as shown in Figure 1.1, are coated with a binder, mixed with ceramic powder, and screened to obtain a uniform ceramic layer around the individual spheres. Figure 1.2 illustrates the coated spheres. The spheres are then cold-pressed on mandrels to form thick-walled cylinders of the approximate diameter required. After removal of the mandrel, the binder was removed by low temperature firing in vacuum. Figure 1.3 illustrates the pressed cylinder after binder removal. Additional firing at high temperatures was performed to achieve partial sintering. In the partially sintered state, the thick-walled cylinders are readily machined to the thin wall configuration required for pressure bonding. Figure 1.4 illustrates the machined cermet cylinder.

Machining of the partially sintered cylinder exposes some of the niobium spheres at the cermet-to-flange interface. During the subsequent high pressure, high temperature autoclave operation, diffusion bonding occurs between ceramic and metal and also at the exposed niobium or niobium 1% zirconium spheres to the niobium 1% zirconium flange area. The joining of the spheres to the flange forms metallic anchors extending into the cermet structure, which increase the mechanical strength at the interface bond. Figure 1.5 illustrates a typical anchor.

The machined cermet cylinder is then encapsulated in niobium 1% zirconium members and autoclaved to form the trilayer assembly illustrated in Figure 1.6. Machining of the individual seals can then be accomplished.

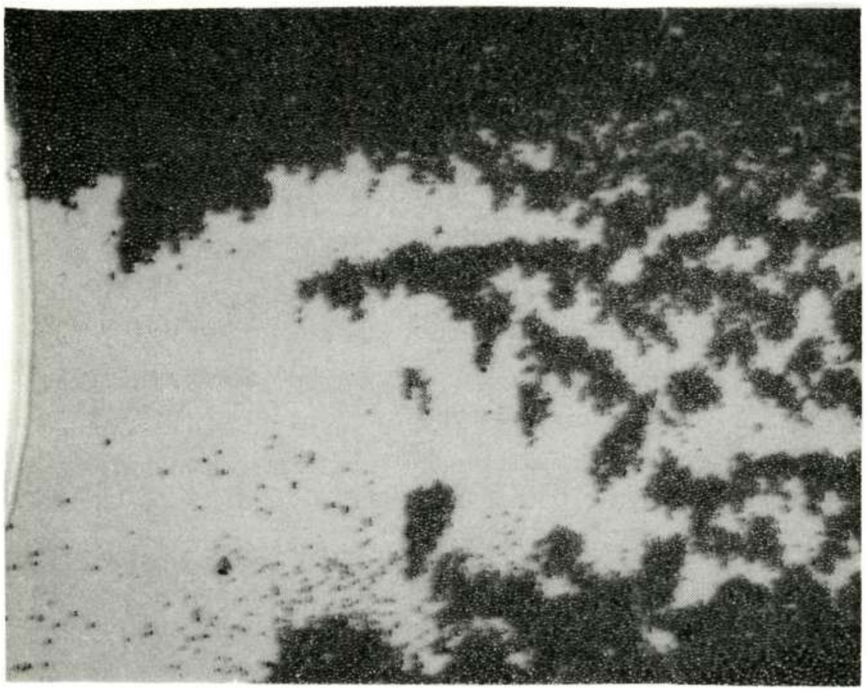

Figure 1.1 Uncoated Metallic Spheres.

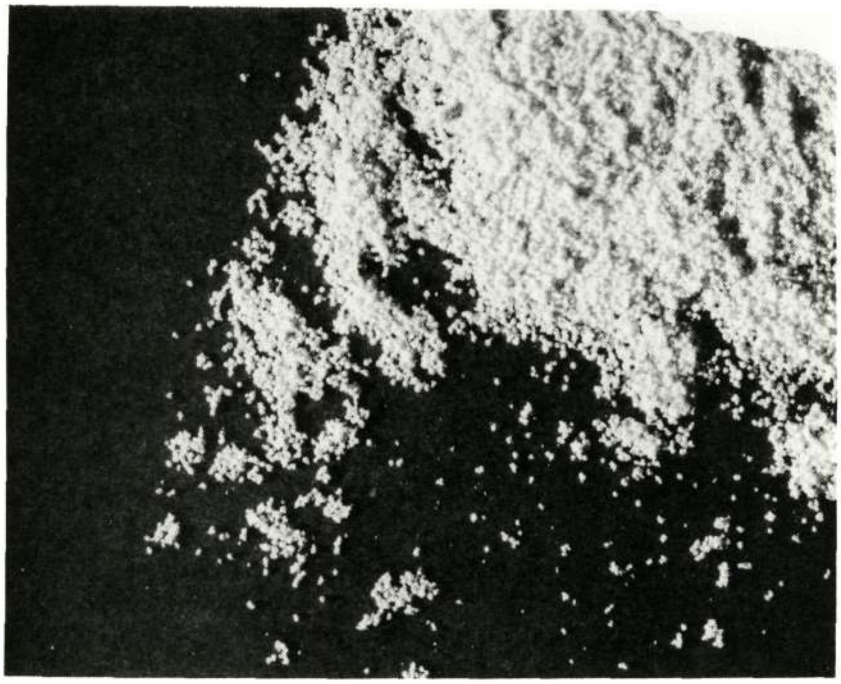

Figure 1.2 Coated Metallic Spheres.

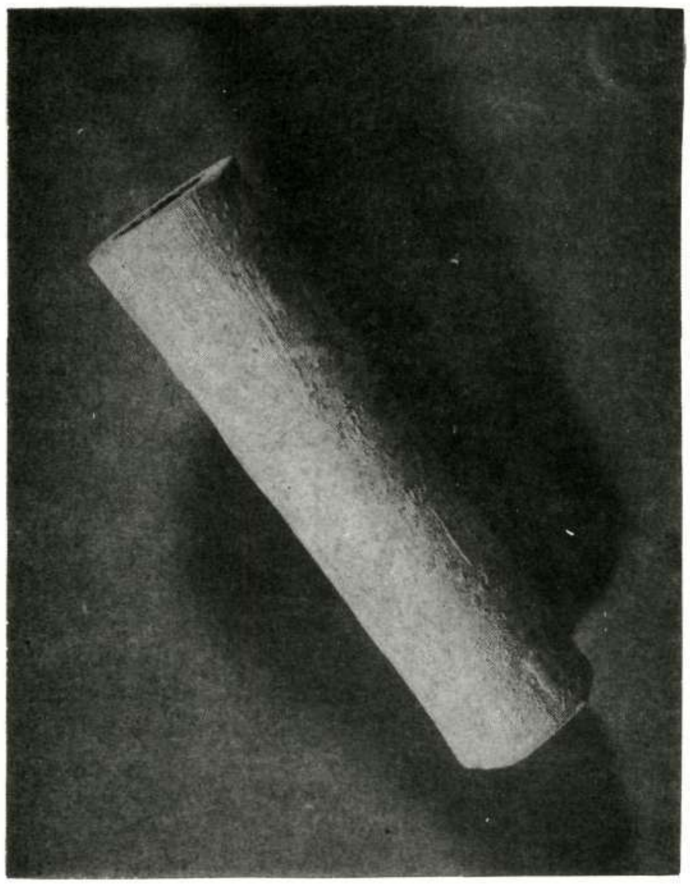

Figure 1.3 Cold Pressed Cermet Cylinder.

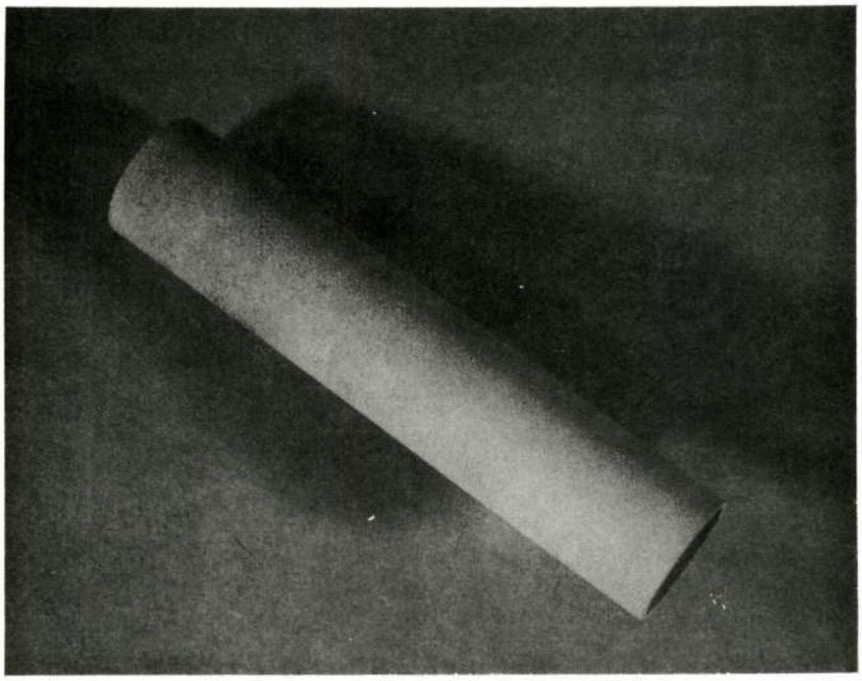

Figure 1.4 Machined, Partially Sintered Cermet Cylinder.

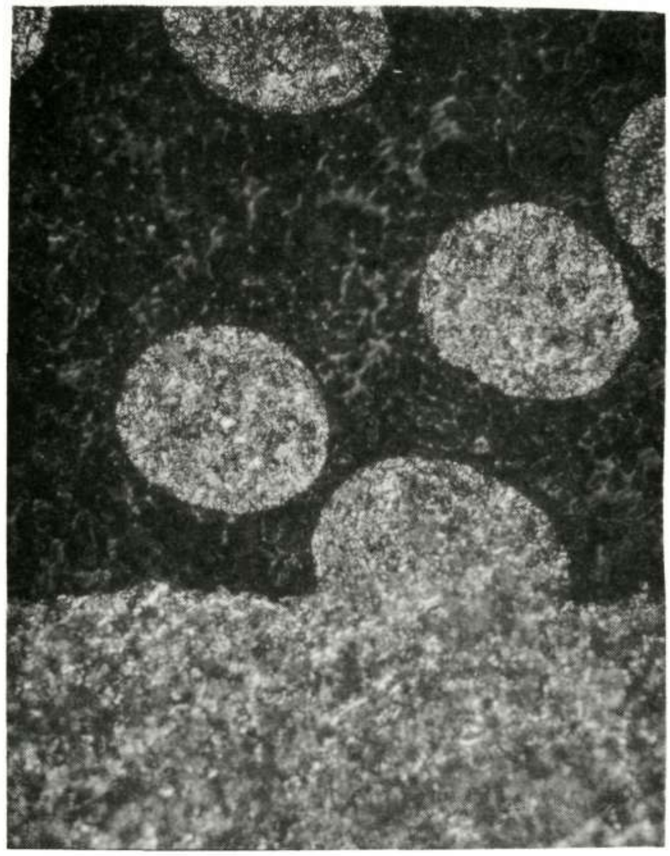

Figure 1.5 Typical Sphere-to-Flange Bond Forming a Mechanical Anchor.

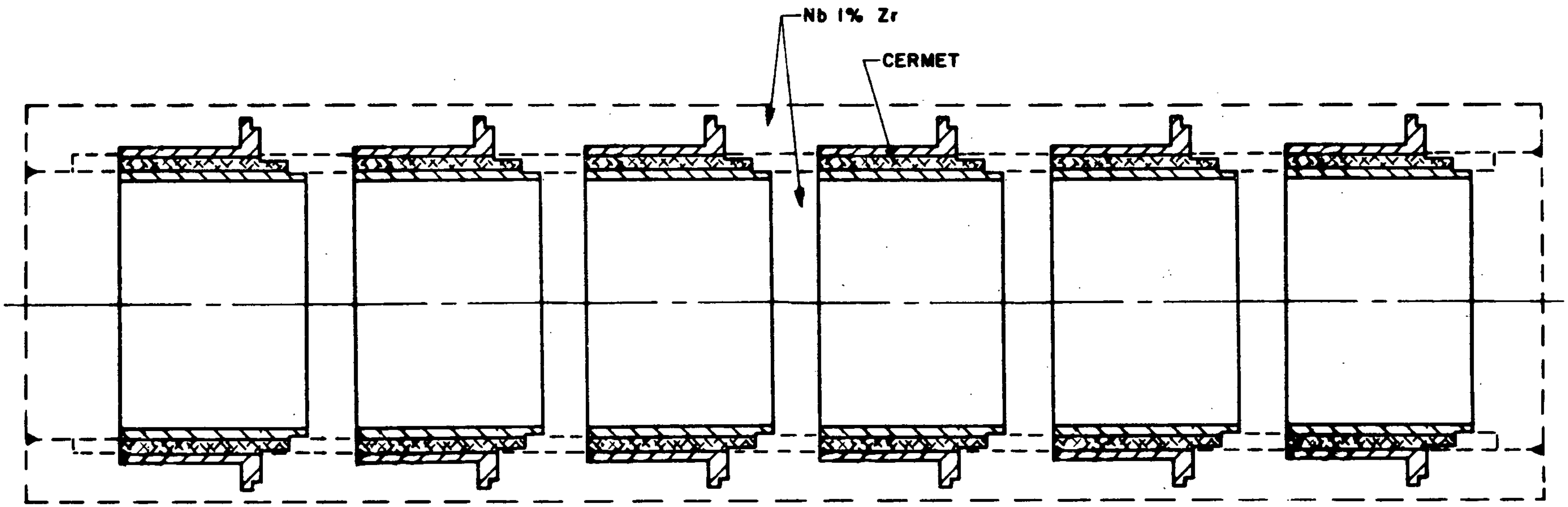

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Figure 1.6 Bonded Trilayer Assembly for the Fabrication of Six Individual Seals.

1.3 SEALS DESCRIPTION

The thermionic diode seal was designed to incorporate the latest fabrication techniques developed for cermet fabrication. Six seals were fabricated and bonded in one assembly. Figure 1.7 illustrates the design. All six seals are machined from one common capsule. The capsule consists of a rod of Nb 1% Zr surrounded concentrically by a cylinder of cermet which is in turn surrounded by a cylinder of Nb 1% Zr. The capsule is welded closed and pressure bonded to form a trilayer assembly. Each seal is sliced off the common trilayer and machined, as shown in Figure 1.6.

