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HIGH TEMPERATURE
THERMOCOUPLE
DEVELOPMENT PROGRAM

By
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Part A

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Part B

prepared for
National Aeronautics and Space Adminstration
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ENGELHARD INDUSTRIES DIVISION
ENGELHARD MINERALS & CHEMICALS CORPORATION

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FINAL REPORT

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NASA Lewis Research Center
Contract NAS 3-10950
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FOREWORD

The work described herein was performed at Engelhard Industries Division of Engelhard Minerals & Chemicals Corporation and National Beryllia Corporation under NASA Contract No. NAS 3-10950, with Mr. Peter Cipollone of NASA Lewis Research Center as Technical Project Manager, and Mr. George Glawe of NASA Lewis REsearch Center as Technical Consultant.

ABSTRACT

The problem of extending the useful life of thermocouples intended for in-core and out-of-core thermionic applications in a vacuum environment at temperatures up to 2273 K for periods of time up to 10,000 hours has been investigated. Many factors that may influence this useful life were examined and a basic probe design was developed. With a few modifications twenty-three thermocouple assemblies were fabricated. Generally the finished thermocouple consisted of solid doped W-3% Re and W-25% Re wires; high purity and high density BeO insulators; and was sheathed in a high purity tantalum tube. In a few probes stranded thermocouple wires were substituted; commercial grade BeO was used; and in two cases CVD W-22% Re tubing was used. Each of the components selected was made of the highest purity material available; was subjected to special cleaning steps and was assembled in a class 10,000 clean room. Pertinent physical and chemical properties were determined on each of the components. Special processing techniques were used by National Beryllia Corp. in the fabrication of the high purity (99.95%), high density (over 95% of theoretical) BeO.

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SUMMARY

The aim of this program was to develop a thermocouple that could be used both in-core and out-of-core in thermionic applications in a vacuum of 1.3 X 15^6 N/m^2 (1 X 10^{-8} Torr.) at temperatures up to 2273 K (2000°C) for periods of time up to 10,000 hours. Previous work, well documented in the technical literature, had shown that tungsten-rhenium thermocouples have been used for short periods of time at temperatures up to 3273 K.

Although the tungsten-rhenium thermocouples suffer from several deficiencies: drift when subjected to neutron flux, relatively brittle after exposure to high temperatures and cannot be used bare above 1900°C in a hard vacuum. Nevertheless, they are the best commercially available combinations that could be considered to meet the objective of this program. A search of the literature as well as unpublished data at Engelhard Industries (obtained in work over the past ten years) show that there may be other interesting combinations, one of which is columbium vs molybdenum, but they are all untried. These may be materials of the future.

The experience of others with tungsten-rhenium thermocouples shed little light on possible long term stability at 2273 K. However, in work performed at CANEL in 1962 it was shown that if great care were taken in preparing components and during assembly (in a clean room) the lives of lower temperature probes (type K) could be extended dramatically.

After due consideration of the many factors concerned in the fabrication of a high reliability thermocouple a probe was designed. Although the basic design called for solid doped W-3% Re and W-25% Re wires insulated with specially prepared high purity BeO and sheathed with a high purity tantalum tube, several variations were made with a number of probes. For example, in some probes stranded wire was used; in two probes a W-22% Re CVD sheath was used; in five of them commercial quality BeO was substituted for the high purity material. In all, twenty-three probes were assembled and shipped to NASA's Lewis Research Center.

To minimize or even eliminate completely the thermocouple failures due to unknown material quality or compatibility, all components were obtained in the highest purity available. These were then subjected to various cleaning and degassing operations. Next the properties, both chemical and physical, were determined.

To further insure achievement of the program objectives, and to minimize loss of thermocouple performance due to handling and fabrication, special assembly procedures were used. All handling, preparation and processing of the probe components was done in a class 10,000 clean room. The final assembly and sealing of the probes was accomplished in a stainless steel glove box containing a high purity inert atmosphere. This glove box was located in the clean room.

Since a question had been raised about the adequacy of the presently available, commercial quality, BeO, a development program was initiated at the National Beryllia Corporation to fabricate high purity BeO insulators. This program consisted of four distinct phases.

In the initial phase, the raw materials to be used in this program were characterized with regard to impurity content and physical characteristics. The second phase dealt with establishing effective material processing methods and fabrication techniques that did not significantly increase impurity content. In the third phase, firing cycles and atmospheres were determined that yielded high fired densities and retained the high purity levels. The final phase consisted of fabricating the specific insulators that were supplied to Engelhard Industries utilizing the techniques developed in this program.

Two high purity raw material ceramic lots, each from a different source, were examined in this study. One lot exhibited a high surface area and was a highly reactive material, while the other possessed a relatively low surface area and was found to be marginally reactive. Techniques were developed that enabled the fabrication of high quality insulators from both raw material sources.

The processing and fabrication aspects of this program dealt with the examination of selected milling conditions, binder systems, mixing techniques, extrusion parameters and drying methods. From these studies, processing and fabrication techniques were developed that yielded insulators of ultra high purity, possessing high density, and controllable dimensional tolerances.

In the firing study, the effects of firing temperature, firing atmosphere and firing time were evaluated with regard to fired density, shrinkage and purity. Conditions were determined for achieving densities in excess of 95% theoretical value and with minimal impurities being introduced from the firing operation.

The final phase of the program consisted of utilizing the information obtained from the experimental work to produce the specific insulators required by Engelhard Industries. The beryllium oxide parts supplied contained less than a 500 parts per million impurity content (assumed to be in the oxide state), were in excess of 95% theoretical density, possessed high strength, exhibited a fine grained microstructure and were dimensionally within the specified tolerances.

INTRODUCTION

Within recent years, the need for reliable means of measuring temperature over 2073 K for both nuclear and non-nuclear environments has become more pronounced. The thermocouple appears to be a favored device for accomplishing this objective.

From the point of view of the user, a thermocouple is one of the simplest means of measuring, indicating and controllint temperature. In addition, the data or information obtained with a thermocouple can be transmitted easily to remote and distant receivers. Probes utilizing the thermoelectric principle have been used successfully at lower temperatures for many years in many fields of endeavor.

For the purpose of high temperature measurement, tungsten-rhenium thermocouples have been extensively investigated. When used with proper insulators these couples have been employed to measure temperatures as high as 3273 K.[1] However, lifetimes of 10,000 hours at temperatures over 2073 K have not been reported. This may be due to several factors. Either the commercially available thermocouples do not have this desired long life or past high temperature applications did not require such long operating times. There is considerable evidence in the literature that points to the first supposition.

Some interesting work on the improvement of life of lower temperature sheathed thermocouples, as reported by Fanciullo and Bliss[2], appears to point to a possible solution. These authors showed that if great care is taken in selecting materials, preparing them for assembly and finally in assembling them under clean room conditions the life of the finished probes may be extended dramatically. For example, EMF stability within 1% can be achieved when sheathed, high quality type K thermocouples are heated at 1477 K (2200°F) for 10,000 hours.

PROGRAM OBJECTIVES AND METHODS OF ACHIEVEMENT

The main objective of this program was to develop technology and fabrication procedures for a thermocouple having improved performance for in-core and out-of-core thermionic applications in a vacuum environment, at temperatures up to 2273 K for periods of time up to 10,000 hours. Improvements sought were increased longevity and long term EMF stability. The thermocouple probe used consisted of doped W-3% Re and W-25% Re wires insulated with BeO and sheathed in tantalum.

To minimize, or even eliminate completely, the thermocouple failures due to unknown material quality or compatibility, a stringent material characterization program was initiated. All materials that were procured were extensively processed and evaluated for quality prior to assembly into probes. The thermocouple insulation that was ultimately used evolved from a special development program at National Beryllia Corporation.

To further insure achievement of the program objectives, and to minimize loss of thermocouple performance due to handling and fabrication, special assembly procedures were used. All handling, preparation and processing of the probe components was done in a class 10,000 clean room. The final assembly and sealing of the probes was accomplished in a stainless steel glove box containing a high purity inert atmosphere. This glove box was located in the clean room.

In all, twenty-three probes were fabricated and shipped to NASA's Lewis Research Center. A detailed description of the materials used, the special processing and assembly procedures employed as well as the special tools, fixtures and apparatus needed for the characterization of the components and fabrication of the finished probes has been described in Part of this report. Information pertinent to the development of procedures for the fabrication of dense, high-purity BeO insulators may be found in Part B.

PART A - THERMOCOUPLE ASSEMBLY

Technical Considerations and Design Criteria

A. Thermocouple Wire

While any two dissimilar conductors forming a couple will develop an EMF when their junctions are at different temperatures, only relatively few thermoelement combinations have been utilized in thermometry. Some of the reasons for a choice of a pair of materials are evident while others may not be quite so obvious. The following criteria play an important part in the selection of a thermocouple combination[3].

1. The melting point of the thermoelements should be higher than the highest temperature at which the thermocouple is to be used. For safety and stability of the couple, the lowest melting point of the thermoelement combination should be at least 100 K above the maximum operating temperature.

2. The thermal EMF of the couple should be large enough to be measured with reasonable accuracy.

3. The thermal EMF of the couple should increase continuously with increasing temperature over the temperature range in which the couple is to be used; preferably approximating a straight line relationship.

4. The couple should be resistant to physical and chemical alteration due

to the medium and the temperature to which it is to be exposed.

5. Each thermoelement must be homogeneous. In the case of alloys, the alloy elements must have reasonable solid solubility in the base material. If this is not the case the resultant thermoelement will show hysteresis on heating and cooling and the alloy in effect will be useless. Also, the EMF of the wire will vary over its length.