1.4 TEST DESCRIPTION

Simple trilayer seals were fabricated for the development phase of the contract. Figure 1.8 illustrates the design. The fabricated seals were first tested for vacuum integrity. The seals were axially leak tested with a leak detector calibrated to 10^{-10} std cc/sec. Electrical resistance measurements were taken from the seals between the inner and outer metal members. These measurements were taken at room temperature.

The seals were then sectioned. One portion of the seal was used to determine the bond strength of the fabricated structure. The samples were brazed with copper to Nb adapters. Figure 1.9 illustrates the fabricated assembly. The tensile test specimens were then installed in a "Super L" tensile tester and evaluated for bond strength. Figure 1.10 illustrates a typical fractured assembly after testing.

Metallurgical examination was conducted on the remaining portion of the seal. It consisted of examination by optical microscope, electron

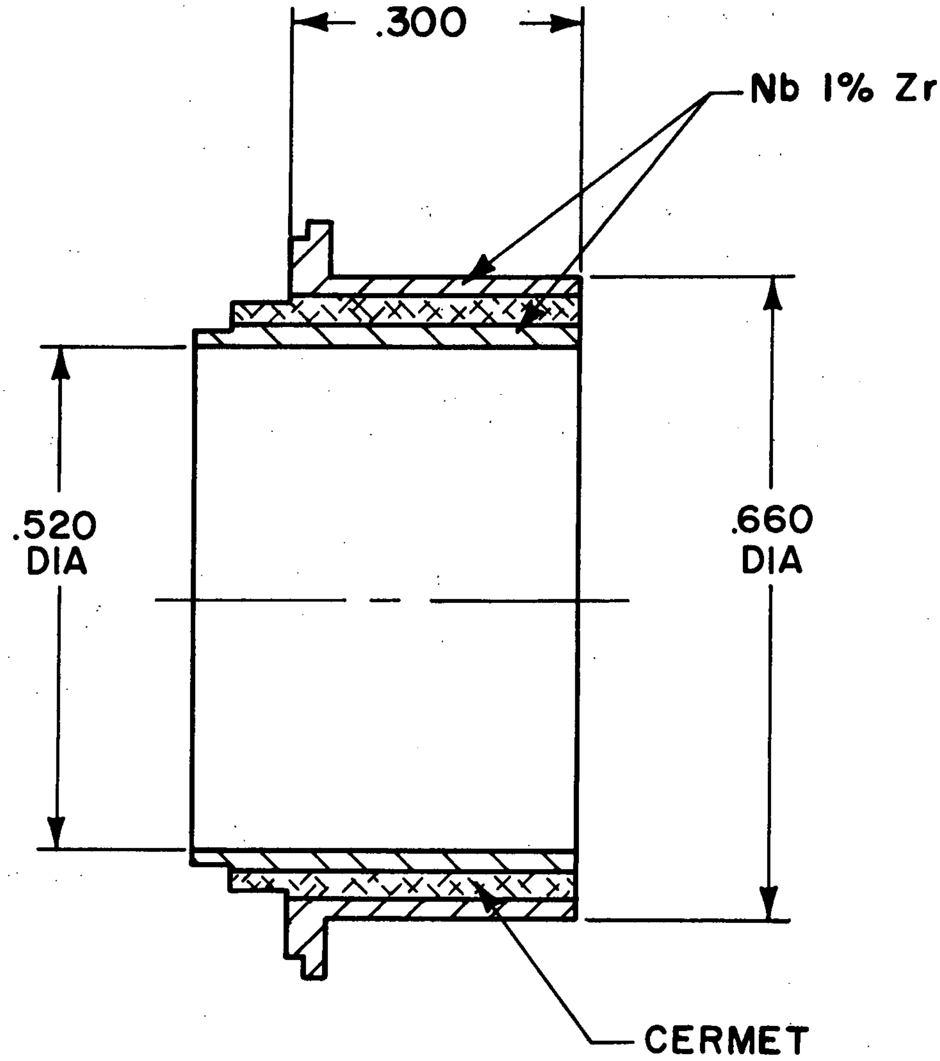


Figure 1.7 Cermet Seal for Thermionic Diodes.

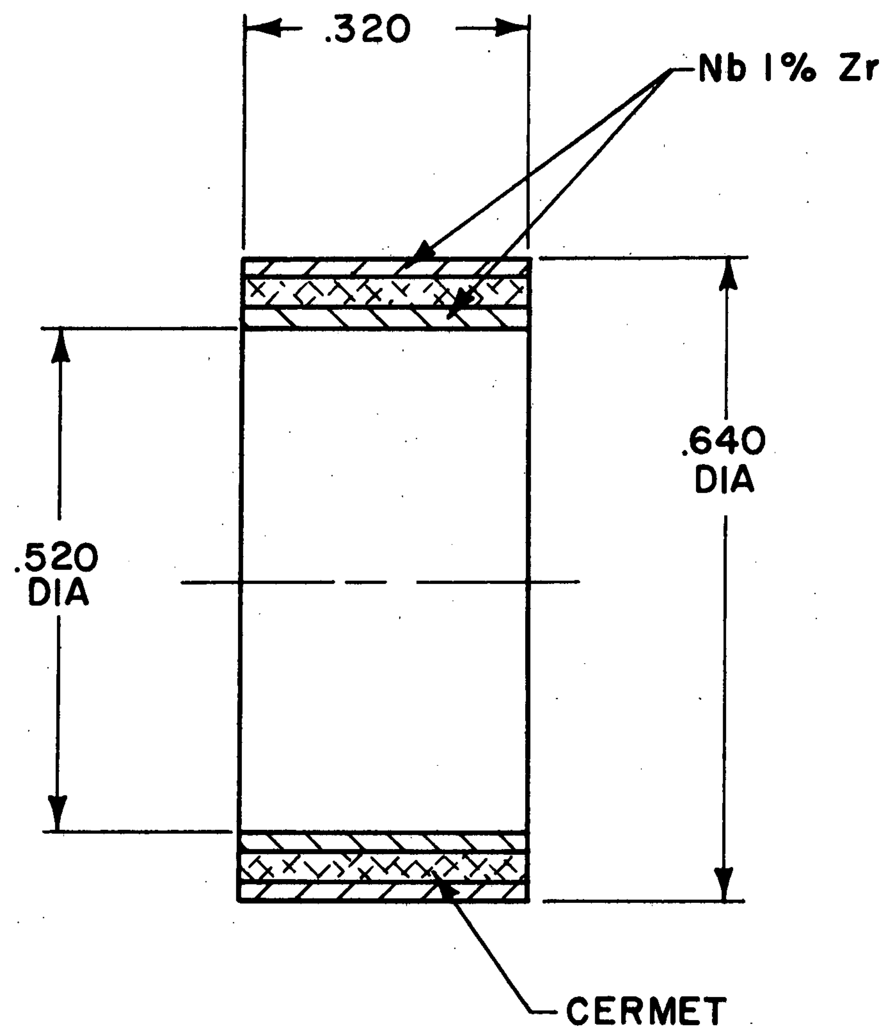


Figure 1.8 Development Seals.

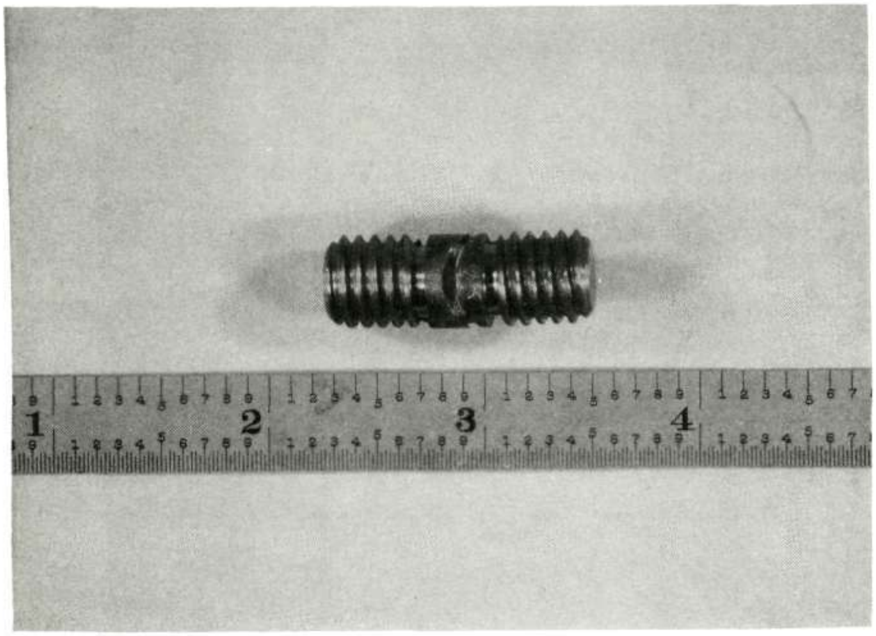


Figure 1.9 Tensile Test Specimen Before Fracture.

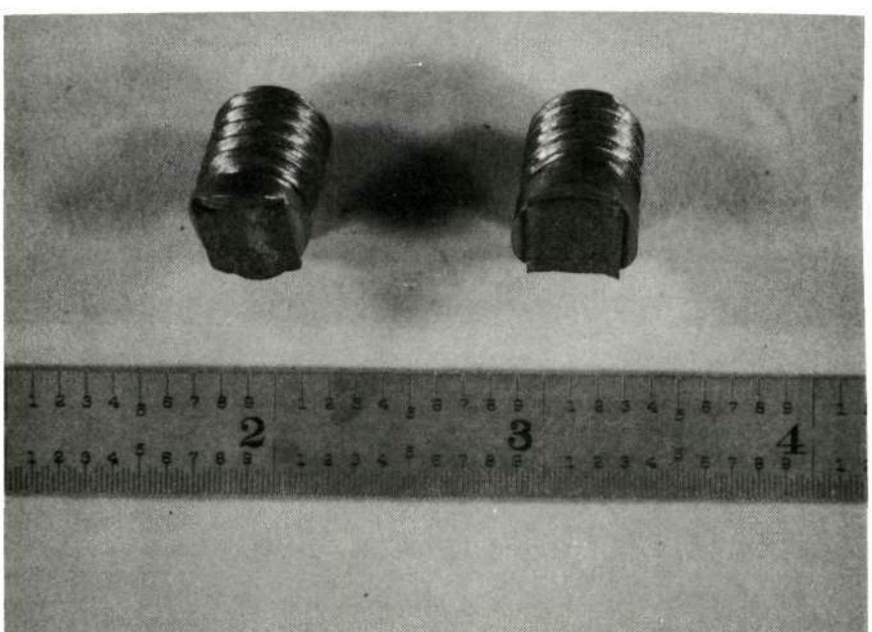


Figure 1.10 Tensile Test Specimen After Fracture.

scanning microscope, microprobe analysis and atomic absorption analysis. Raw material was analyzed for trace element impurities by spectrographic techniques.

1.5 SUMMARY OF DATA

Eight types of cermets were evaluated. Four types were eliminated after the second bonding cycle in order that a concentrated effort could be put forth on the four most promising cermets. Table I summarizes the bond strengths of all samples. A summary of the most promising cermet type insulator seals follows:

<u>Type 3: 1 Micron Al_2O_3 with Nb 1% Zr Spheres</u>

- Both 30% and 50% by volume niobium 1% zirconium sphere insulators can be fabricated. 30% cermets can be fabricated reproducibly; 50% cermets are difficult to fabricate and are not as reproducible as 30%.
- Nb 1% Zr spheres are superior to Nb spheres.
- Bond strengths as high as 21,500 psi were realized.
- Grain size was 10 microns.
- Porosity was $\sim 1\%$.
- Vacuum tight.
- Electrical resistance > 500 meg Ω.
- Grain boundary fracture.
- 3-hour pressure-temperature shutdown cycle is recommended for this cermet type.

TABLE I

BOND STRENGTH

Cermet Type	3-Hour Pressure Shutdown Cycle (psi)	6-Hour Pressure Shutdown Cycle (psi)	3-Hour Pressure-Temp. Shutdown Cycle (psi)	3-Hour Temperature Shutdown Cycle (psi)
1	8,900	8,000	-	-
2	15,000	16,700	-	-
3	9,000	15,700	21,500	> 2,600**
4	17,500	> 20,000**	-	-
5	4,600	4,700	4,000	2,000*
6	8,500	6,500	-	-
7	10,000	7,200	4,800	-
8	8,000	-	16,500	9,500*

* These insulators were fabricated with 30% by volume Nb 1% Zr spheres. All other cermets were 50% Nb 1% Zr spheres.

** Braze failed.

Type 5: Pure Y_2O_3 with Nb 1% Zr Spheres

- Electrically insulated 50% by volume Nb 1% Zr sphere cermets cannot be fabricated at this time.
- Electrically insulated 30% by volume Nb 1% Zr sphere cermets can be fabricated.
- Bond strengths as high as 4700 psi were realized.
- Porosity was ~ 2%.
- Vacuum tight.
- Electrical resistance >500 meg Ω.
- Transgranular fracture, highest strength structure possible.
- Grain size 2 microns.
- 3-hour pressure shutdown cycle recommended.

Type 6: Y_2O_3 3% ZrO_2 with Nb 1% Zr Spheres

Type 7: Y_2O_3 10% ZrO_2 with Nb 1% Zr Spheres

- Electrically insulated 50% by volume Nb 1% Zr sphere cermets cannot be fabricated at this time.
- Electrically insulated 30% by volume Nb 1% Zr sphere cermets can be fabricated.
- Bond strengths as high as 10,000 psi were realized.
- Porosity was ~2%.
- Vacuum tight
- Electrical resistance >500 meg Ω.
- 3 hour pressure shutdown cycle recommended

Type 8: ZrO_2 12% Y_2O_3 with Nb 1% Zr Spheres

- Electrically insulated 50% by volume Nb 1% Zr sphere cermets cannot be fabricated at this time.
- Electrically insulated 30% by volume Nb 1% Zr sphere cermets can be fabricated.
- Bond strengths as high as 16,500 psi were realized.
- Porosity was ~ 2%.
- Vacuum tight.
- Electrical resistance can be >500 meg Ω.
- Grain size 1 to 5 microns.
- Grain boundary fracture.
- 3-hour pressure-temperature cycle recommended.

2. SPECIMEN PREPARATION

Six different raw materials were used in this program. 200 Å alumina, commercially known as "ALOM" and 1 micron alumina known as "POLY" alumina were the two types of aluminas investigated. Both niobium and niobium 1% zirconium spheres were also investigated. Yttria and zirconia were used both as base materials and as stabilizing materials. Table II lists the trace impurities of the materials used.