6. Electrical resistance of the thermoelements should not be too high and thereby limit their use.

7. The thermocouple should maintain its EMF-stability during calibration and in use within acceptable limits.

8. The thermal EMF should not be altered during use by internal physical or chemical changes or by contamination from material of the environment. Because of the high temperature at which the couple in this project will be used, it is important that it be compatible with the insulating and sheath materials.

9. It should be possible to melt or compact the thermoelements from their raw materials and to fabricate wire or any other desired shape without undue difficulty.

10. The thermoelements should be reproducible in the quantities desired and be of uniform quality.

Keeping the above criteria in mind, as well as the desired operating conditions (2273 K, 10,000 hours, nuclear environment), the list of commercially available high temperature thermocouples (see Table 1) was examined. Although all combinations shown are still considered non-standard, an appreciable amount of information is available in the technical literature.

If a high operating temperature was the only criterion then the iridium-rhodium vs iridium, iridium vs tungsten and tungsten-rhenium combinations could be considered. However, the Ir-Rh vs Ir couples, although being the only ones that could be used in air to 2273 K for short periods of time without undergoing catastrophic failure, would have to be ruled out mainly because of the high thermal neutron capture cross sections of iridium and rhodium as well as long half lives of the irradiated isotopes. Other shortcomings are low total EMF and low sensitivity as well as brittleness in the iridium leg after exposure to high temperatures. The iridium vs tungsten is also subject to similar problems (except low sensitivity and low total EMF). This leaves only the W-Re combinations for consideration.

The thermocouples that are generally used today at temperatures over 2073 K are ones where either one thermoelement or both contain tungsten and rhenium. These are:

tungsten vs tungsten - 26% rhenium
tungsten - 5% rhenium vs tungsten - 26% rhenium
doped tungsten - 3% rhenium vs tungsten - 25% rhenium

Although there are no official "standard tables" prepared by national standardizing laboratories, these thermocouples may be obtained to meet standard EMF vs temperature values (within 1%) prepared by the respective manufacturers.[4-6]

The tungsten and W-5% Re thermoelements are not supplied to the user in a stabilized (recrystallized) condition; therefore, a small change in EMF is encountered at the operating temperature. In the case of the doped W-3% Re doped W-5% Re, W-25% Re and W-26% Re thermoelements, these are supplied in a stabilized (recrystallized) condition. Some of the properties of all three W-Re thermocouple combinations are shown in Table II. Properties which may have bearing on the design of thermocouple probes are shown in Table III for W-3% Re vs W-25% Re. Other pertinent information may be found in the literature.[9-21]

Because of the relative brittleness of the positive leg of the W-Re thermocouples (in particular W) and the instability of the W-Re thermocouples in a nuclear environment considerable amount of research was conducted during the past ten years to develop improved thermoelements.

In one of these efforts Kuhlman[22] sought to develop mechanically stronger thermoelements. He determined the EMF versus temperature for a number of these. In each case the EMF was determined in respect to W-26% Re. Materials used were: Re, Re-6% W, Re-9% W, Re-12% W, Re-15% W, Re-10% Ru, Re-5% Ru, Re-10% Rh, Re-20% Rh, Re-10% Pt, Re-30% Ir, Re-5% Mo, Re-10% Os, Re-20% Os, Mo-10% W, Mo-20% W, Mo-10% Re, Ir-20% Re, Ir-20% Re. Of the alloys studied Re-10% Ru and Re-12% W showed the greatest potential for high-temperature thermocouple applications. All of these materials were tested in rod form, approximately 30.48 cm (12 inches) X .318 cm (1/8 inch) in diameter.

Bliss [23] and co-workers studied a number of potential high temperature thermoelements to improve stability and provide resistance to radiation. Candidate materials were selected on the basis of melting point, nuclear cross-section, thermoelectric power, availability. Metals tested out of pile, versus platinum 27 were columbium (niobium), vanadium, titanium, zirconium and yttrium. These researchers concluded that the molybdenum versus columbium combination shows considerable promise. They determined a tentative EMF vs temperature table over the range of 810.7 K (1000oF) to 1654 K (2500°F).

For the past ten years, in work outside this contract, the authors have investigated a number of metals and alloys as potential thermoelements. This work has had a dual aim. First of all, a positive leg having improved mechanical properties was sought for the W-Re thermocouply. Secondly, thermocouple combinations capable of stability under nuclear irradiation were examined. Various metals and alloys were tested. Details of the results obtained have been published.[24-26]

At this time, based on our work as well as a knowledge of what is available in the literature, we feel that, although there are promising combinations which may prove to be eminently successful in the future, there are no commercially proven couples that are better than the three W-Re combinations (with all of their known deficiencies) for use over 2073 K in a nuclear environment.

B. Sheath Material

The choice of a thermocouple sheath material is governed by the following parameters:

1. Availability
2. High melting point
3. Compatability with thermocouple insulation and wires
4. Compatability with use environment
5. Ease in handling
6. Ease of fabrication
7. Cost

For this application, the list of possible materials would include tungsten, rhenium, osmium, tantalum, molybdenum, colombium, ruthenium. Osmium, rhenium and ruthernium would be eliminated due to the lack of availability in the form of tubing and in reasonable quantities. Molybdenum would be eliminated due to its relatively high vapor pressure at the design temperature and vacuum conditions. Columbium has an edge over tantalum as far as nuclear applications are concerned, but the latter has a superior melting temperature, and thus a higher use temperature.

Tantalum has a considerable advantage as a sheath material. It has a high melting point, 3269 K, and can be worked easily into various shapes. Electron beam melted tantalum of a high purity is available commercially.

Because of its good workability, tantalum tubing can be drawn to small sizes and thin wall thicknesses. This is of considearable importance in thermocouple applications.

Tantalum has one big drawback; its reactivity with N_2, O_2, H_2 and carbon, which can result in the embrittlement of the tantalum. For this reason, great care must always be exercised to insure that it does not come in contact with these contaminants when it is exposed to high temperatures as for example in annealing operations or in thermocouple applications.

Another interesting possible candidate for thermocouple sheathing is tungsten-rhenium vapor deposited material. This material may be obtained in small sizes and with good dimensional control. Its relative brittleness is offset by sufficient handling strength, desirable high melting point and nuclear properties.

There is probably no material which can be classified as an ideal one for use as a thermocouple sheath at high temperatures and for long periods of time. Usually, selection is based on material properties and is influenced by prior experience. For this program it was decided to use high purity tantalum primarily, but with a limited inclusion of tungsten-rhenium as a back up material.

C. Ceramic Oxide Insulation

Only a relatively few ceramic oxides are available for use to 2273 K and these are ceria (fusion temperature approx. 2273 K), yttria (F.T. 2683 K), thoria (F.T. 3323 K), zirconia (F.T. 2823 K) and beryllia (F.T. 2843 K). Of these, ceria and yttria can be ruled out because they are relatively untried while zirconia should not be considered because it becomes a conductor at higher temperatures.

The remaining two refractory oxides, thoria and beryllia, both have good high temperature properties; for example good chemical stability (thoria is the better of the two) and high fusion temperatures. However, for use to 2273 K (near the upper limit of use temperature of beryllia) beryllia enjoys one decisive advantage - it has a much higher electrical resistivity than does thoria. For this reason, plus its other good high temperature properties, beryllia appears to be the best refractory insulating material than can be used to achieve the program objectives. A few of the interesting properties of beryllium oxide are:

1. Desirable nuclear properties.

2. Has a better resistance to thermal shock than most other ceramic materials.

3. Higher melting point than any metal except tungsten, osmium, tantalum, rhenium and molybdenum. Its melting points is approximately 773 K higher than its proposed use temperature (2273 K).

4. Has a high electrical resistivity.

5. Has a high chemical stability and a particularly high resistance to reduction.

6. As far as it can be ascertained (there are some conflicting reports), BeO is compatible with W, Re and Ta to the use temperature in this project (2273 K). However, this compatibility has been ascertained for relatively shorter times than the desired 10,000 hours. It appears also that when incompatibility was noted between BeO and W, Re or Ta, it could have been attributed to impurities present and not to the BeO.

7. Its high thermal conductivity, comparable to that of some metals, coupled with a moderate and uniform thermal expansion, makes it very resistant to thermal shock.

8. Beryllia has a relatively low vapor pressure.

9. Beryllium oxide is stable in air, hydrogen, carbon monoxide, argon, nitrogen or vacuo to temperatures above 1973 K.

D. Compatibility

Selection of the right thermocouple material, sheath or insulator must be made with reference to the environment in which it will be used and to the particular application. This is especially true at high temperatures and wherever contact is made with many of the refractory metals and materials.

Generally speaking, the higher the temperature, the greater the potential for different materials to react and interdiffuse, and the higher the temperature and the longer the time, the greater is the extent to which reaction and diffusion occur. Chemical reaction between the thermocouple and its insulators, sheath or environment can substantially reduce the effectiveness of the couple, or perhaps result in its early failure. In addition, it may alter the mechanical properties on which the design of the couple or structure is based.

What may happen in a given case under a given set of time-temperature-pressure conditions will depend on the thermodynamics of the system and its kinetics. With the use of thermodynamics, we can usually determine the direction in which a given reaction has the potential to go. However, since reliable thermodynamic data may be lacking, and since there may be insufficient knowledge regarding solubility limits and intermediate phases at the high temperatures at which the thermocouple systems may be used, it is often very difficult to make reliable predictions. Also, kinetic theory has not evolved to the point where good predictions can be made for interaction rates between the materials of interest and temperature of concern. For these reasons, the "rules of thumb" and the experimental approach are usually relied upon very heavily.