Initial work in the fabrication of the eight types of cermet centered around past development work on alumina cermets. It became very obvious that techniques that performed well with "ALCOA" alumina, used previously, did not necessarily perform well with the two aluminas, Y_2O_3 and ZrO_2, being evaluated. Every ceramic reacted differently. Cold pressing pressures had to be adjusted for

TABLE II

RAW MATERIAL ANALYSIS

Element	Nb Spheres (ppm)	Nb 1% Zr Spheres (ppm)	"ALOM" Alumina (ppm)	"POLY" Alumina (ppm)	Y_2O_3 (ppm)	ZrO_2 (ppm)
Ca	80	100	20	30	~0.5	~0.5
Mg	3	2	102	160	10	20
Si	6	4	1500	120	78	850
Fe	200	60	1300	37	3	4
Na	–	–	–	200	330	–
Ba	–	–	–	8	32	135
Cu	3	3	84	7	12	13
Cr	100	110	110	0.7	–	8
Ga	–	–	155	12	–	–
Mn	–	–	10	5.1	–	2.8
Pb	–	–	–	3.0	–	–
Al	–	–	major	major	~18	~3
Y	–	–	–	–	major	–
Zr	–	9200	–	~3	–	major
B	–	–	44	–	–	–
Ni	5	3	125	–	–	–
Ti	–	–	52	–	–	–
V	–	–	36	–	–	–
N_2	22	38	–	–	–	–
H_2	16	42	–	–	–	–
O_2	1750	1340	–	–	–	–

each type of ceramic. For instance, if 60,000 psi was used for Y_2O_3 as was used for the Al_2O_3, the Y_2O_3 cylinder would fracture on the mandrel. Partial sintering of the pressed cylinders also proved to be difficult. Sintering temperatures had to be found for each ceramic type. For instance, if ZrO_2 was sintered at the same temperature as the Al_2O_3, it would be very soft and break during the machining operation. Both sintering temperatures and times were adjusted to arrive at conditions which were adequate for machining.

A considerable amount of difficulty was encountered in trying to coat the metallic spheres uniformly with ceramic. Each type of ceramic again proved to react differently. A thorough description of each technique used would be too lengthy for the context of this report, in that over 30 different techniques were tried.

A brief summary of areas investigated follows. Several binders were tried such as PVA alcohol, aqueous soap solutions, amyl-acetate, paraffin, solution of acid to achieve a high PH, electrostatic charging, and nitro-cellulose diluted with Butyl alcohol and Butyl acetate. Of these, paraffin proved to be the most favorable.

Several different sized sieves were also tried to improve the coating process. Cold pressing the powder before use, after binder application, and also after sieving with the spheres was also tried. Conglomerating the raw powder with paraffin and with aqueous soap solutions was also tried. Of these, cold pressing the raw powder without binders proved to be the more desirable technique.

Another serious problem arose in trying to obtain spheres. "NUMEC" was the supplier of spheres in work previously done on cermets. New management policies at "NUMEC" discouraged small orders on an R and D basis; they would only consider fabricating large quantities of spheres at a substantial cost. An alternate supplier was sought. "TAFA," located in New Hampshire, agreed to develop the techniques required to fabricate the spheres. The first batch of spheres received from them was inferior to "NUMEC" spheres in that they had difficulty in fabricating spheres of the correct size and uniformity. These spheres could not be coated adequately and resulted in electrically shorted insulator assemblies. More development work was carried out at "TAFA" and finally they were able to produce uniform spheres of the correct size.

Reproducible coating techniques to fabricate 50% by volume cermet structure have not as yet been developed. 30% by volume cermet structures can be fabricated using alumina, yttria or zirconia ceramic. The lesser volume of metallic sphere reduces the possibility of metal contact, yielding electrically insulated cermet structures. More development work is required to arrive at adequate coating techniques for 50% by volume cermet structures.

3. 3-HOUR PRESSURE SHUTDOWN CYCLE

Eight development seals were fabricated and pressure bonded for three hours. The pressure-temperature cycle is illustrated in Figure 3.1. Results of the examination of the seals are presented below.

<u>Type 1: 1 Micron Al_2O_3 with 50% Nb Spheres</u>

- Bond strength was 8900 psi.
- Reaction zone between the Al_2O_3 and the Nb 1% Zr outer and inner sheath.

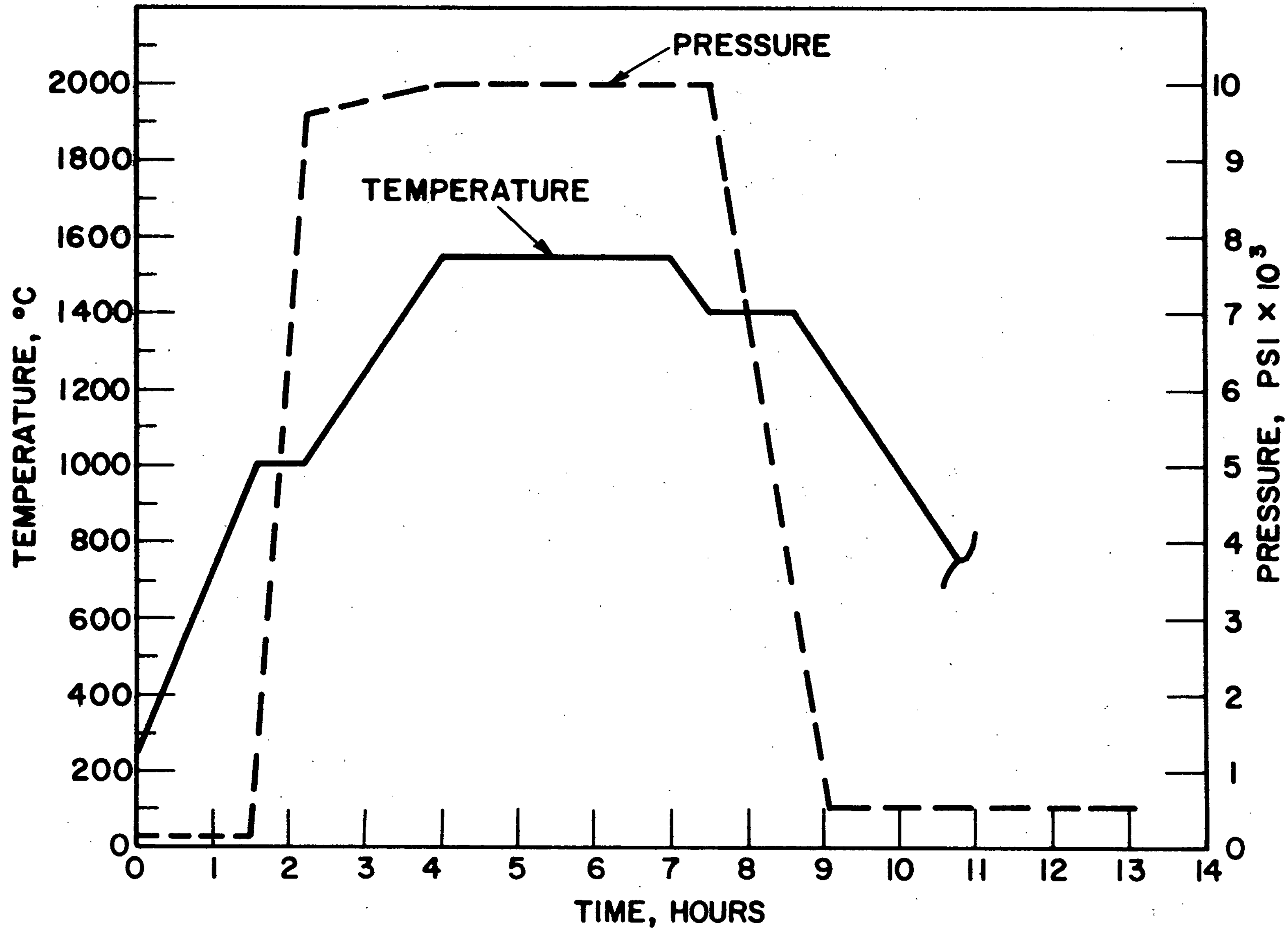


Figure 3.1 Pressure Shutdown Cycle.

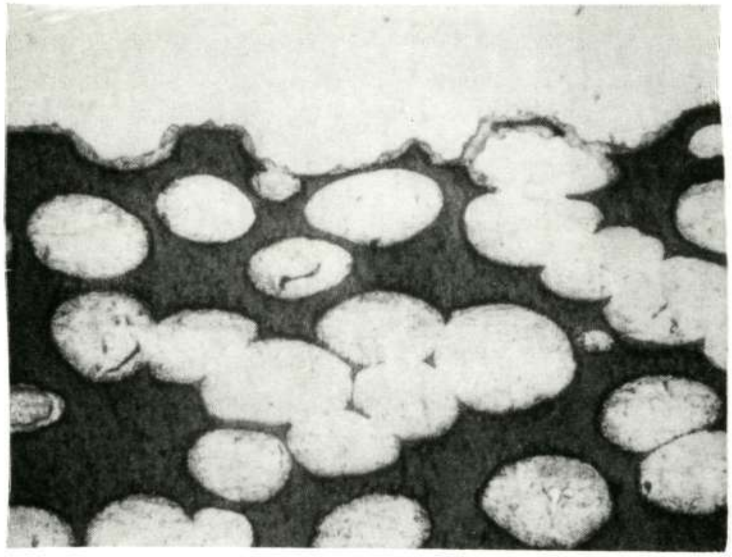
- Very fine uniform ceramic matrix with no detectible grains using optical microscope.
- Electrically insulated (>500 meg Ω).
- Vacuum tight.

Type 2: 200 Å Al_2O_3 with 50% Nb Spheres

- Bond strength was 15,000 psi.
- Reaction zone between the Al_2O_3 and the Nb 1% Zr outer and inner sheath (see Figure 3.2)
- Very fine uniform ceramic matrix with no detectible grains using optical microscope (see Figure 3.3).
- Electrically shorted.
- Vacuum tight.

Type 3: 1 Micron Al_2O_3 with 50% Nb 1% Zr Spheres

- Bond strength 9000 psi.
- Reaction zone between the Al_2O_3 and the Nb 1% Zr outer and inner sheath (see Figure 3.4).
- Very fine uniform ceramic matrix with no detectible grains using optical microscope (see Figure 3.5).
- Electrically shorted.
- Vacuum tight.



Nb 1% Zr Flange

Figure 3.2 3-Hour Pressure Shutdown Cycle. Type 2 Cermet, etched (280x).

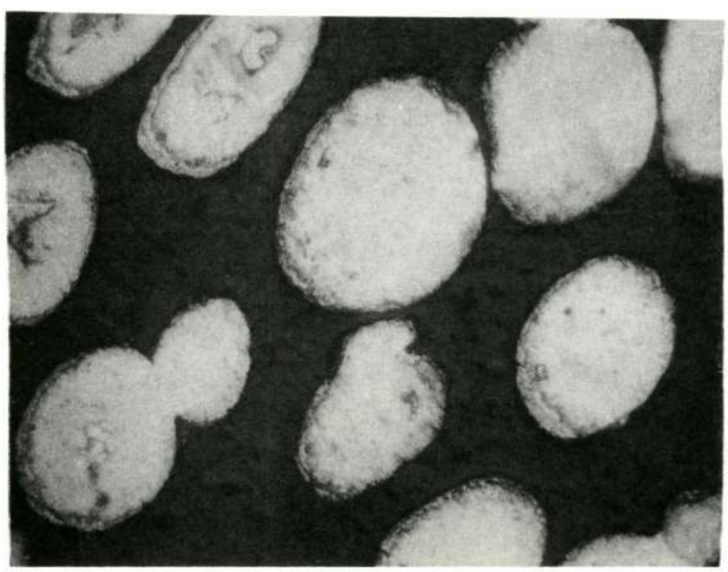


Figure 3.3 3-Hour Pressure Shutdown Cycle. Type 2 Cermet, etched (540x).

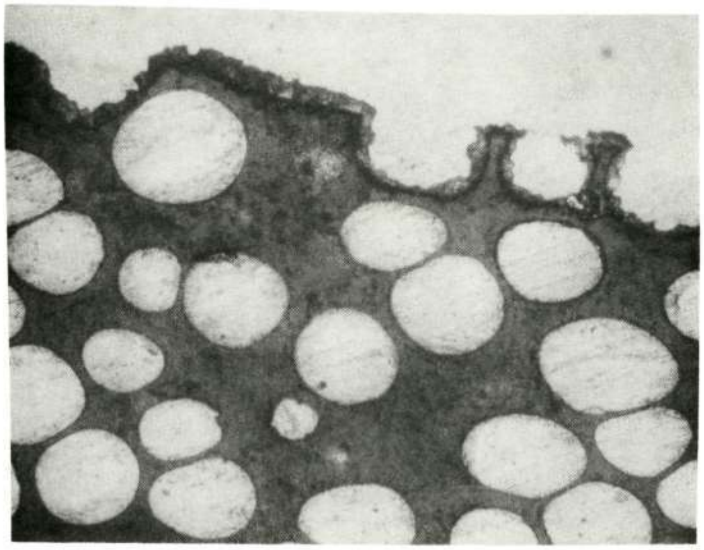


Figure 3.4 3-Hour Pressure Shutdown Cycle. Type 3 Cermet, etched (280x).

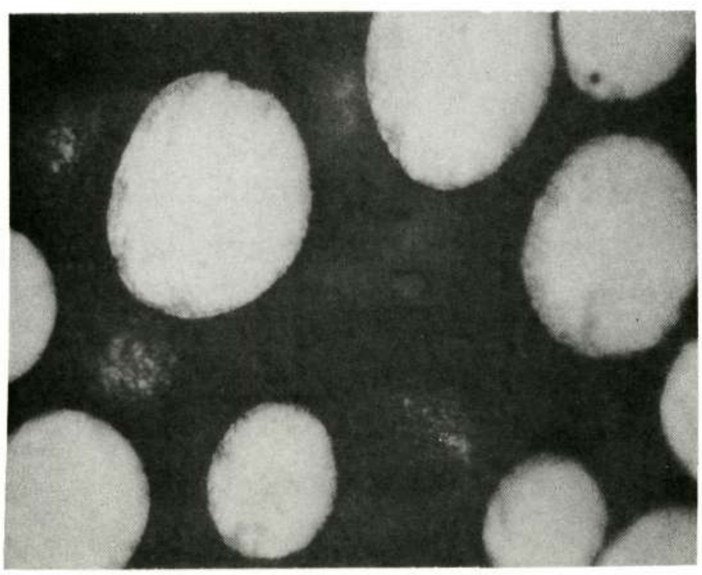


Figure 3.5 3-Hour Pressure Shutdown Cycle. Type 3 Cermet, etched (540x).

Type 4: 200 Å Al_2O_3 with 50% Nb 1% Zr Spheres

- Bond strength was 17,500 psi.
- Reaction zone between the Al_2O_3 and the Nb 1% Zr outer and inner sheath.
- Very fine uniform ceramic matrix with no detectible grains using optical microscope.
- Electrically shorted.
- Vacuum tight.

Type 5: Pure Y_2O_3 with 50% Nb 1% Zr Spheres

- Bond strength was 4600 psi.
- No reaction zone (see Figure 3.6).
- Very fine uniform ceramic matrix with no detectible grains using optical microscope.
- Electrically shorted.
- Vacuum tight.

Type 6: Y_2O_3 3% ZrO_2 with 50% Nb 1% Zr Spheres

- Bond strength was 8500 psi.
- No reaction zone (see Figure 3.7).
- No definite grains were apparent. Different crystal sizes were observed dispersed throughout the matrix.
- Vacuum tight.

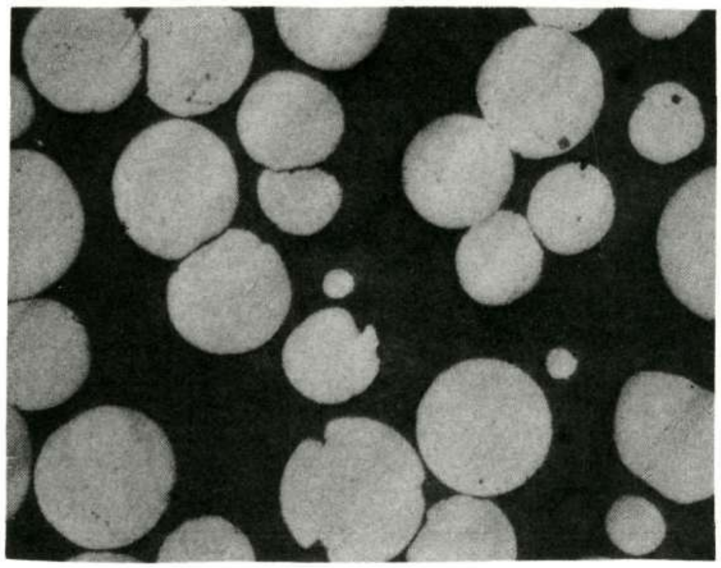


Figure 3.6 3-Hour Pressure Shutdown Cycle. Type 5 Cermet (280x).

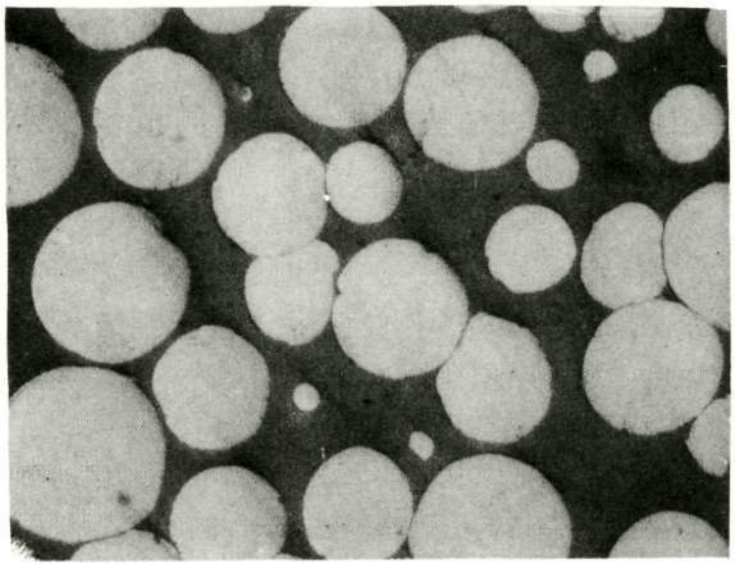


Figure 3.7 3-Hour Pressure Shutdown Cycle.
Type 6 Cermet (280x).

Type 7: Y_2O_3 10% ZrO_2 with 50% Nb 1% Zr Spheres

- Bond strength was 10,000 psi.
- No reaction zone.
- No definite grains were apparent. Different crystal sizes were observed dispersed throughout the matrix (see Figure 3.8).
- Electrically shorted.
- Vacuum tight.

Type 8: ZrO_2 12% Y_2O_3 with 50% Nb 1% Zr Spheres

- Bond strength was 8000 psi.
- No reaction zone.
- No definite grains were apparent using optical microscope.
- The ceramic matrix had a significant amount of micro cracks (see Figure 3.9).
- Electrically shorted.
- Vacuum tight.

The tensile test specimens evaluated clearly showed that in all cases failure occurred in the ceramic matrix and not at the bond interface between the metal sheath and the cermet.

Atomic absorption techniques were employed to determine the percent of theoretical density of the cermet structure. Difficulty was encountered in trying to dissolve the Y_2O_3 cermets. Several acids

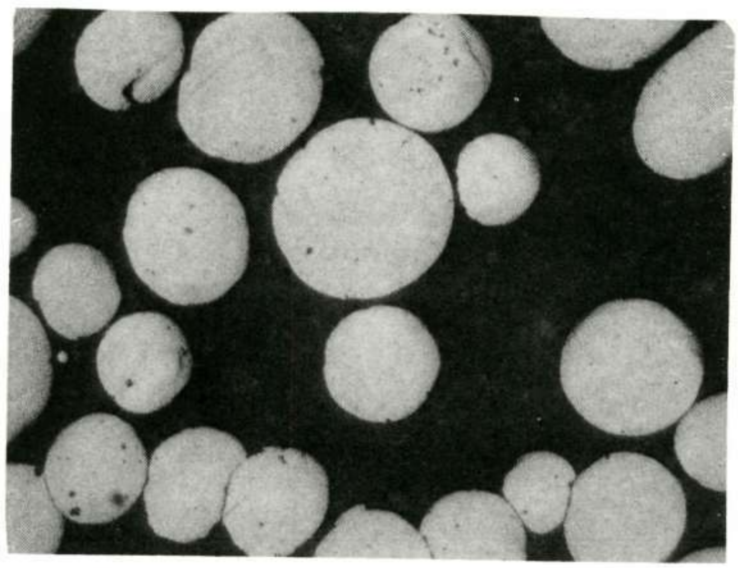


Figure 3.8 3-Hour Pressure Shutdown Cycle.
Type 7 Cermet (280x).

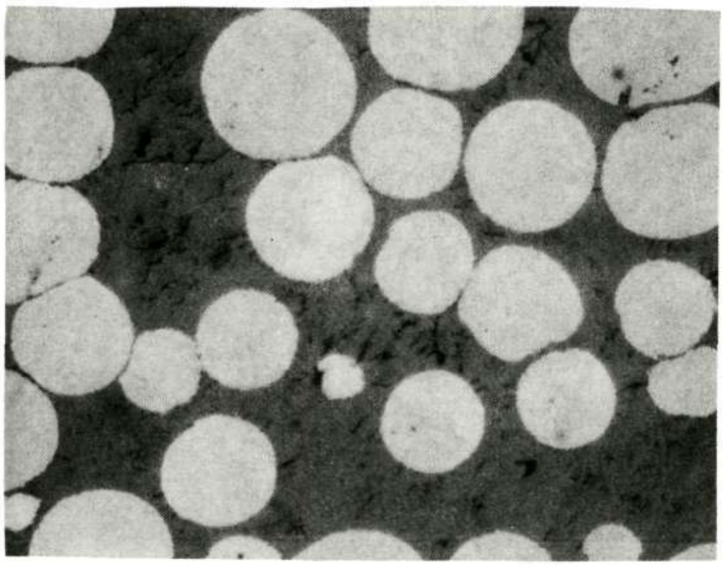


Figure 3.9 3-Hour Pressure Shutdown Cycle. Type 8 Cermet (280x).

such as HF, HCL, H_2SO_4, etc. were tried unsuccessfully. Fused NH_4HF_2 biofluoride, fused Na_2O_2, fused $KHSO_4$, fused Na_2CO_3, etc. were also tried unsuccessfully. The work in trying to dissolve the Y_2O_3 cermets indicate that we had produced a very stable Y_2O_3 ceramic body. Erroneous results were obtained from the analysis of the Al_2O_3 samples and could not be accepted. Atomic absorption techniques to analyze the cermets could not be used. Other techniques are not accurate to the degree required to determine the percent of theoretical density.

Poor coating techniques as well as poor sphere dispersion in the matrix was attributed to improperly sized spheres.

4. 6-HOUR PRESSURE SHUTDOWN CYCLE

Eight development seals were fabricated and pressure bonded for six hours. The pressure-temperature cycle is illustrated in Figure 4.1. Results of the examination of the seals are presented below.

Type 1: 1 Micron Al_2O_3 with 50% Nb Spheres

- Reaction zone between the Al_2O_3 and the Nb 1% Zr outer and inner sheath.
- Detectible grains less than 10 microns in size.
- Vacuum tight.
- Electrically insulated (> 500 meg Ω).
- Bond strength was 8,000 psi.

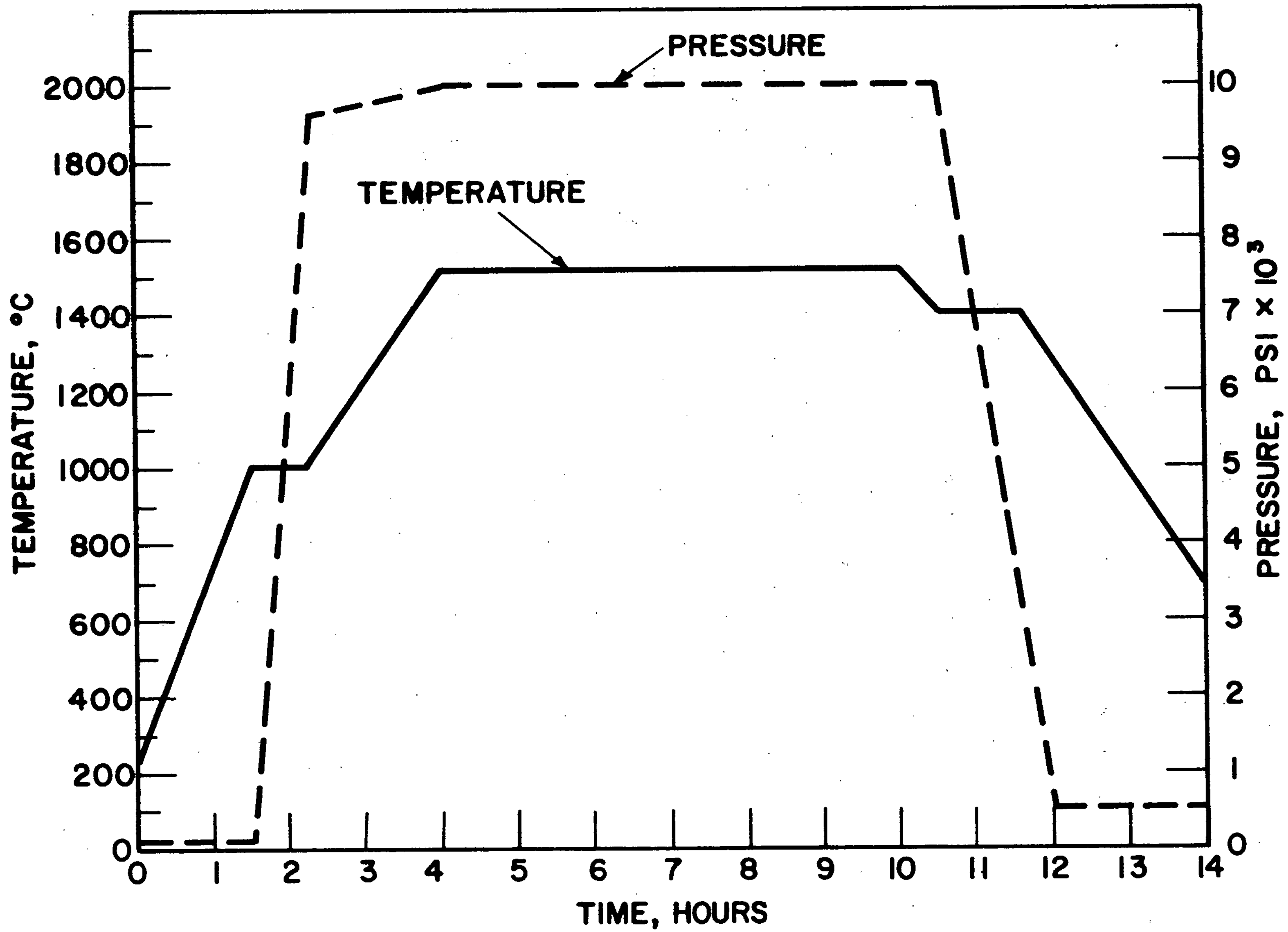


Figure 4. 1 6-Hour Pressure Shutdown Cycle.

Type 2: 200 Å Al_2O_3 with 50% Nb Spheres

- Reaction zone between the Al_2O_3 and the Nb 1% Zr outer and inner sheath (see Figure 4.2).
- Vacuum tight.
- Detectible grains less than 5 microns in size.
- Bond strength was 16,700 psi.
- Electrically shorted.

Type 3: 1 Micron Al_2O_3 with 50% Nb 1% Zr Spheres

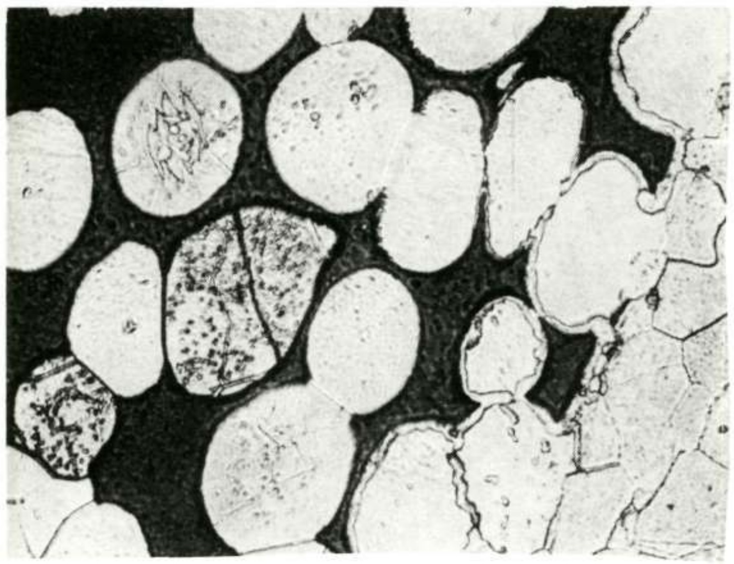
- Electrically shorted.
- Vacuum tight.
- Bond strength was 15,700 psi.
- See Figure 4.3.