E. Thermocouple Design

After consideration of many of the factors concerned in the fabrication of a high reliability thermocouple, a probe was designed. This is shown in Figure 1 and is indicative physically of the twenty-three (23) probes produced and shipped to NASA LeRC.

However, in order to broaden the experiment, the type and quality of probe companents as well as the environment surrounding the components in the sheath were varied. For example, two of the probes were sheathed in W-22%Re tubing which was fabricated by chemical vapor deposition and twenty-one in tantalum. In eighteen of the probes, a high purity BeO specially prepared by National Beryllia Corporation (see Part B of this report for details) was used. For comparison purposes, commercial grade BeO insulators, obtained from two other sources, were used in five probes.

To see whether there would be any benefit in using stranded thermocouple wire, it was used in three probes, while solid wire was used in twenty others. Likewise, three of the probes were assembled without any special precautions in an attempt to simulate what may be called commercially assembled probes.

B

PREPARATION OF MATERIALS

Thermocouple Wire

Two different thermocouple wires were used; solid wire and stranded wire. Sufficient material was obtained at .254 cm diameter and .0076 cm from one ingot to minimize uncertainties that may be introduced by minor differences between different lots of ingots. Samples of these wires were calibrated to obtain a basis for preliminary acceptance. The resultant calibration agreed with the published EMF-temperature relationship to within 1%. Having passed this preliminary criteria for acceptance, the wire material was released for processing and characterization prior to thermocouple assembly.

Processing of the thermocouple wire was initiated by extensive surface cleaning. A three stage surface cleaner was employed. The reason for the cleaning operation was to remove all possible films or surface inclusions of a contaminating nature. In operation, the wire to be cleaned was passed through three battery jars containing the cleaning agents. Ultrasonic agitation was imparted to expedite the cleaning operation. The as received wire was first passed through chloroform to remove oils and fatty films; next it was subjected to mild abrasion with an aluminum oxide slurry (-325 mesh in water); in turn followed by a distilled water rinse. The aluminum oxide slurry gently polishes the wires, and this is evident by their bright surface appearance.

After this operation the wire was subjected to a second pass through the cleaning facility. In this pass the aluminum oxide abrasion tank was replaced with a NaOH solution (20%). Electrical contact was made with the wire through a conducting pulley and slip ring assembly through which current flows to electrolytically etch the wire. A current density of about 0.868 amperes/cm^2 was employed to further clean the surface of any contaminants not removed by the slurry abrasion process. From this stage of the processing operation, the wires were handled only with protective covering on the hands.

Annealing of the thermocouple wires followed the cleaning operation. Annealing (continuous) was accomplished in a test facility which permits heating the wire to any desired temperature in a protective environment. At the outset only a small sample of each wire was annealed. After a preliminary evaluation of the EMF-temperature relationship and mechanical properties, the remainder of the wire was annealed at temperatures from 1948 K (for W25Re) to 2148 K (for W3Re) in an $7H_2 93N_2$ gas.

At this point samples of the wires were calibrated in order to provide reference data gainst which assembled probes could be compared. The calibration between the as received samples, i.e., before surface cleaning, and the final bare wire calibration of the cleaned and annealed wires agreed to within experimental uncertainty.

After the cleaning and calibration of the thermocouple wires was completed, they were tested for homogeneity. Testing was accomplished on a test facility (Figures 2 and 3) specifically designed for this purpose. The wire was passed through a one inch long heat zone, nominally at 1223 K, in a neutral environment at a rate of .0076 M/sec. Electrical contact was made with the wire by conductive pulleys and slip ring assemblies. The generated signal was amplified and supplied to a zero centered recorder. A permanent record (Figure 4) was provided of the generated signal due to inhomogeneity in the individual conductors. The resultant maximum error of temperature measurement due to the inhomogeneity found in this test was determined to be 2.1 K.

Seven strands of the .0076 cm diameter thermocouple wire were heated to approximately 973 K and twisted ten turns in 2.54 cm to provide the stranded cable. The stranded cable was subjected to the same cleaning, handling and testing procedures as was the solid one. All electrical tests on the stranded wire agreed with the solid wire to within experimental uncertainty.

The final processing operation on the thermocouple wire was vacuum degassing. This was accomplished in an ion pumped vacuum chamber (Figure 5) which housed, vertically suspended, up to eight lengths of wire. Connected to the vacuum chamber was a "V" tube residual gas analyzer employed to monitor the outgassing constituents. In this vacuum processing, like all others, the residual gas analyzer was used to control the operation. The optimum time at temperature was determined when the spectrum of vacuum quality approached known background levels. Using this as a criteria it was assumed that the degassing process, either of absorbed or adsorbed gases, had gone to completion for that particular temperature.

At times, the temperature at which a certain material was processed was governed by comparing expected gains versus mechanical degradation due to thermally induced structure changes. This was found to be the case with vacuum degassing the thermocouple wires. Ideally, theory would predict that a de-gas temperature of 2073 K to 2273 K would be optimum but to do so at the upper temperature would probably alter the chemical composition by preferential rhenium volatilization.

A number of vacuum degassing tests were conducted at temperatures from 1273 K to 2073 K at various times at temperature. Evaluation of the residual gas analyzers spectrum indicated that for this particular lot of material, degassing was completed, to within the instruments sensitivity and confidence, within one hour exposure at temperatures from 1275 K for the W3Re to 1723 K for the W25 Re.

It was concluded after much experimentation that vacuum degassing of this particular lot of thermocouple wires would serve little or no purpose other than liberating adsorbed surface gases. This condition has been subsequently found not necessarily true for other types or lots of thermocouple materials.

To prevent the thermocouple wires from readsorbing atmospheric contaminants, a method was developed whereby the wires could be removed from the system under protective gas cover and transported to an environmentally controlles storage area. This was accomplished by fabricating a polyethylene bag with glove ports heat sealed in. The vacuum system was let up to atmospheric with high purity argon (research grade, nominally 99.999%). With the bag attached to the entry flange, the flange would be "cracked", permitting the argon to flood the bag. The bag would be flushed a minimum of three times by collapsing it against the argon flow and permitting the bag to expand. Working through the inflated bag, the wire samples would be removed from their electrical clamps and sealed into a tantalum tube previously installed in the bag.

At the completion of certain preparation stages, samples of the thermocouple wire were submitted for analysis, chemical as well as physical. Chemical properties were determined at Battelle Columbus Laboratories by Solid Mass Spectrographic Techniques. Seventy-seven elements in the periodic table were sought with a detection limit of about .003 ppm. Only those elements detected in excess of the detection limit are presented. Classified techniques such as Vacuum Fusion, Combustion and Kjeldahl were used by Battelle for the determination of oxygen, hydrogen, carbon and nitrogen.

The surface purity condition was investigated at Engelhard Industries with the application of Electron Beam Micro-Probe Analysis techniques. Automatic 2 θ scans were made on the surface of the sample to determine the presence of selected contaminants (C, Fe, Cr, Ni, Al, Si and Ca), and a manual elemental scan procedure was then employed to determine the distribution of the detected foreign elements. The results of the scans are reported in terms of a number of contamination particles and relative content of the contamination in the particle. The content of the contamination in the particles was rated as H, M, L; referring to high (more than 50%), moderate (10-50%) or low (less than 10%) respectively.

The results reported for the Electron Beam Micro Probe Analysis should be considered to be semi-quantitative. The data tend to crudely indicate the relative improvement in surface quality as a function of various cleaning and processing steps.

Tables IV to VIII present the results of the chemical analysis. Table IX shows the mechanical properties for the thermocouple wires. Figures 6 to 25 show the results of metallographic examination of the material after heat treatment.

Sheath Material

The tantalum tubing was procured from a commercial source under written specifications (see Appendix) which called for certain maximum impurity levels and certain minimum fabrication controls. However, since all suppliers took exception to one or more aspects of the specification, the material was accepted on best available basis. The tantalum from which the sheath tubing was fabricated was electron beam consolidated stock. The W22Re tubing was obtained also from a supplier and was produced by chemical vapor deposition technique. This tubing is supposed to be indicative of what was available commercially at that time (1969).

Preliminary surface cleaning of the tantalum tubing was accomplished by subjecting it to the following cleaning procedure:

1. Ultrasonic agitation in warm chloroform, 60 minutes.
2. Ultrasonic agitation in warm water (flowing), 10 minutes.

3. Ultrasonic agitation in warm acid solution, 10 minutes.
4. Ultrasonic agitation in warm water (flowing), 10 minutes.
5. Rinse with alcohol.
6. Rinse with chloroform.
7. Dry with flowing argon.

Various acid solutions were evaluated for apparent activity. Most of these were mixtures of hydrofluoric and nitric acids. A solution of 25HF, 25HNO_3 bal. H_2O was found suitable. Because the cleanliness of the inside surface of the sheath was of paramount concern, special methods were developed to insure the elimination of stagnated solution areas inside the tubing. A specially designed ultrasonic cleaning tank was obtained with a highly concentrated bank of transducers located in a central location. Positioning the vertically suspended tubes over the transducer bank caused convection currents to rise through the bore thus insuring a continuous wash of the inside surface.

The tantalum tubing was vacuum processed, after surface cleaning in a manner similar to that for the wire. The tubing was suspended in the process chamber employed for wire processing. It was heated to various temperatures and held for periods of time decided upon the analysis of the vacuum quality. A number of preliminary heating tests were conducted to optimize the process for maximum degassing and maintenance of minimum acceptable mechanical properties. Figures 26 and 27 show the relative outgassing constituents for process runs to 2108 K and 2363 K respectively.