Type 4: 200 Å Al_2O_3 with 50% Nb 1% Zr Spheres

- Electrically shorted.
- Vacuum tight.
- Bond strength was >20,000 psi (braze failed).

Type 5: Pure Y_2O_3 with 50% Nb 1% Zr Spheres

- No reaction zone.
- Very fine uniform ceramic matrix with no detectible grains using optical microscope.
- Electrically shorted.



Nb 1% Zr
Flange

Figure 4.2 6-Hour Pressure Shutdown Cycle.
Type 2 Cermet, etched (400x).

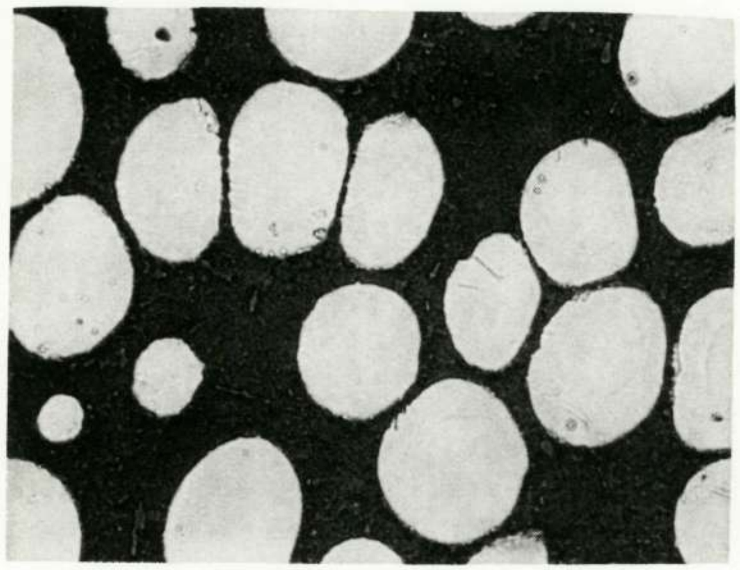


Figure 4.3 6-Hour Pressure Shutdown Cycle. Type 3 Cermet (400x).

- Micro-cracks (see Figure 4.4).
- Vacuum tight.
- Bond strength was 4,700 psi.

Type 6: Y_2O_3 3% ZrO_2 with 50% Nb 1% Zr Spheres

- No reaction zone.
- Vacuum tight.
- Very fine uniform ceramic matrix with no detectible grains using optical microscope.
- Electrically shorted.
- Micro-cracks (see Figure 4.5).
- Bond strength was 6,500 psi.

Type 7: Y_2O_3 10% ZrO_2 with 50% Nb 1% Zr Spheres

- No reaction zone.
- Vacuum tight.
- Very fine uniform ceramic matrix with no detectible grains using optical microscope.
- Electrically shorted.
- Bond strength was 7,200 psi.
- Micro-cracks (see Figure 4.6).
- Different crystal sizes were observed dispersed throughout the matrix.

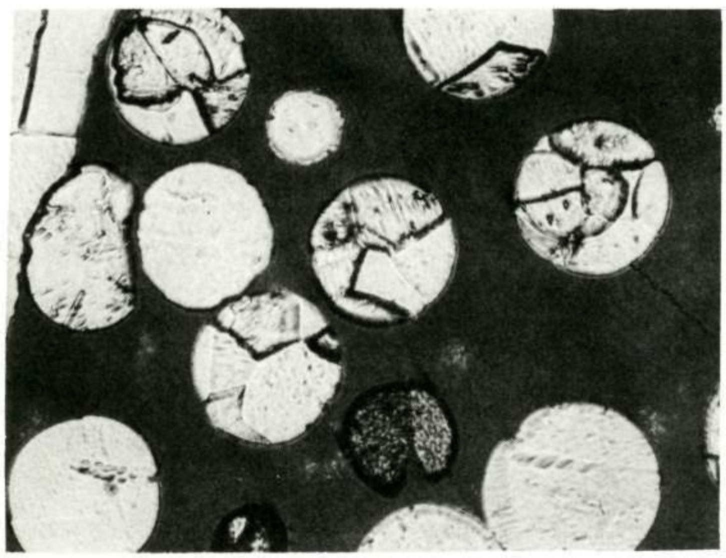


Figure 4.4 6-Hour Pressure Shutdown Cycle. Type 5 Cermet, etched (400x).

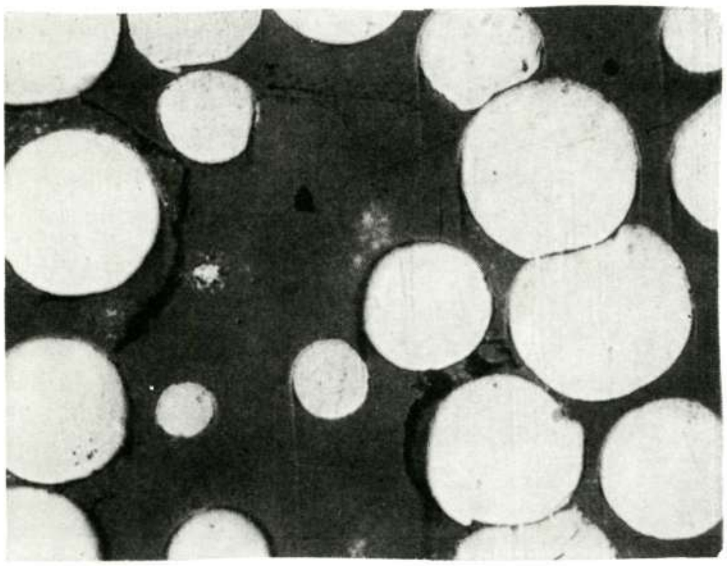


Figure 4. 5 6-Hour Pressure Shutdown Cycle. Type 6 Cermet (400x).

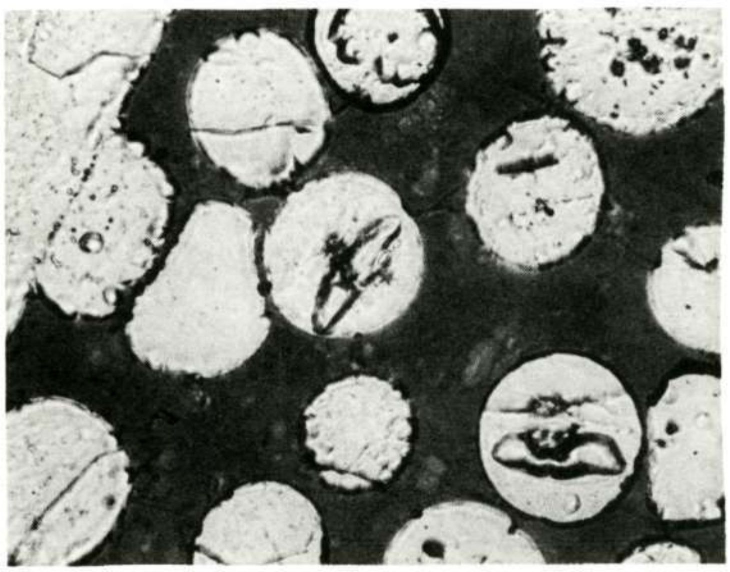


Figure 4.6 6-Hour Pressure Shutdown Cycle. Type 7 Cermet, etched (400x).

Type 8: ZrO_2 12% Y_2O_3 with 50% Nb 1% Zr Spheres

- Capsule leaked during pressure bonding - cermet was not bonded and cracked badly.

The tensile test specimens evaluated clearly showed that in all cases failure occurred in the ceramic matrix and not at the bond interface between the metal sheath and the cermet.

The six-hour bonding run has improved the sintering of the alumina cermets; grains are more discernible.

Poor coating techniques as well as poor sphere dispersion in the matrix were attributed to improperly sized spheres.

5. THREE-HOUR PRESSURE-TEMPERATURE SHUTDOWN CYCLE

Four development seals were fabricated and pressure bonded for three hours. The pressure-temperature cycle is illustrated in Figure 5.1. Three different shutdown cycles were evaluated to determine the effects of pressure and temperature reduction during the bonding cycle on the fabricated seals. The first shutdown cycle is presented in Section 3, while the second shutdown cycle is evaluated in this section and the third and final shutdown cycle is evaluated in Section 6.

Four of the eight cermet types were eliminated from further development work in order that a concentrated effort could be put forth on the most promising four. Type 2 and Type 4 were eliminated because of the unsuccessful previous attempts to fabricate those types electrically insulated. A considerable amount of work would be required to successfully fabricate them. Type 1 was eliminated because results thus far

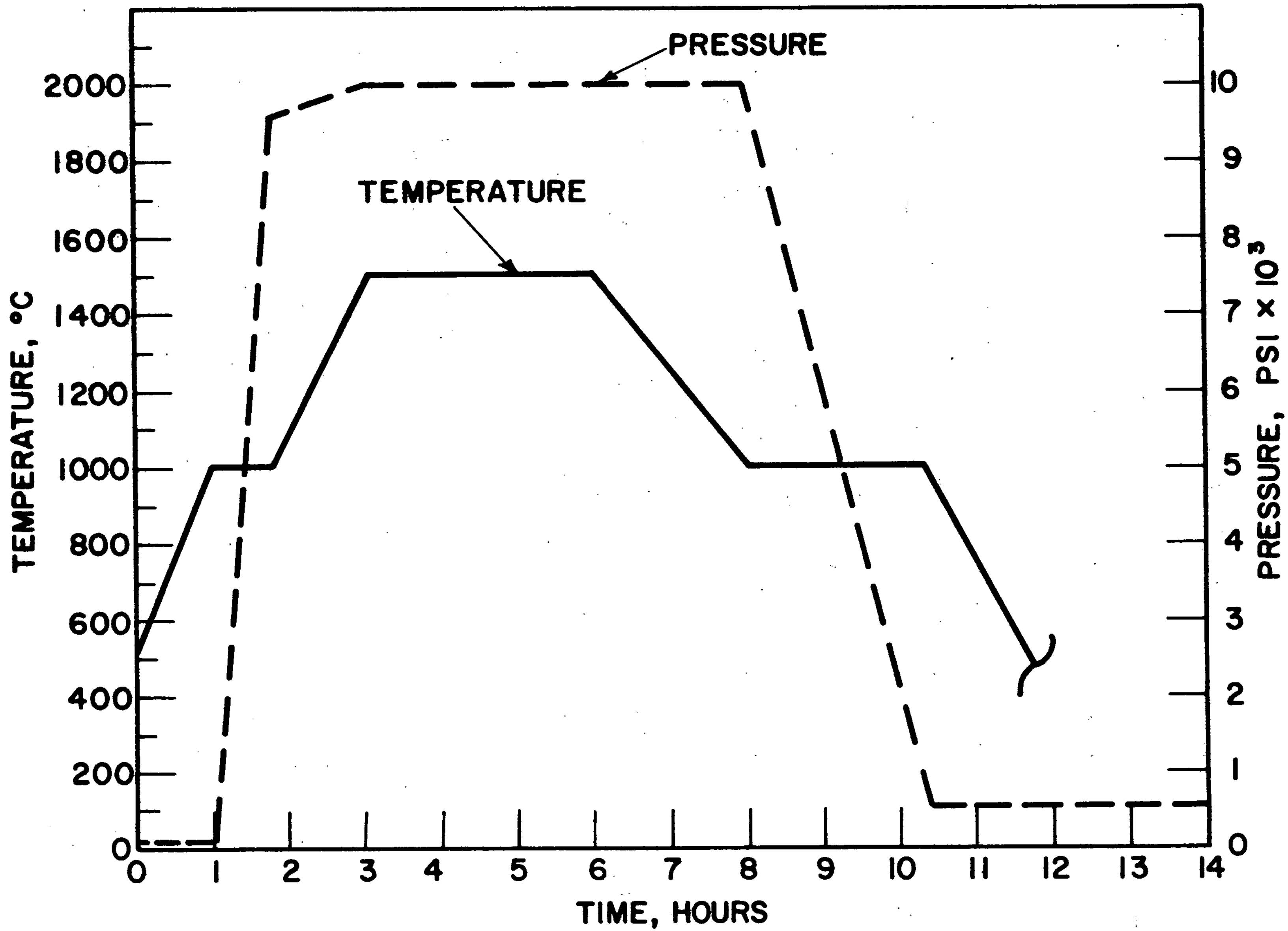


Figure 5.1 3-Hour Pressure-Temperature Shutdown Cycle.

indicated that Nb 1% Zr spheres were superior to pure Nb spheres. Type 6 was eliminated because of its similarity to Type 7.

Results of the examination of seals for the second shutdown cycle are presented below.

Type 3: 1 Micron Al_2O_3 with 50% Nb 1% Zr Speres

- Bond strength was 21,500 psi.
- Vacuum tight.
- Electrically shorted.
- Grain size approximately 10 microns (see Figure 5.2).
- Small amount of porosity (approximately 1%).
- Ceramic crystal pattern was impressed on the Nb 1% Zr spheres (see Figure 5.4).
- In some cases the sphere fractured and a portion of the sphere remained bonded to the ceramic matrix (see Figure 5.5).
- Porosity was observed in the Nb 1% Zr sphere (see Figure 5.6).
- Grain boundaries of the spheres were very discernible. Large grain boundaries of the spheres are shown in Figure 5.3.
- Fracture occurred at the Nb 1% Zr-to-alumina interface.
- Fracture occurred at the grain boundaries (see Figure 5.7).
- Very well formed alumina crystals.