While low confidence must be placed on the absolute quantities plotted in the above figures, a relative indication of the "outgassing" constituents can be obtained. Theory would predict that hydrogen would be liberated from tantalum at temperatures greater than 473 K, CO at temperatures greater than 1573 K, and nitrogen at temperatures greater than 2173 K. The present traces clearly show a rather marked increase in hydrogen content as we approach 773 K. Total pressure readings indicate a saturation level existing, i.e., very slow pressure recovery to base. This condition exists to approximately 1273 K where the relative percentage of hydrogen becomes less due to the increase in the CO content. The CO is the predominant gas for the remainder of the test run. Little indication of nitrogen gas was noted. The reason for this deviation from theory is uncertain.

It must be noted that the lines drawn through the plotted points of Figures 26 and 27 are for clarity in following trends only. They must not be considered in the usual sense as representing a continuation of data.

The two process runs presented are but a sample of all tests conducted. It was concluded after reviewing all test run data that equivalent results would be obtained by heating the tubing to approximately 2073 K and holding for about one hour after a soak at 1873 K for 16 hours. This schedule was followed for the processing of all tantalum sheath tubes used in the fabrication of thermocouples for this program. Heating the tubes to temperatures greater than 2073 K did not seem to liberate any significant gas but did materially affect the grain size of the tantalum. ASTM grain size for the nominal 2073 K outgas temperature was found to be No. 2, while an ASTM No. 1 was realized when the tubing was processed to 2363 K (see Figures 28 through 33).

Removal of the tantalum shield tubes from the vacuum chamber was accomplished using the same techniques as described in the wire secition, i.e., covering the system with an inflated "bag" and sealing the tubes in a receptacle containing an inert atmosphere. This method was employed to minimize, or prevent the adsorption of atmospheric water vapor and the formation of the passive tantalum oxide on the tubes.

Characterization of the tantalum was conducted on samples of the material at various process stages. Figures 28 through 33 show the results of metallographic examination in the as received and vacuum processed condition. Solids mass spectrogrphic analysis was conducted by Battelle on as received, after surface cleaning, and after vacuum degas samples. Table X shows the results of this investigation. Mechanical properties such as ultimate tensile strength, yield strength, elongation and hardness may be found in Table XI.

A special analysis by Ion Microprobe Solids Analytical Spectroscopy was conducted by GCA Technology Division, GCA Corporation on the surface cleaned and vacuum degassed tubing. This technique provided a layer-by-layer analysis across the tube wall for certain selected elements. In addition, a more comprehensive analysis was obtained at a depth of .0076 cm and .013 cm from the outside surface for a slightly larger number of possible contaminants. Figures 34 and 35 graphically show the impurity distribution across the wall of the test samples. Tables XII and XIII present the analysis at .0076 cm and .013 cm depth.

It must be noted that the data presented here are for an "Energy Window" setting of 200 electron volts. With this setting, the observed, and reported, quantity of impurity elements would be higher than realized. Also, for simplification, a monatomic combination was assumed for all elements. This will result in some elements appearing higher in content than would actually be realized. For this reason, it is suggested that the bulk analysis as supplied by Solids Mass Spectrographic Techniques be used as the "true" indication of the impurity content while the data presented here be taken as the apparent distribution of them.

Electron Beam Microprobe analyses of the inside diameter surface of as received, surface cleaned and vacuum degassed tantalum samples were obtained at Engelhard Industries. The findings of this study are as follows:

<u>As Received Ta Sample</u>

1. Fe was the most commonly detected foreign element. The Fe concentrations varied in a wide range from very low to very high.
2. Al was the second major foreign element with concentrations varying from low to moderate.
3. Mg particles were detected a number of times, but the concentrations were relatively low.
4. Low concentrations of O were found always combined with the detected Fe, Al or Mg.
5. Carbonaceous film or particles were detected many times. The maximum C content detected in these particles was at the level of about 30%. This is probably due to the residual drawing lubricant.

Surface Cleaned Sample

1. Negligible amount of particles containing carbon was detected. Very faint traces of carbon were detected in the general area surveyed.
2. In the 1.91 cm of tubing scanned, only 2 iron particles were found and were rated medium to low.
3. The Cr and Ca particles were practically negligible.
4. One moderate particle of Ni was detected and three (moderate to low) particles of Si and Al were found.

Vacuum Processed Tubing

1. Si, Al and Fe were detected as contaminants.
2. Through the entire cross-section length of the tube, about 1.91 cm, a total of four impurity particles were detected. Some particles contained the combination of contaminants; some just a single contaminant.
3. The concentration of the contaminants varied in a wide range, from very low levels to relatively high levels of more than 50%, in the areas being analyzed.

W22Re Sheath Processing

Four samples of W22Re vapor deposited tubing were processed in a manner similar to that for tantalum. Surface cleaning was accomplished by degreasing with warm chloroform, agitated by ultrasonic means and followed by acid cleaning. Acid cleaning techniques were as described in the tantalum section. A dip in a solution of 50% HCL, 50% H_2O for 15 minutes was followed by a one minute dip in 1 HF, 1 HNO_3, 3 H_2O. The tubes were then successively rinsed in running water, alcohol, chloroform and then dried with flowing helium. Considerable activity was noted in the HF-HNO_3 bath. Surface condition appeared mottled. It was further noted that the effervescent activity due to the acid was concentrated about these mottled surfaces. This may be due to the surface being rhenium rich, or perhaps to the formation of preferred crystal orientation as a result of the vapor deposition.

Samples of this material were vacuum processed in a manner similar to the wire and tantalum procedures. Figure 36 shows the vacuum quality-temperature data for this run.

Unlike tantalum which liberated large quantities of hydrogen, starting at low temperatures, the W-Re tubing showed only slight gas liberation until approximately 1373 K was reached. The gas liberated below 1373 K is believed to be surface water and adsorbed gases though some question of this remains. The pressure rise and decay was extremely rapid, too fast to record with the RGA.

At 1273 K a gradual increase in CO was noted, indicating a possible reduction of the oxides and carbides. This continued to the maximum process temperature of 2196 K. It is believed that CO would continue to be liberated at higher temperatures, but due to the vapor pressure of Re (approximately 10^{-6}N/m^2 at 2573 K) it was decided not to proceed further. Instead, the samples were permitted to "soak" at 2196 K until the total pressure decayed to the base value.

An increase in hydrogen was observed at about 1573 K which tended to remain constant (except for the soak time at 2206 K) for the test duration.

Documentation of the quality of the W22Re tubing may be found in Table XIV and Figures 37-43. Table XIV presents the solids Mass Spectrographic Analyses for samples of this material in the as received and vacuum degassed condition. The rhenium content was determined by sublimination of rhenium oxide and conversion of tungsten to tungsten oxide at 1023 K. This method has been applied in the past and has given accuracies of 2% or better. This accuracy is considered adequate for the purpose of determining the nominal rhenium content.

An examination of the results show that with the exception of O, F, Al and Si, no substantial changes in impurity elements were noted. The drop in oxygen in the WR-VP (vacuum processed) sample may possibly be attributed to the vacuum processing. No explanation can be given for the apparent pick up of F, Al and Si. However, two different samples, one of which was in the as received condition while the other was vacuum processed, were employed, hence these anomolies may be attributed to specimen differences.

Photomicrographs for the nominal W-22%Re vapor deposited tubing in the as received condition (Figures 37-38) and the vacuum processed at 2196 K conditions (Figures 39-41) are also shown. Samples of W-Re tubing used in actual probes are shown in Figures 42 and 43.

Equiaxed grains are visible in both the "as received" and vacuum processed samples. Preliminary examination of the vacuum processed sample at low magnification (100x, Figures 39-40) discloses what appears to be excessively large grain boundaries. Further examination under oblique light at 2000x (Figure 41) shows a number of grains in relief, thus explaining the apparent large grain boundaries observed at low magnification.

The photomicrographs reveal what appears to be a discontinuity of deposit. This condition was noted in three of the four tubes to various degrees.

An electron beam microprobe analysis was conducted across this area in an attempt to ascertain the nature of this discontinuity. At first glance it would appear that the discontinuity was due to porosity or voids, but this was not born out by analysis. It was found that the discontinuity was richer in rhenium, and lower in tungsten, than that indicated by the average analysis (22%Re). The tungsten content on the inside surface of the sample is slightly lower than the outside surface, while the rhenium content varies in an opposite manner. It would appear that an interruption of deposition was the cause of this discontinuity of structure.

Due to the limited amount of sample material available no mechanical property tests were conducted.

Ceramic Processing

Extruded and fired twin bore BeO ceramics, in three grades, were received from National Beryllia Corp. This material was carefully prepared using the highest purity raw materials available (see Section B of this report). The twin bore insulators, 99.95 + % BeO, classified as S-11, CF-1 low and CF-1 high, were intended for thermocouple insulation, while a single bore tube was intended for use as thermocouple junction sleeving. The properties and analyses for each of these types of BeO ceramic are shown in Section B.

Segments of twin bore tubing were laser beam cut to a length of .127 cm. These small pieces were used as a sheath end plug upon which the thermocouple junction rested. The balance of the insulation was supported from this end plug by approximately .508 cm long single bore segments which surrounded the wire junction.

All material from a given lot of ceramic insulation, twin bore, as well as single bore, and cut end plugs, were loaded into a BeO crucible in preparation for vacuum firing. The crucible was fabricated from S-11 powder to minimize contamination of the thermocouple insulation by "cross talk" between itself and the surroundings.

A furnace using a turbo-molecular vacuum pump was employed for the final ceramic degassing operation (Figure 44). Preliminary experimental ceramic degassing runs disclosed problems with the use of ion pumps. During processing, large gas evolutions were experienced which tended to saturate the ion pump resulting in very long process times. The turbo pump, being mass transport in principle, rather than scavenger, did not suffer this problem and subsequently provided a greatly shortened time schedule. In addition, due to the elimination of the ion pump's regurgitation characteristic, residual gas analysis studies were more indicative of the sample under study and not the massed system.