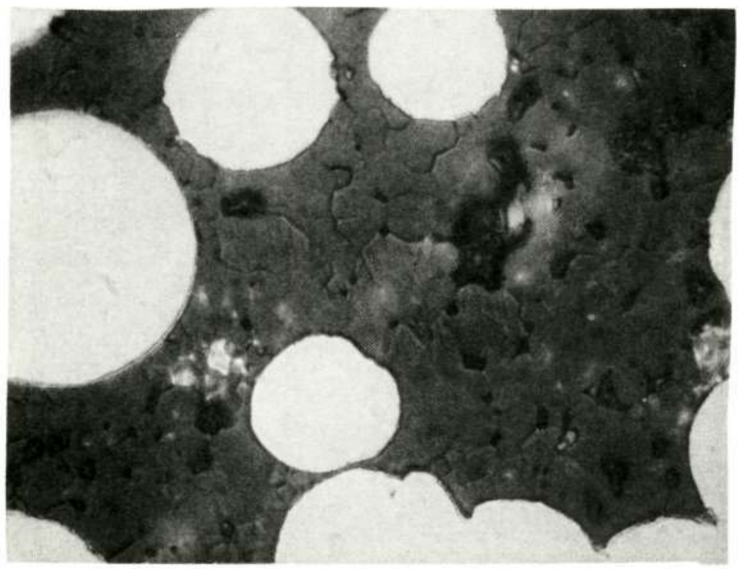


Figure 5.2 3-Hour Pressure/Temperature Shutdown Cycle. Type 3 Cermet (540x).

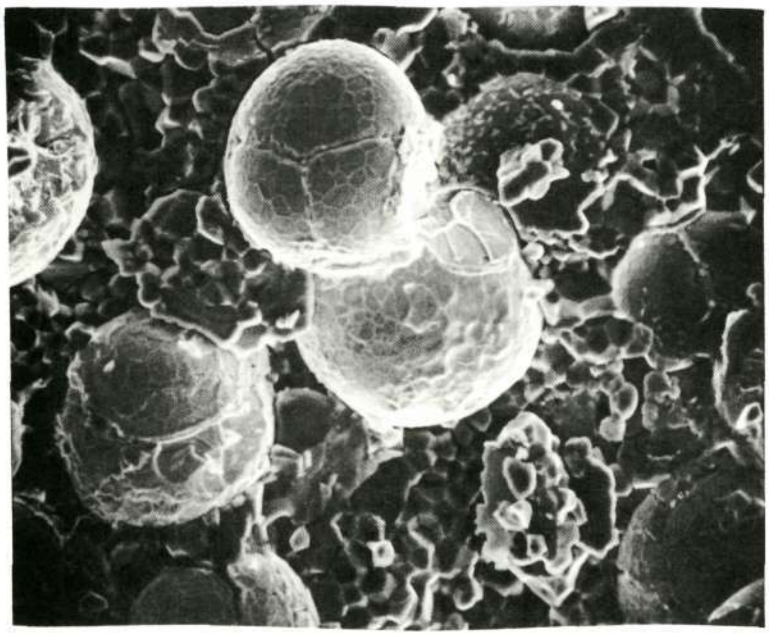


Figure 5.3 3-Hour Pressure/Temperature Shutdown Cycle. Type 3 Cermet (500x)

Figure 5.4 3-Hour Pressure/Temperature Shutdown Cycle. Type 3 Cermet (2000x).

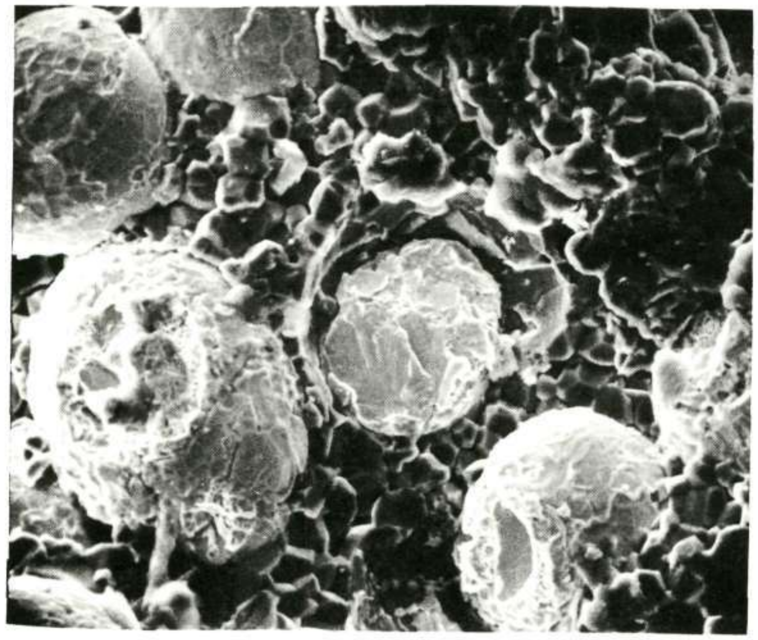


Figure 5.5 3-Hour Pressure/Temperature Shutdown Cycle. Type 3 Cermet (500x).

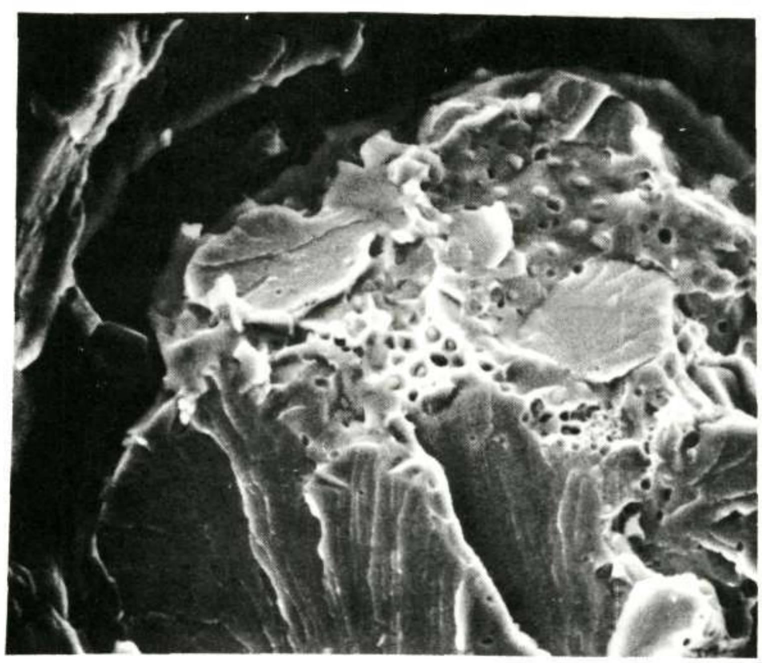


Figure 5.6 3-Hour Pressure/Temperature Shutdown Cycle. Type 3 Cermet (2000x).

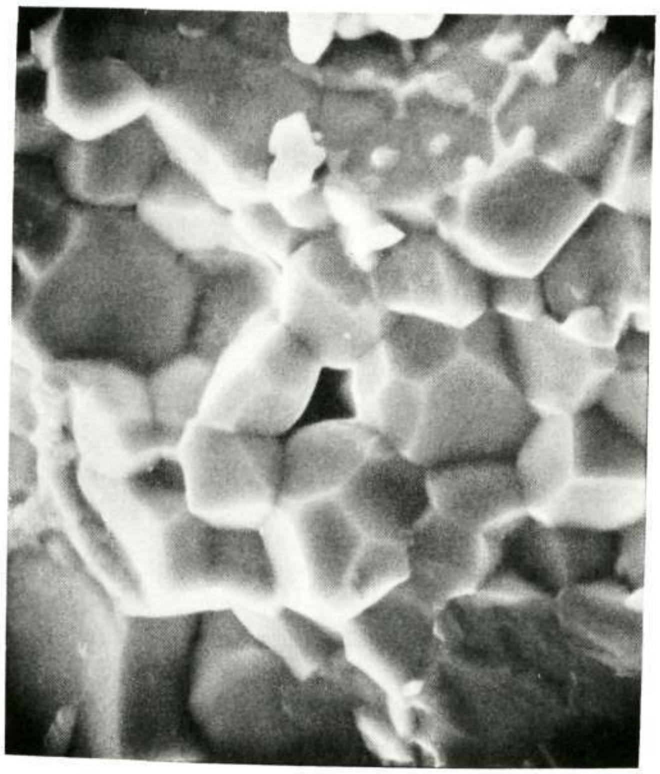


Figure 5.7 3-Hour Pressure/Temperature Shutdown Cycle. Type 3 Cermet (2000x).

Type 5: Pure Y_2O_3 with 50% Nb 1% Zr Spheres

- Bond strength was 4,000 psi.
- Vacuum tight.
- Electrically shorted.
- Grain size approximately 2 microns (see Figure 5.8).
- Small amount of porosity - approximately 2% (see Figure 5.8).
- The fracture occurred in the matrix of the Y_2O_3. Figures 5.9 and 5.10 illustrate that the spheres are coated.
- See Figure 5.11 for optical micrograph of surface.
- Well formed Y_2O_3 crystals.
- Fracture occurred transgranularly, indicating as strong a structure as can be fabricated. The crystals are well bonded at the grain boundaries. High bond temperatures don't appear to be necessary to improve the strength. Figure 5.8 illustrates the transgranular fracture.

Type 7: Y_2O_3 10% ZrO_2 with 50% Nb 1% Zr Spheres

- Bond strength was 4800 psi.
- Vacuum tight.
- Electrically shorted.
- Two different grain sizes: the Y_2O_3 grains were not very discernible; the Y_2O_3 and ZrO_2 grains were larger and more discernible (see Figure 5.12).

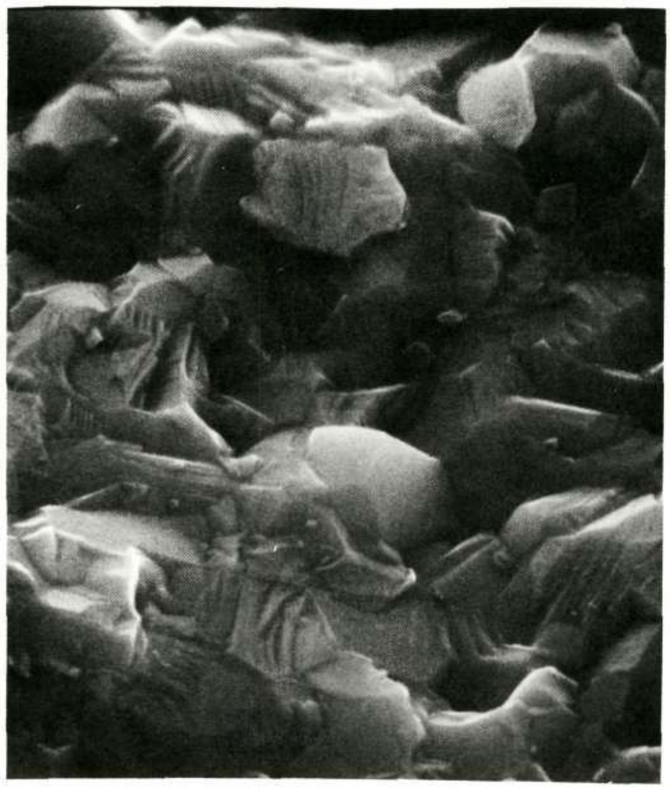


Figure 5.8 3-Hour Pressure/Temperature Shutdown Cycle. Type 5 Cermet (10,000x).

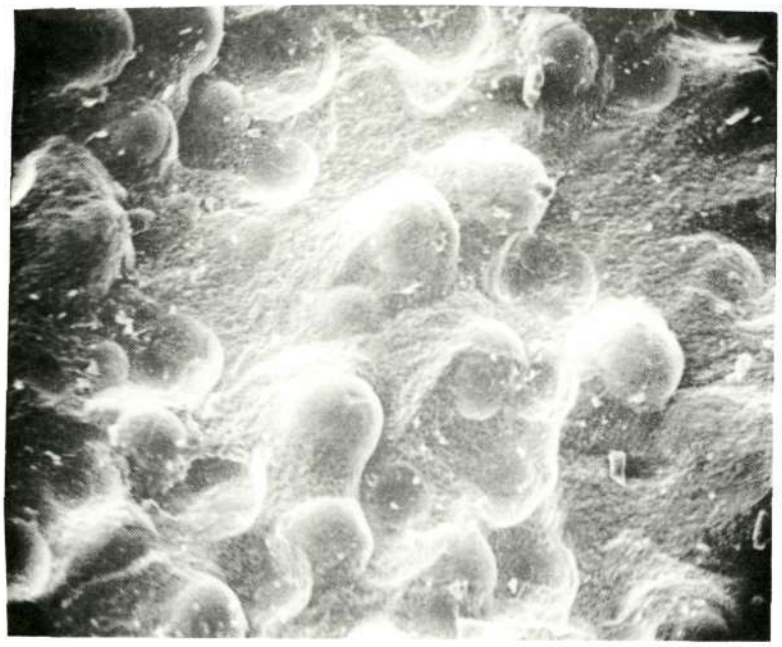


Figure 5.9 3-Hour Pressure/Temperature Shutdown Cycle. Type 5 Cermet (200x).

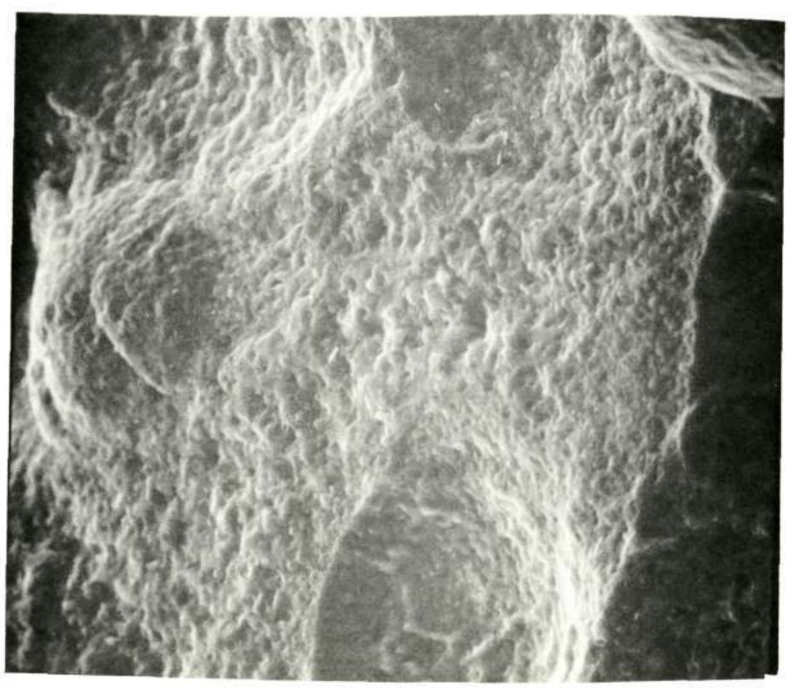


Figure 5.10 3-Hour Pressure/Temperature Shutdown Cycle. Type 5 Cermet (1000x).