A number of experimental runs were conducted prior to the final process run. One fact obtained from these experiments was the relative difficulty in analyzing the outgassing constituents of the ceramic in questions due to the overshadowing presence of the crucible. The crucible was approximately 60% to 75% dense and consisted of approximately 50 times the mass of the material under test. The majority of the outgassing indications were attributed to the crucible rather than the thermocouple insulators.

Repeated tests with the empty crucible disclosed that a typical outgassing spectrum could be expected for a fixed set of handling conditions. Relative indications of sample outgassing were obtained by comparing "empty" and "full" crucible process runs and deducting the effect of crucible from that of the insulators.

In general, it was found that the ceramic could be expected to liberate large quantities of water vapor, moderate amounts of normal air, a slight quantity of excess oxygen and an even smaller quantity of light hydrocarbon. It is speculated that the hydrocarbon content may be due to residuals from the binder system employed. A temperature of between 973 K and 1073 K was required to cause the outgassing constituents to reduce to a level below the instrument's sensitivity. This tends to indicate that the evolution products are but weakly held on the ceramic, or that they are readily mobile through the ceramic.

Repeat process runs where the ceramic in question was exposed to atmospheric conditions for 18 hours and reprocessed, disclosed nearly identical results except for the liberation of hydrocarbons, which were not evident. This would tend to indicate a surface liberation.

Repeat tests in which the vacuum system was brought up to atmospheric pressure with either argon or helim and the ceramic then exposed to air, disclosed that the repetitive water-air-excess oxygen liberation to be reduced. Ceramic so processed and exposed to air for a number of hours and reprocessed liberated only slightly detectable quantities of these expected constituents. In their place was a marked increase in either argon or helium, depending on the species of the backfilling gas.

Having obtained sufficient background experience with the particular grades of ceramic in question and with the process equipment, a standardized procedure was employed for the processing of the thermocouple insulators used in the probes. All ceramics were subsequently processed at about 1623 K ± 50 and held from 24 to 36 hours at a pressure in the low $10^{-5}N/m^2$ range.

Due to the indication that the ceramic "picked up" atmospheric contaminants, methods of removal and transport to the assembly area were developed to minimize exposure. A polyethylene "bag" was fabricated with three arm ports heat sealed to it. This bag was taped to the main entry flange of the process chamber (Figure 45). The vacuum system was brought up to a pressure slightly higher than atmospheric with research grade argon at which time the entry flange was "cracked" permitting the collapsed bag to inflate. After inflating completely, the bag was compressed and re-inflated a number of times with the research grade argon to purge or flush any remaining atmosphere.

Working one arm port, the bolts and washers were removed, along with the entry flange, and placed in the opposite arm port. The arm ports were then tied off. It was then possible to reach into the system and remove the BeO crucible and its contents by working through the third arm port. The crucible was withdrawn into the arm port, which was twisted off and finally heat sealed shut. The bagged crucible and processed insulators were then placed into the transport tube of the stainless steel glove box in preparation for thermocouple assembly.

The transport tube was evacuated and backfilled with argon approximately three times, or until an oxygen meter connected to the glove box facility indicated that the oxygen content of the transport tube was below 5 ppm. The main valve was then opened permitting the crucible and its contents to be drawn into the glove box proper. The polyethylene bag, into the crucible was sealed, usually ruptures during this operation. This is due to the expansion of the sealed bag by reason of the pressure difference across it during the evacuation of the transport tube. This insured that the crucible and its contents arrive in the glove box in the same environment. Once inside the glove box the BeO pieces were inspected and sorted - hot end tubulations, plugs and insulators - and stored within rigid containers until final assembly.

Hermetic Seal

A hermetic seal assembly was required to provide a barrier so that atmospheric contaminants would not gain access to the processed materials in the final probe assembly. However, great difficulty was experienced in obtaining a usable seal.

Initially, a metallized and brazed BeO seal was designed after consultation with a number of authoritative seal manufacturers. Three different design configurations were tried without success. This resulted in a substantial loss of time.

Since time was rapidly running out, an alternate approach was tried. A hermetic seal assembly was fabricated using Varian Torr Seal Epoxy. The seals were fabricated and leak tested with helium after the performance of qualitative brazing tests. All passed this test and appeared to be leak tight.

Subsequent to the termination of the contract, but prior to the writing of the final report (a time lapse of approximately two years), it was discovered that the Torr Seal Epoxy lost hermeticity. It is uncertain at this time as to the cause of the failure of the seal. Perhaps it may be due to the aging of the epoxy and loss of adhesion. In any event, the seal was repaired using a G. E. Vacuum Leak Sealer (GEVAC). This epoxy seal appears to be effective at the time of the writing of this report.

ASSEMBLY

All assembly operations, performed after vacuum processing of the basic components, were conducted in the stainless steel glove box (Figure 46). All probes were assembled as shown in Figure 1.

The sheath material was brazed to the stainless steel vacuum gland with an 82% gold-18% nickel alloy, using a plasma torch in an argon gas environment. After this brazing operation, the braze area was leak tested. A Veeco MS-12 helium leak tester was connected to a valved "feed-through" into the glove box by .735 cm copper tubing and "Swagelok" fittings. The "feed-through" was in turn connected to a leak test manifold. The manifold, as shown in Figure 47, received the sheath-gland subassembly for testing. Next the manifold was evacuated and helium was "sprayed" through the sheath-gland bore. This process effectively tests the braze area of the sheath to nickel tubulation; retests the weld between the nickel tubulation and the stainless steel vacuum glad; and tests a portion of the sheath for porosity.

After passing the braze leak test, the sheath and vacuum glad assembly was cut to length in preparation for sealing the "hot end" portion. This was accomplished by holding the surplus portion of sheath with a pin vise and cutting the tubing in a specially modified cutter.

The cutter (Figure 48) is a commercially available tubing cutter intended for fine tubes. A tantalum block was fitted to the bearing surfaces to prevent "pick-up" between the sheath tubing and the cast aluminum housing. In addition, the cutting wheel was modified so that the tube was partially "spun" shut prior to the final parting. Figure 49 shows an "as-parted" and a welded sheath for comparison.

The cut sheath was then clamped in a spring loaded copper chill block and fused shut using the plasma welder. After fusing the end of the sheath, the assembly was again leak tested.

The thermocouple wires were junctioned by forming a twist in a specially provided jig (Figure 50) by procedures previously qualified. Qualification tests were performed by spacing the wires on a center line distance equal to that of the insulation and rotating them in an appropriate jig four full turns. Excess twist was cut from the assembly and the final welding accomplished with the twisted portion held between copper chill blocks. The resulting junction consisted of a minimum of 1.5 turns and the weld bead (see Figure 51). The thermocouple wires could be flexed 180° apart when held one inch from the twist without juncture fracture.

The insulators were then "strung" on the T/C wires; the hot end ceramic tube placed over the junction; the hot end plug positioned on the tube; and the assembly slipped into the prepared sheath. The hermetic seal subassembly was then slipped over the wires and fitted to the stainless steel vacuum gland.

The thermocouple was then placed into a jig for the brazing operation which affixed the seal to the vacuum gland. An alloy containing 60% Ag, 30% Cu and 10% Sn was the brazing material. Finally the tubulations which seal the thermocouple wires were brazed shut. Again the same alloy was used as the brazing material. These final brazing operations, which seal the probe, were conducted in high purity argon. An oxygen meter was connected and "energized" throughout the fabrication and sealing operations. Normal oxygen content at the time of the final seal brazing was less than 10 ppm except for certain sample fabrications where deliberate excursions were desired.

When the probes had been sealed, they were removed from the glove box for final leak testing. This final test was accomplished by pressurizing the entire probe to approximately 690,000 N/m^2 of helium pressure, holding the pressure for 15 minutes and then exposing it to atmosphere. The probes were washed with alcohol to remove any residual surface helium and then placed in a container which was connected to the leak tester. Having passed this test, teflon insulation was placed on the T/C wire and a code number was affixed. For the final operation, the tips of the probes were x-rayed and the junctions located.

Since the program was terminated by NASA prior to full unit testing, no further attempt was made to evaluate the completed probes. Only the cursory leak tests described in the preceding paragraph were tried. All probes appeared to be leak tight.

In all, twenty-three (23) probes were assembled and shipped to NASA. Pertinent data relating to these probes are shown in Table XV.

The BeO insulators obtained from National Beryllia, S-11 and CF-1, are 99.95 + % pure. These code letters indicate two different high purity BeO powder lots obtained from two different sources. The S-11 insulators were fabricated with a high density (99% of theoretical). On the other hand, the CF-1 powder was used to fabricate low density (93% of theoretical) insulators. Details relating to purity and fabrication procedures for these insulators will be found in Section B of this report.

SUMMARY AND CONCLUSIONS

1. In order to realize the potential from the use of high purity components in high temperature (over 1873 K) thermocouple probes, great care must be taken during the processing of components as well as during the assembly of them into a finished probe.

2. In many cases ceramic insulators as received by the thermocouple fabricator may be unsuitable for use in high reliability, high temperature, thermocouple assemblies. Impurities that may be found in the raw material and contained in the hard fired or crushable insulators, hydrocarbons from unburned binder, adsorbed and absorbed gases, surface contaminants resulting from abrasion of the packing material or fingerprints from handling, are some of the problem areas that should concern the assembler.