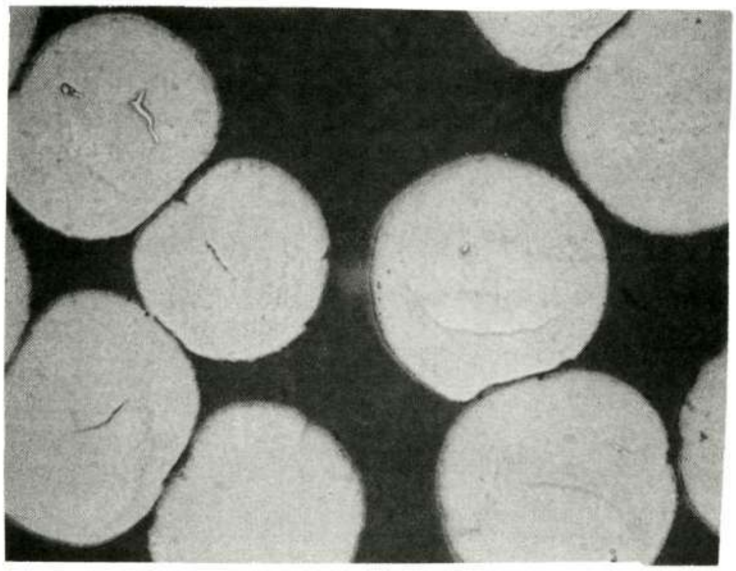


Figure 5.11 3-Hour Pressure/Temperature Shutdown Cycle. Type 5 Cermet (560x).

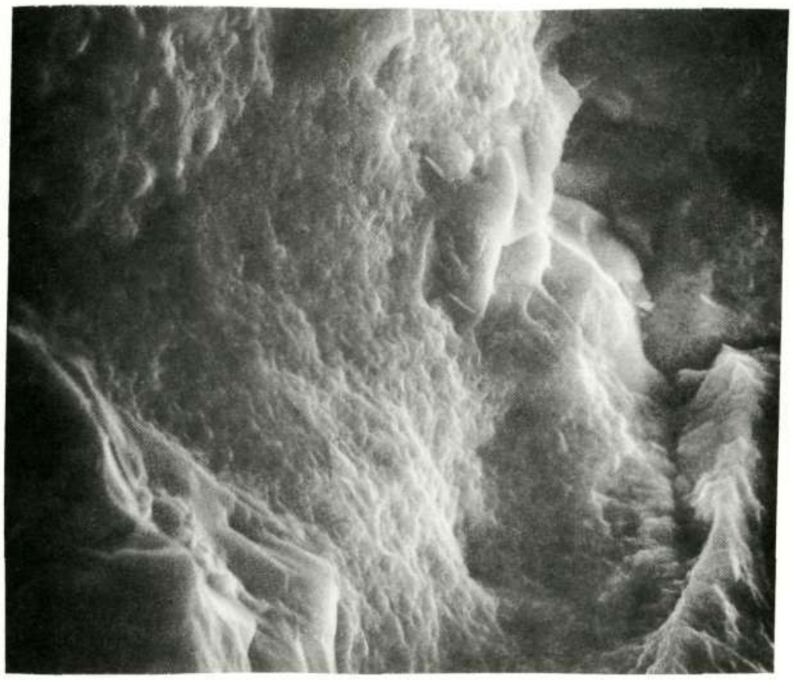


Figure 5.12 3-Hour Pressure/Temperature Shutdown Cycle. Type 7 Cermet (3000x).

Figure 5.13 3-Hour Pressure/Temperature Shutdown Cycle. Type 7 Cermet (500x).

- Microprobe analysis indicated that the small grains were pure Y_2O_3 and the larger grains were Y_2O_3 and ZrO_2.
- Spheres were coated with the matrix material as can be seen in Figure 5.13.
- Fracture occurred in the matrix and not at the Nb 1% Zr ceramic interface.
- Small amount of porosity approximately 2% (see Figure 5.14).
- Microcracks - see Figure 5.15.

Type 8: ZrO_2 12% Y_2O_3 with 50% Nb 1% Zr Spheres

- Bond strength was 16,500 psi.
- Vacuum tight.
- Electrically shorted.
- Minor amount of microcracks (Figures 5.16 and 5.17).
- Two different grain sizes - see Figure 5.18.
- Microprobe analysis indicated that the small grains (1 micron) were pure ZrO_2 and that the larger grains (5 microns) were ZrO_2 and Y_2O_3.
- Grains were very discernible, well formed crystals.
- The spheres were coated with the matrix material as can be seen in Figures 5.19 and 5.20.
- Fracture occurred in the matrix and not at the Nb 1% Zr-ceramic interface.
- Small amount of porosity - approximately 2%.

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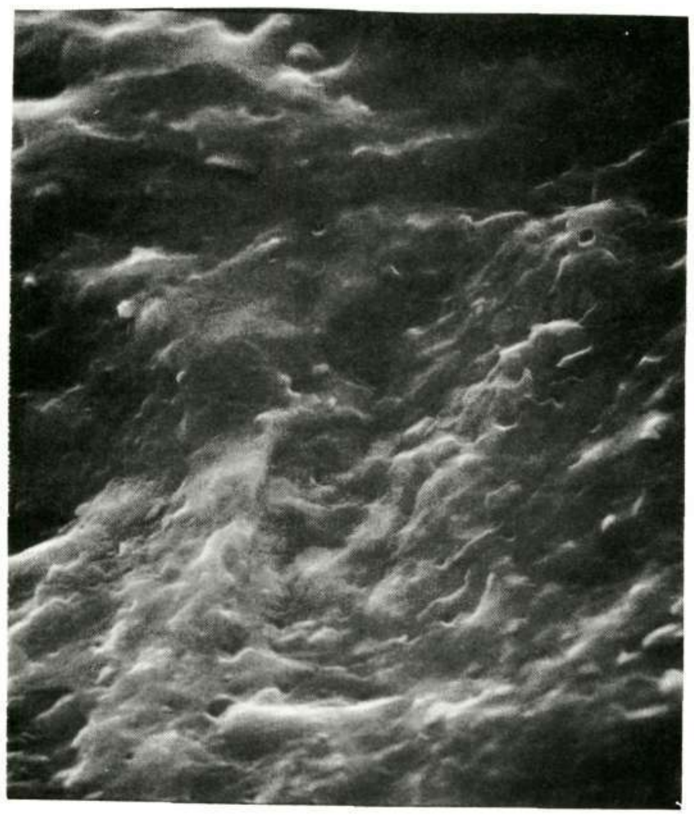

Figure 5.14 3-Hour Pressure/Temperature Shutdown Cycle. Type 7 Cermet (10,000x).

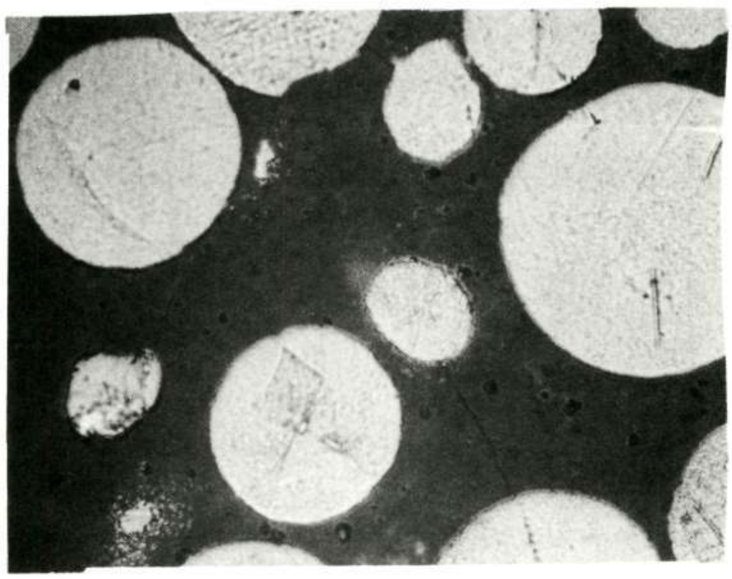

Figure 5.15 3-Hour Pressure/Temperature Shutdown Cycle. Type 7 Cermet, etched (560x).

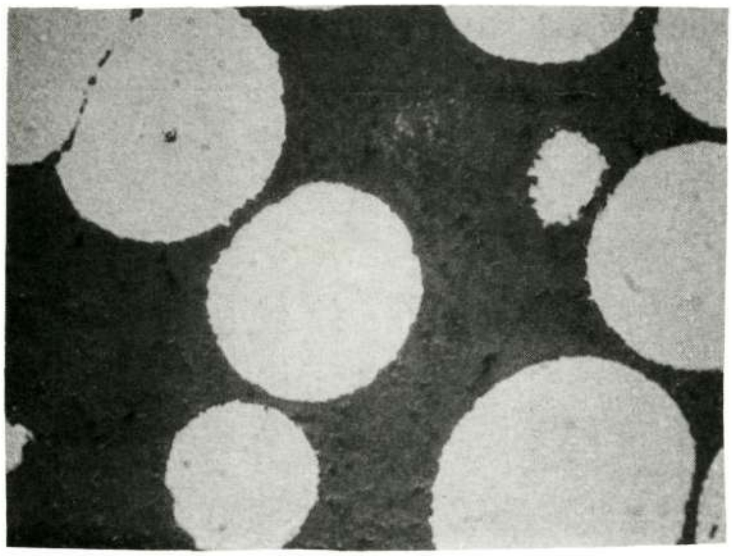

Figure 5.16 3-Hour Pressure/Temperature Shutdown Cycle. Type 8 Cermet (560x).

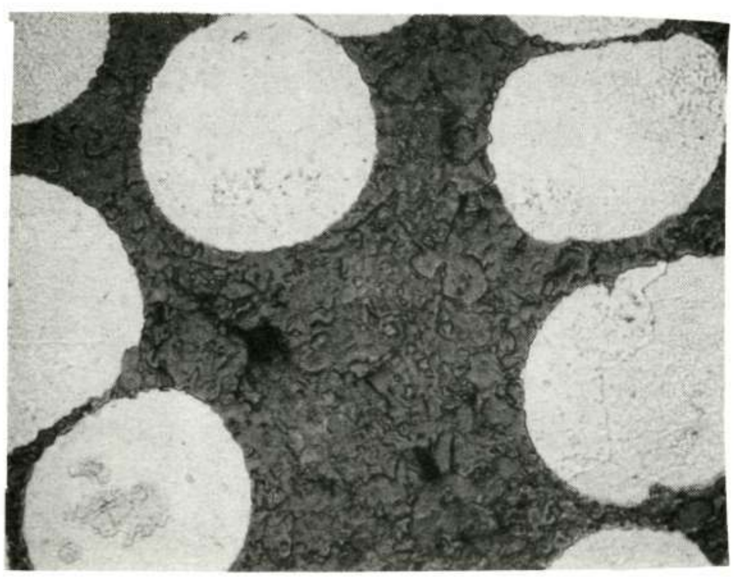

Figure 5.17 3-Hour Pressure/Temperature Shutdown Cycle. Type 8 Cermet, etched (560x).

SPHERE MATRIX

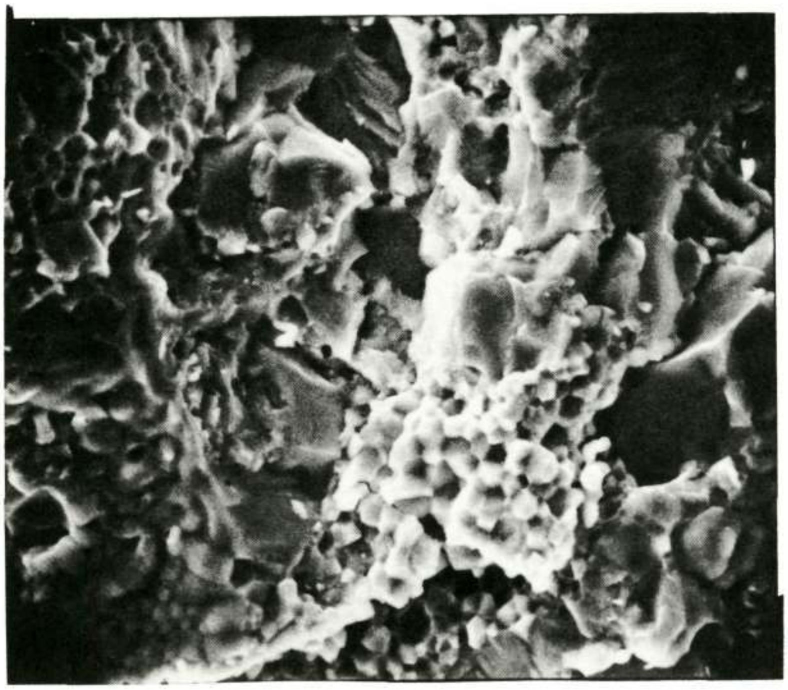

Figure 5.18 3-Hour Pressure/Temperature Shutdown Cycle. Type 8 Cermet (2000x).

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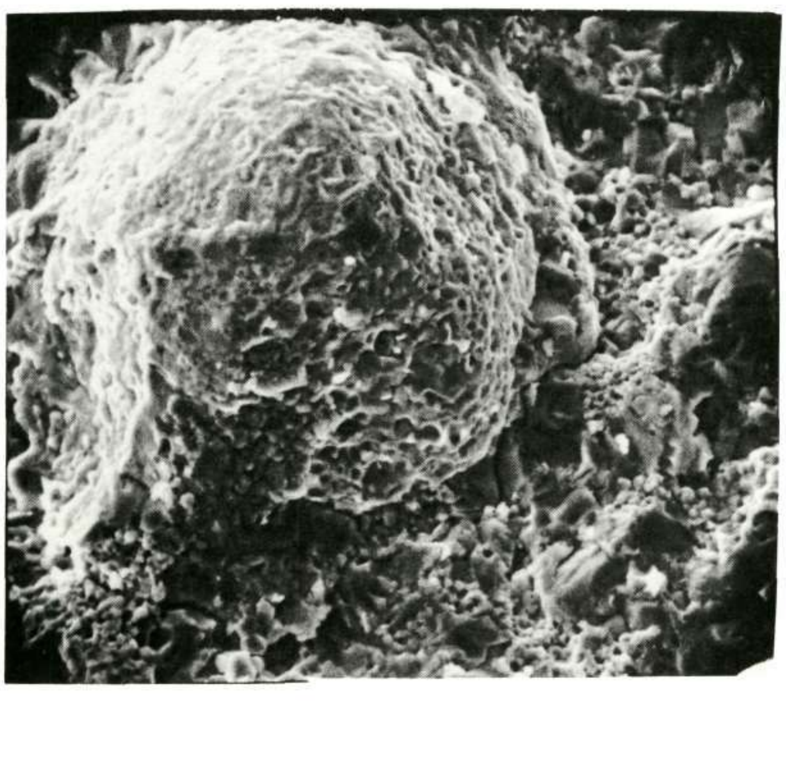
Figure 5.19 3-Hour Pressure/Temperature Shutdown Cycle. Type 8 Cermet (200x).

SPHERE



MATRIX

Figure 5.20 3-Hour Pressure/Temperature Shutdown Cycle. Type 8 Cermet (1000x).

Tensile test specimens evaluated clearly showed that in all cases failure occurred in the ceramic matrix and not at the bond interface between the metal and the cermet.

This stress relieving cycle has improved the bond strength of the Type 3 cermet. The highest bond strength previously realized was 15,700 psi for Type 3.

Bond strengths for Type 5 and 7 were somewhat lower than the previous work. The bond strength of Type 8 was significantly higher than data from previous work.

6. THREE-HOUR TEMPERATURE SHUTDOWN CYCLE

Four development seals were fabricated and pressure bonded for three hours. The pressure-temperature cycle is illustrated in Figure 6.1. Three of the four seals were fabricated with 30% by volume spheres in order to determine whether the cause of electrical shorting was a result of too many spheres or whether it was a result of the type of ceramic being used.

Results of the examination of the seals are presented below.

<u>Type 3: 1 Micron Al_2O_3 with 50% Nb 1% Zr Spheres</u>

- Bond strength was > 2600 psi (braze failed).
- Vacuum tight.
- Electrically shorted.
- Grain size approximately 10 microns.
- Macro-cracks.
- See Figure 6.2 and 6.3.

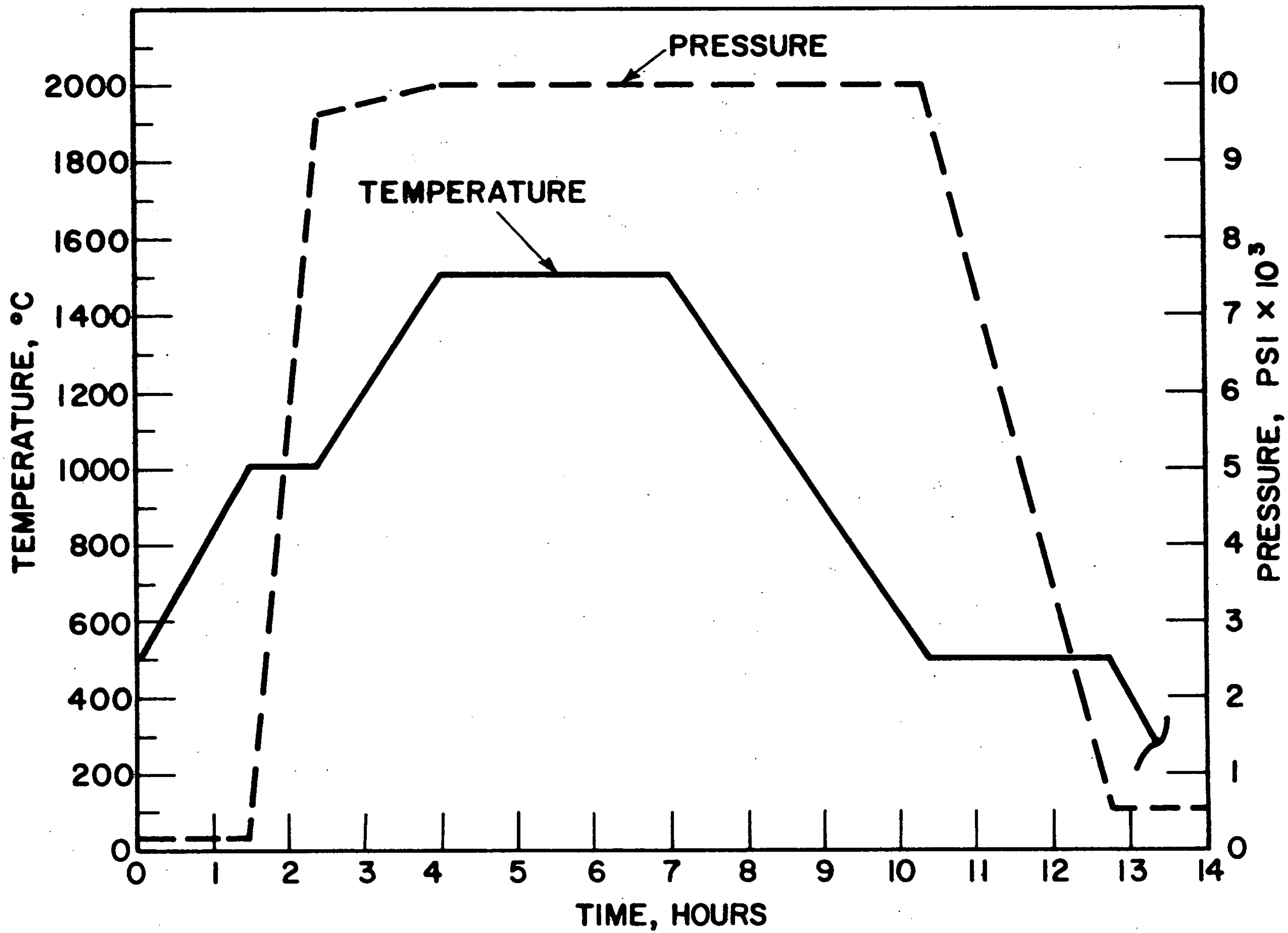


Figure 6. 1 3-Hour Temperature Shutdown Cycle.

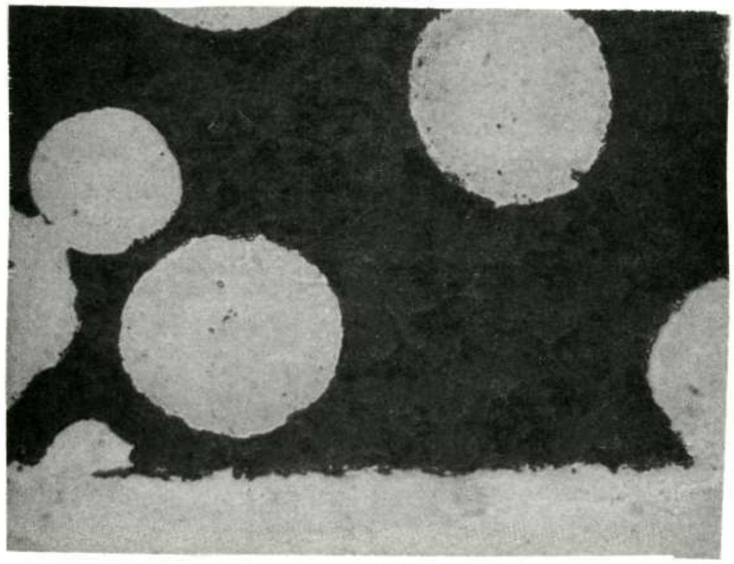


Figure 6.2 3-Hour Temperature Shutdown Cycle. Type 3 Cermet (540x).

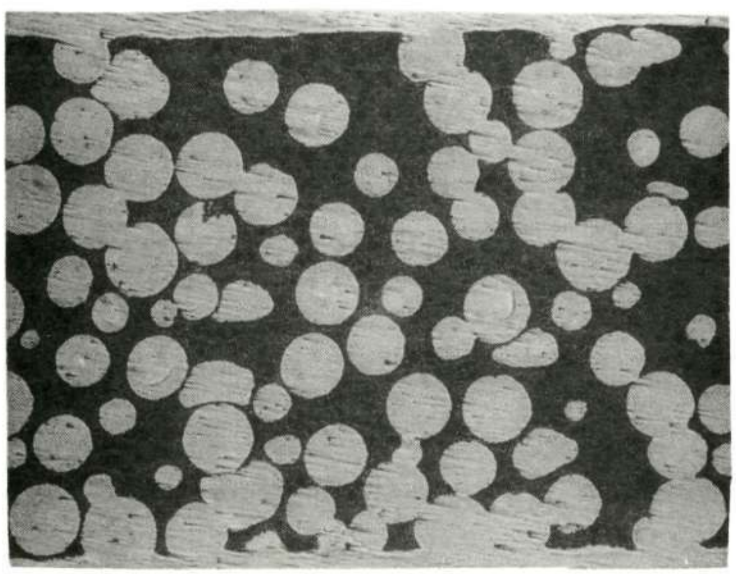


Figure 6.3 3-Hour Temperature Shutdown Cycle. Type 3 Cermet (140x).

Type 5: Pure Y_2O_3 with 30% Nb 1% Zr Spheres

- Bond strength was 2000 psi.
- Vacuum tight.
- Electrically insulated, >500 meg Ω
- Macro-cracks (see Figure 6.4).

Type 7: Y_2O_3 10% ZrO_2 with 30% Nb 1% Zr Spheres

- Bond strength - broken at assembly.
- Vacuum tight.
- Electrically insulated, > 500 meg Ω.
- Macro-cracks (see Figure 6.5).

Type 8: ZrO_2 12% Y_2O_3 with 30% Nb 1% Zr Spheres

- Bond strength was 9500 psi.
- Vacuum tight.
- Electrical resistance, 1 Ω.
- Micro-cracks (see Figure 6.6).
- Macro-cracks.

The tensile test specimens evaluated clearly showed that in all cases failure occurred in the ceramic matrix and not at the bond interface.

This stress relieving schedule is not recommended to fabricate cermet seals. Very large macro-cracks as well as micro-cracks were present in every specimen.

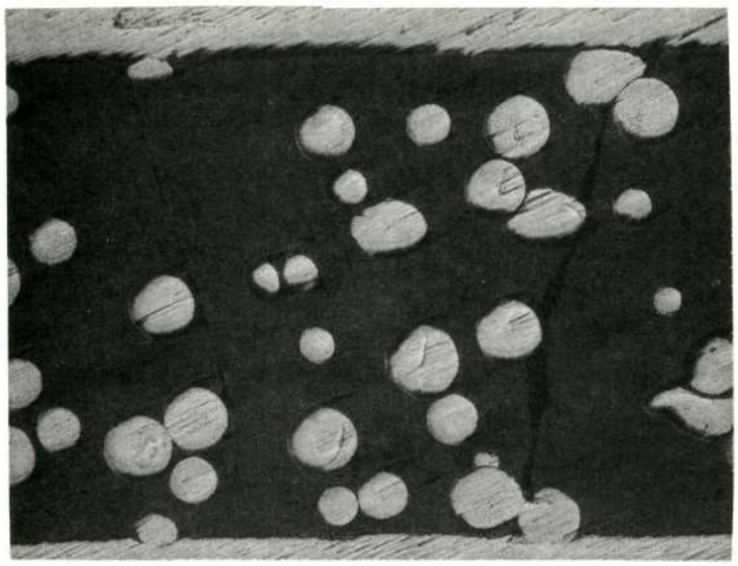


Figure 6.4 3-Hour Temperature Shutdown Cycle. Type 5 Cermet (140x).

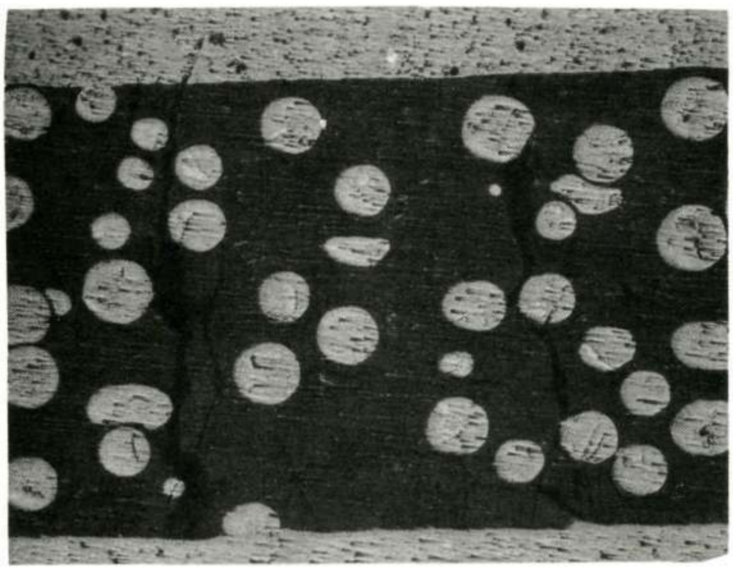


Figure 6. 5 3-Hour Temperature Shutdown Cycle. Type 7 Cermet (140x).

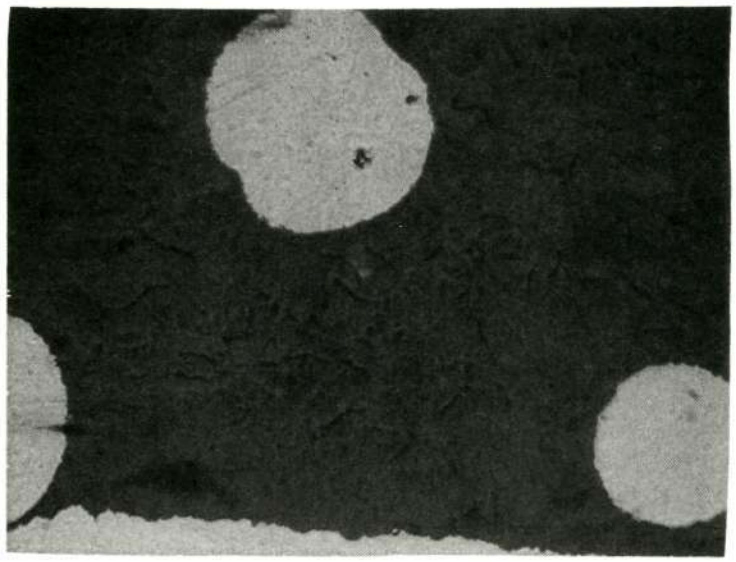


Figure 6.6 3-Hour Temperature Shutdown Cycle. Type 8 Cermet (560x).

Electrically insulated cermet specimens can be fabricated with 30% by volume Nb 1% Zr spheres. Electrical shorting of samples appears to be a result of too many spheres.