3. Thermocouple wires may have a relatively high surface contamination due to pick-up from drawing dies, spooling devices and from general handling. The best way to correct this is to remove the contaminated surface by abrasion or chemical means.

4. The outer and inner surfaces of high purity metallic sheath materials may be contaminated in varying degrees. The amount of contamination may be kept to a minimum if greater care is taken during fabrication and annealing. This may not be possible for a number of reasons, and for this reason the removal of contaminated surfaces may be the only solution.

5. Vacuum processing of the components, in particular the ceramic insulators, is one way of improving the quality of as received materials. Assembly of the components in a clean room, in a clean work station or in a glove box will maintain this purity.

6. Vacuum degassed components, particularly the ceramics, should be transported from the vacuum degassing facility to the glove box in a way so that the components are not recontaminated by contact with the atmosphere. The method employed in this project for this purpose was very successful.

7. In all of the vacuum degassing studies conducted, a residual gas analyzer, connected to the process chamber, was found to be indispensable. Only by study of the indicated vacuum quality and outgassing constituents could intelligent process schedules for a particular lot be formulated. Variation in material quality, even from the same supplier, rules out the use of standardized process schedules.

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APPENDIX

Engelhard Minerals and Chemicals Corporation
Engelhard Industries Division
Temperature Sensing Department
Carteret, New Jersey

Material Specification 100 May 1, 1968

Tantalum Tubing

1. Scope

This specification covers seamless tantalum tubing of a type suitable for nuclear and high reliability applications.

2. Fabrication

Tubing shall be made by a seamless method from electron beam melted raw material to meet the requirements of this specification.

3. Definition

3.1 Maximum outside diameter (D). The nominal outside diameter of the tube plus tolerance in inches.

3.2 Minimum inside diameter (d). The nominal inside diameter of the tube minus tolerance in inches.

3.3 Lot. All tubing of the same nominal dimensions, type, and obtained from the same heat or ingot.

4. Chemical Composition

The manufacturer's analyses on a sample from each finished tubing lot shall be considered the chemical analysis for products supplied under this specification. The sampling procedure selected shall be such that it will yield the most representative sample of the lot being examined.

The chemical composition shall conform to the requirements as prescribed in Table 1. The elements listed in the primary group shall be assumed present at the minimum levels of detection if not detected above these levels. The elements listed in the secondary group shall be assumed to be not present if the element content is below the minimum detection level. The minimum detection levels for the elements listed are to be specified by the manufacturer of the tubing.

TABLE II

Chemical Requirements
Tantalum 99.97% or Higher

Primary Group

Element	Maximum Impurity Level, ppm
O	150
C	50
Fe	50
Mo	50
Nb	200
Si	30
F	10
Cl	10
Al	25
Cr	25
Co	50
H	10
N	50
B	10
S	10

Secondary Group

Element	Maximum Impurity Level, ppm
Na, K, Ca, Bi, Cd, Pb, Pd, Pt, Rh, V, Zn, Li, Sb, Ag	Less than 10 ppm total
Ni	50
Cu	50
Mn	10
Mg	10
Ti	25
Zr	25
W	100

5. Temper

5.1 Tubing covered by this specification shall be in the as drawn, straightened and cleaned condition.

6. Tolerances

6.1 Diameter and wall thickness. The permissible variations in diameter and wall thickness shall not exceed those prescribed in Table II. Out of round conditions shall not exceed .00025 mm in any tubing diameter.

6.2 Length - When tubing is ordered to length, a variation of 3.175 mm - 0" will be permitted up to 152.4 mm, and lengths over 152.4 mm, a variation of + 73.50 mm - o" is acceptable.

6.3 Straightness - Tubes shall be free of bends or kinks and the maximum bow shall not exceed .254 mm per foot or .662 mm in any 662 mm section.

6.4 Quantity - For orders requiring up to 254 cm of finished tubing, the manufacturer may overship by 10%. When the order is for quantities up to 2540 cm, the manufacturer may overship an order by 5%. The permissible overshipment shall be negotiated for orders larger than these quantities.

TABLE II

Permissible Variation in Diameter and Wall Thickness Measured at Any Location (a)

Nominal OD	O.D. Variation ±	I.D. Variation ±	Wall Variation ±
Up to but not incl. 2.388 mm	.025 mm	.001 mm	10%
2.388 mm to but not incl. 4.724 mm	.051 mm	.051 mm	10%
4.724 mm to but not incl. 15.86 mm	.066 mm	.066 mm	10%

(a) Tolerances are applicable to only two dimensions as specified by the procurement document.

7. Quality and Finish

7.1 The finished tubing shall be free from oxide, grease, oil, drawing compounds and other extraneous materials and shall be furnished "thermocouple clean".

The term "thermocouple clean" refers to a level of cleanliness of the I.D. of the tubing which will permit a white lint-free cloth swatch or nylon "butterfly" soaked in acetone, methyl-ethyl ketone or isobutyl ketone to be drawn thru the entire length of the tube and show no discoloration visible to the unveiled eye. Evidence of discoloration shall be cause for rejection.

7.2 Tubes shall exhibit freedom from cracks, seams, slivers, inclusions, blisters, burrs and other imperfections having a depth exceeding 10% of the nominal wall thickness or .025 mm, whichever is greater. For wall thickness from .75 mm to .51 mm the maximum permissible depth is .052 mm.

7.3 When specified on purchase order, tubing shall be tested by applying an internal pneumatic pressure equal to 80% of the pressure calculated for yielding.

7.4 Unless otherwise mutually agreed, inspection to determine conformance with Section 7 of this specification may be limited to ordinary visual inspection at magnification of not less than 10x. In this case, the magnitude of the discontinuity shall be determined by metallographic examination at 100x or higher, or by optical comparator. Alternate methods which can be specified in the order are ultrasonic, eddy current, fluorescent penetrate, dye penetrant and borescopic examination.

8. Sampling

8.1 Samples must be taken from the applicable material to determine conformance to the specification. The samples shall be representative of the finished product.

8.2 Care should be taken to insure that the samples selected for testing are not contaminated by the sample procedure. Sampling techniques and methods for analysis shall be as agreed upon by the manufacturer and the purchaser.

9. Retest

9.1 If any sample or specimen exhibits obvious surface contamination or improper preparation disqualifying it as a truly representative sample, it shall be discarded and a new sample or specimen substituted.

9.2 In case of failure, retest two additional specimens. If both specimens conform to the specification, discard the original values and consider the material acceptable.

9.3 If the inspection results of a lot are not in conformance with the requirements of this specification, the lot may be reworked at the option of the manufacturer. A lot shall be acceptable if results of all tests after reworking conform to the specification.

10. Marking

Each bundle, box or carton shall be legibly and conspicuously marked or tagged with the number of this specification, purchase order number, type, temper, heat or ingot number, nominal size and the gross, net and tare weights.

11. Packaging

Immediately after the last cleaning operation, both tubing ends shall be plugged with suitable caps and packed in such a manner as to insure safe delivery to its destination when properly transported by any common carrier.

12. Reports

If requested, the manufacturer shall supply at least three copies of a report of the chemical analysis of each lot represented in the shipment. The report should include the purchase order number, this specification number and quantity and number of items covered by the shipment.

13. Rejection

Material not conforming to this specification or to authorized modifications shall be subject to rejection. Unless otherwise specified, rejected material may be returned to the manufacturer at the manufacturer's expense unless the purchaser receives within three weeks of notice of rejection other instructions for disposition.

14. Referee

In the event of a disagreement between the manufacturer and the purchases on the conformance of material to the requirements of this specification or any special test specified by the purchaser, the mutually acceptable referee shall perform the test in question. The results of the referee's testing shall be absolute and binding on both parties.

TABLE I

Physical Properties of Alloying Elements Having High Melting Points

Element	Melting Point Deg. C	Crystal Structure	Group in Periodic Table	Structure Outer Electron Shell	Electro Negativity	Atomic Radius Å	Thermal Neutron Capture Cross Section Barns
Tungsten	3410	bcc	V1a	5d.4.2	2.0	1.41	19.2
Rhenium	3180	hcp	V11a	5d.5.2	2.2	1.37	84.0
Osmium	3000	hcp	V111a	5d.6.2	2.0	1.35	14.7
Tantalum	2996	bcc	Va	5d.3.2	1.7	1.47	21.3
Molybdenum	2610	bcc	V1a	4d.5.1	2.1	1.40	2.5
Columbium	2468	bcc	Va	4d.4.1	1.7	1.47	1.1
Iridium	2447	fcc	V111b	5d.7.2	2.1	1.35	430.0
Ruthenium	2310	hcp	V111a	4d.7.1	2.0	1.34	2.46
Hafnium	2222	hcp	1Va	5d.2.2	1.4	1.59	105.0
Boron	2030		111a	2p.1	2.0	.97	755.0
Rhodium	1963	fcc	V111b	4d.8.1	2.1	1.34	150.0
Vanadium	1900	bcc	Va	3d.3.2	1.9	1.36	4.98
Chromium	1875	bcc	V1a	3d.4.2	2.2	1.28	2.9
Zirconium	1852	hcp-bcc	1Va	4d.4.2	1.5	1.60	0.18
Platinum	1772	fcc	V111c	5d.8.2	2.1	1.38	8.1
Thorium	1750	fcc	1Va	6d.2.2	1.4	1.80	7.45
Titanium	1668	hcp-bcc	1Va	3d.2.2	1.6	1.46	5.6
Palladium	1554	fcc	V111c	4d.10	2.0	1.37	8.0

TABLE II

Tungsten-Rhenium Thermocouples

	W Vs W-26%Re	W-3%Re Vs W-25%Re	W-5%Re Vs W-26%Re
Nominal operating temperature range, in:			
Reducing atmosphere (non-hydrogen)	N.R.[a]	N.R.	N.R.
Wet hydrogen	N.R.	N.R.	N.R.
Dry hydrogen	3030K	3030K	3030K
Inert atmosphere	3030K	3030K	3030K
Oxidizing atmosphere	N.R.	N.R.	N.R.
Vacuum[b]	3030K	3030K	3030K
Maximum short-time temperature	3270K	3270K	3270K
Mean, over nominal operating range	16.7/°K	17.1/°K	16.0/°K
At top temperature of normal range	12.1/°K	9.9/°K	8.8/°K
Melting temperature, nominal:			
Positive thermoelement	3680K	3630K	3620K
Negative thermoelement	3393K	3393K	3393K
Stability with thermal cycling	Good	Good	Good
High-temperature tensile properties	Good	Good	Good
Stability under mechanical working	Fair	Fair	Fair
Ductility (of most brittle thermoelement after use)	Poor	Poor to good depending on atmosphere or degree of vacuum	Poor to good depending on atmosphere or degree of vacu
Resistance to handling contamination	Good	Good	Good
Extension wire	Available	Available	Available

a - Not recommended

b - Preferential vaporization of rhenium may occur when bare (unsheathed) couple is used at higher temperatures and high vacuum. Check vapor pressure of rhenium at operating temperature and vacuum before using bare couple.

TABLE III

PROPERTIES OF W-3%Re and W-25%Re

	97%W-3%Re Leg	75%W-25%Re Leg
Nominal Composition, Wt.%Re	3% nominal, remainder doped tungsten	25% nominal, remainder tungsten
Density, 20°C	19.4 gm/cc	19.65 gm/cc
Electrical Resistivity 20°C, microhm-cm	9.7	27.9
Ultimate tensile strength, 25°C, N/m^2 (wire samples)	$1.24 \times 10^8 - 1.38 \times 10^8$	$1.44 \times 10^8 - 1.58 \times 10^8$
Elongation, in 5.08 cm (wire samples), %	10 - 30	15 - 25
Hardness, DPH	321	396
Melting Point, °K	3633	3393

TABLE IV

MASS SPECTROGRAPHIC ANALYSIS OF .0254 cm W/Re WIRE

(ppmw)

Element	As Received		As Surface Cleaned	
	W-3%Re	W-25%Re	W-3%Re	W-25%Re
Li	<0.001	<0.001	<0.001	<0.001
Be	<0.002	<0.002	<0.002	<0.002
B	<0.006	<0.006	0.006	0.006
C	60.	60.	60.(a)	60.(a)
N	1.	3.	0.3(a)	0.3(a)
O	30.	100.	30.(a)	50.(a)
F	0.03	0.03	0.03	0.03
Na	0.3	1.	1.	0.3
Mg	0.4	0.4	0.5	0.4
Al	1.	2.	1.	2.
Si	<4.	10.	10.	10.
P	<0.2	6.	6.	2.
S	0.4	0.6	0.6	0.6
Cl	0.1	0.1	1.	0.2
K	15.	10.	10.	10.
Ca	1.	1.	1.	0.6
Sc	<0.02	<0.02	<0.02	<0.02
Ti	≤1.	≤3.	≤3.	≤3.
V	0.1	0.03	0.03	0.03
Cr	0.3	1.	1.	3.
Mn	0.03	0.2	0.3	0.1
Fe	2.	5.	5.	3.
Co	0.02	0.03	0.02	0.02
Ni	0.2	5.	5.	5.
Cu	<0.03	0.04	0.2	0.04
Zn	<0.1	0.1	0.2	0.1
Ga	<0.2	<0.2	<0.02	<0.2
Ge	<0.04	<0.04	<0.04	<0.04
As	<0.01	0.1	0.1	0.1
Se	<0.03	<0.03	<0.03	<0.03
Br	<0.03	<0.03	<0.03	0.03
Rb	0.03	0.2	0.7	0.3
Sr	<0.02	<0.02	<0.02	<0.02
Y	<0.02	0.03	<0.02	<0.02
Zr (b)	<10.	<10.	<10.	<10.
Nb (b)	<50.	<50.	<50.	<50.
Mo	10.	60.	60.	60.
Ru	<0.2	<0.2	<0.2	<0.2
Rh	<0.05	<0.05	<0.05	<0.05
Pd	<0.2	<0.2	<0.2	<0.2
Ag	<0.1	<0.1	<0.1	<0.1

TABLE IV (Continued)

Element	As Received		As Surface Cleaned	
	W-3%Re	W-25%Re	W-3%Re	W-25%Re
Cd	<0.2	<0.2	<0.2	<0.2
In	<0.06	<0.06	<0.06	<0.06
Sn	<0.2	<0.2	<0.2	<0.2
Sb	<0.1	<0.1	<0.1	<0.1
Te	<0.2	<0.2	<0.2	<0.2
I	<0.06	<0.06	<0.06	<0.06
Cs	<0.06	<0.06	<0.06	<0.06
Ba	<0.1	<0.1	<0.1	<0.1
La	<0.06	<0.06	<0.06	<0.06
Ce	<0.06	<0.06	<0.06	<0.06
Pr	<0.06	<0.06	<0.06	<0.06
Nd	<0.2	<0.2	<0.2	<0.2
Sm	<0.2	<0.2	<0.2	<0.2
Eu	<0.2	<0.2	<0.2	<0.2
Gd	<0.3	<0.3	<0.3	<0.3
Tb	<0.1	<0.1	<0.1	<0.1
Dy	<0.3	<0.3	<0.3	<0.3
Ho	<0.1	<0.1	<0.1	<0.1
Er	<0.3	<0.3	<0.3	<0.3
Tm	<0.1	<0.1	<0.1	<0.1
Yb	<0.3	<0.3	<0.3	<0.3
Lu	<0.1	<0.1	<0.1	<0.1
Hf	<0.2	<0.2	<0.2	<0.2
Ta (c)	2.	2.	1.	0.5
Os	<0.2	<0.2	<0.2	<0.2
Ir	<0.2	<0.2	<0.2	<0.2
Pt (b)	<4.	<4.	<4.	<4.
Au (b)	<2.	<2.	<2.	<2.
Hg (b)	<5.	<5.	<5.	<5.
Tl	<0.1	<0.04	<0.04	<0.04
Pb	<0.6	0.6	1.	1.
Bi	≤0.1	≤0.2	≤0.2	≤0.3
Th	<0.1	<0.1	<0.1	<0.1
U	<0.1	<0.1	<0.1	<0.1

(a) Samples baked overnight.
(b) Interference - see text.
(c) Possible contamination from Ta electrode holders.
(<) The "less than" symbol indicates that the element was not seen. The value following is the detection limit at the time of the analysis.

TABLE V

VACUUM FUSION, COMBUSTION AND KJELDAHL ANALYSIS OF W/Re

(ppmw)

Sample	Oxygen	Hydrogen	Nitrogen	Carbon
W-25%Re Surface Cleaned	80	<1	30 (<10)*	10
W-3%Re Surface Cleaned	30	<1	5 (<10)	10

*Kjeldahl determination in parentheses.

TABLE VI

MASS SPECTROGRAPHIC ANALYSIS OF W/Re STRANDED THERMOCOUPLE WIRES

(ppmw)

Element	Surface Cleaned		Element	Surface Cleaned	
	W-25%Re	W-3%Re		W-25%Re	W-3%Re
Li	0.04	0.04	Rh	<0.06	<0.06
Be	0.02	0.02	Pd	<0.2	<0.2
B	0.02	0.06	Ag	<0.04	<0.04
C	140.	70.	Cd	<0.1	<0.1
N	2.	2.	In	<0.2	<0.2
O	50.	30.	Sn	<0.07	<0.07
F	0.03	<0.03	Sb	1.	<0.04
Na	10.	3.	Te	<0.1	<0.1
Mg	6.	2.	I	<0.02	<0.02
Al	4.	3.	Cs	<0.02	<0.02
Si	20.	6.	Ba	<0.1	<0.03
P	5.	0.06	La	2.	<0.03
S	2.	1.	Ce	2.	<0.03
Cl	2.	1.	Pr	0.3	<0.03
K	30.	60.	Nd	1.	<0.1
Ca	4.	2.	Sm	<0.1	<0.1
Sc	<0.1	<0.1	Eu	<0.06	<0.06
Ti (a)	<10.	<4.	Gd	<0.1	<0.1
V	0.5	0.3	Tb	<0.03	<0.03
Cr	6.	3.	Dy	<0.1	<0.1
Mn	0.6	0.03	Ho	<0.03	<0.03
Fe	20.	20.	Er	<0.1	<0.1
Co	0.05	0.05	Tm	<0.03	<0.03
Ni	6.	1.	Yb	<0.1	<0.1
Cu	1.	0.05	Lu	<0.03	<0.03
Zn	<0.1	<0.2	Hf	<0.1	<0.1
Ga	<0.2	<0.02	Ta	5.	2.
Ge	<0.04	<0.04	W	-	-
As	0.5	<0.01	Re	-	-
Se	<0.1	<0.03	Os	<0.1	<0.1
Br	<0.1	<0.03	Ir	<0.2	<0.05
Rb	1.	0.1	Pt (c)	<3.	<10.
Sr	<0.05	<0.05	Au (d)	<3.	<1.
Y	0.3	0.1	Hg	<0.04	<2.
Zr	<10. (b)	<10. (b)	Ti	<0.1	<0.1
Nb	(b)	(b)	Pb	<0.6	<0.6
Mo	100.	70.	Bi	<0.1	<0.3
Ru	<0.06	<0.06	Th	<0.04	<0.1
			U	<0.04	<0.1

(a) Interference from Mo^{+n}
(b) Interference from W^{+n}
(c) Interference from WC^{+}
(d) Memory from previous samples
(e) Interference from WO^{+} and photoplate fog

TABLE VII

ELECTRON MICROPROBE EXAMINATION OF W-Re ALLOY THERMOCOUPLE WIRES

	W-3%Re				W-25%Re			
	0.0076 cm dia. SC	.025 cm dia. SC	.0076 cm dia. AR	.025 cm dia. AR	.025 cm dia. SC	.025 cm dia. AR	.0076 cm dia. SC	.025 cm dia. AR
Contaminants	R-1	R-2	R-7	R-10	R-3	R-6	R-8	R-9
C General Area	1%	1.5%	1%	1%	1.5%	3%	1.5%	1%
C Particles	1(M)	6(M)	6(M L)	2(L)	5(M L)	8(H M)	2(M L)	4(M)
Fe Particles	3(H M L)	3(M L)	2(L)	3(M L)	1(L)	10(H M L)	4(M L)	4(H M)
Cr Particles	-	2(L)	-	2(L)	-	3(M L)	2(L)	3(M L)
Ni Particles	1(M)	3(L)	-	3(L)	-	5(M L)	2(L)	2(L)
Zr & Ti	-	-	-	-	-	-	-	-
Si	X		X	X	X	X		
Al	X		X					
Ca							X	
Cl							X	

H - High content in particle (50%)*
M - Moderate content in particle (10-50%)*
L - Low content in particle (10%)*
* - The values are given to permit a relative comparison and are only estimates and are not to be considered quantitative.
X - Particles detected during the scanning for the 6 primarily interesting contaminants. No particular attention was paid to the scanning of Si, Al, Ca and Cl.
SC - Surface cleaned.
AR - As received.

TABLE VIII

ELECTRON MICROPROBE EXAMINATION OF W-Re STRANDED THERMOCOUPLE WIRES

Contaminants	W-3%Re Surface Cleaned	W-25%Re Surface Cleaned
C General Area	0.5%*	1.5%*
C Particles	Neg.	Neg.
Fe Particles	Neg.	3(M L)
Cr Particles	Neg.	Neg.
Ni Particles	Neg.	1(L)
Si Particles	Neg.	3(H M L)

H - High content in particle (50%)*
M - Moderate content in particle (10-50%)*
L - Low content in particle (10%)*
Neg. - Practically negative.
* - The values are given to permit a relative comparison and are only roughtly estimated due to the reason stated in the text. Do not consider the percentage figures as quantitative results.

TABLE IX

PROPERTIES OF W-Re WIRES

W-3%Re, .0076 cm diameter (nominal)	
As received	3.1×10^9 N/m^2
Ultimate Tensile Strength (UTS)	(450,000 psi)
% Elongation, (5.08 cm gage length)(2")	1
Microhardness, DPH, longitudinal sec.	700
After cleaning, annealing, stranding, recleaning and	1.38×10^9 N/m^2
vacuum processing	(200,000 psi)
UTS (one strand)	
% Elongation (5.08 cm gage length)(2")	18
Microhardness, DPH, longitudinal sec.	500
transverse sec.	515
W-25%Re, .0076 cm diameter (nominal)	
As received	2.77×10^9 N/m^2
UTS	(402,000 psi)
% Elongation (5.08 cm gage length)(2")	1
Microhardness, DPH, longitudinal sec.	795
After cleaning, annealing, stranding, recleaning and	
vacuum processing	1.23×10^9 N/m^2
UTS (one strand)	(197,000 psi)
% Elongation (5.08 cm gage length)(2")	4
Microhardness, DPH, longitudinal sec.	475
transverse sec.	480
W-3%Re, .0254 cm diameter (nominal)	
As received	2.46×10^9 N/m^2
UTS	(356,000 psi)
% Elongation, (5.08 cm gage length)(2")	4
Microhardness, DPH, longitudinal sec.	700
After cleaning, annealing and vacuum processing	1.45×10^9 N/m^2
UTS	(210,000 psi)
% Elongation (5.08 cm gage length)(2")	26
Microhardness, DPT, longitudinal sec.	400
transverse sec.	410
W-25%Re, .0254 cm diameter (nominal)	
As received	1.84×10^9 N/m^2
UTS	(267,000 psi)
% Elongation, (5.08 cm gage length)(2")	21
Microhardness, DPT longitudinal sec.	510
After cleaning, annealing and vacuum processing	1.64×10^9 N/m^2
UTS	(238,000 psi)
% Elongation, (5.08 cm gage length)(2")	12
Microhardness, DPH, longitudinal sec.	450
transverse sec.	465

Notes:

1. UTS and % elongation determined in Instron Tensile Tester, Model TM-1. Cross head speed was .508 cm per minute. The average of three tests is reported.
2. Microhardness tests were performed on a Tukon, Model M. A 100 gram load was used. The average of five indentations, randomly selected on the mounted specimen, is reported.

TABLE X

SOLIDS MASS SPECTROGRAPHIC ANALYSIS
TANTALUM TUBING

	As Received	Surface Cleaned	Vacuum Processed
H		*2.5	* 0.5
Li	0.01	<0.004	<0.004
Be	0.02	<0.005	<0.005
B	0.2	0.6	0.006
C	200.0	*70.	*7.
N	80.0	*9.	*6.
O	100.0	*180.	*110.
F	0.1	3.	3.
Na	1.0	<1. (T)	1.
Mg	0.2	0.4	0.4
Al	0.4	0.6	2.0
Si	5.	20.0	20.0
P	<0.5	≤0.6	≤0.6
S	0.6	2.	1.0
Cl	1.0	0.6	0.6
K	1.	2.	1.0
Ca	0.1	0.2	0.6
Sc	<0.01	<0.1	<0.1
Ti	<1.	<10.	<10.
V	0.2	0.6	0.6
Cr	0.3	1.	3.
Mn	0.03	0.1	0.1
Fe	3.0	15.	15.
Co	0.01	0.06	0.2
Ni	1.0	5.	2.
Cu	2.0	4.	1.
Zn	0.04	<0.07	<0.07
Ga	<0.02	<0.02	<0.02
Ge	<0.04	<0.04	<0.04
As	<0.01	<0.01	<0.01
Se	<0.02	<0.03	<0.03
Br	<0.02	<0.03	<0.03
Rb	<0.03	<0.03	<0.03
Sr	<0.02	<0.06	<0.06
Y	0.2	0.4	0.4
Zr	<1.0	<3.	<3.
Nb	80.0	200.	200.
Mo	20.	100.	100.
Ru	<0.2	<0.6	<0.6
Rh	<0.06	<0.2	<0.2
Pd	<0.2	<0.2	<0.2
Ag	<0.1	<0.1	<0.2
Cd	<0.2	<0.07	<0.07
In	<0.06	<0.02	<0.02
Sn	<0.2	<0.07	<0.07
Sb	<0.1	<0.04	<0.04
Te	<0.02	<0.07	<0.07
I	<0.01	<0.2	<0.2
Cs	<0.01	<0.02	<0.03
Ba	<0.03	<0.04	<0.04
La	<0.02	<0.03	<0.03
Ce	<0.02	<0.03	<0.03
Pr	<0.02	<0.03	<0.03
Nd	<0.1	<0.1	<0.1
Sm	<0.1	<0.1	<0.1
Eu	<0.06	<0.06	<0.06
Gd	<0.1	<0.1	<0.1
Tb	<0.03	<0.03	<0.03
Dy	<0.1	<0.1	<0.1
Ho	<0.03	<0.03	<0.03
Er	<0.1	<0.1	<0.1
Tm	<0.03	<0.03	<0.03
Yb	<0.1	<0.1	<0.1
Lu	<0.03	<0.03	<0.03
Hf	<0.3	<0.1	<0.1
W	200.	60.	60.
Re	0.3	0.2	0.6
Os	<0.2	<0.07	<0.07
Ir	<0.2	<0.1	<0.1
Pt	<1.	<1.	<1.
Au	<2.	-	-
Hg	<0.1	<0.3	<0.3
Tl	<0.05	<0.2	<0.2
Pb	<0.2	<0.2	<0.2
Bi	<0.04	<0.1	<0.1
Th	<0.04	<0.04	<0.04
U	<0.04	<0.04	<0.04

Note: Results indicated by an asterisk were determined by chemical means.

Combustion - carbon
Kjeldahl - nitrogen
Vacuum fusion - hydrogen, oxygen

TABLE XI

MECHANICAL PROPERTIES OF TANTALUM TUBING

TENSILE STRENGTH

Table Model Instron
Model TM-L

Cross Head Speed: .508 cm (2 inches) per min.
Three Samples

Ta annealed at 2363K

UTS 1.58 X 10^8 N/m^2 (23,000 psi)
Yield Strength, .2% offset (21,000 psi) 1.45 X 10^8 N/m^2
% elongation, 5.08 cm (2") gage length 23-26%

Ta annealed at 2073K

UTS 1.93 X 10^8 N/m^2 (28,000 psi) 1.51 X 10^8 N/m^2
Yield Strength, .2% offset (22,000 psi)
% elongation, 5.08 cm (2") gage length 16-20%

MICRO-HARDNESS TESTS

Tukon - Model "M"
.1 kilogram (100 gram) load

Ta annealed at 2363K

DPH	82

Ta annealed at 2073K

DPH	101

TABLE XII

COMPOSITION OF Ta TUBING Ta-Sc
Surface Cleaned

At Dept of .0076 cm From Outer Surface

Element	PPM By Weight
H	1
B	20
C	180
N	60
O	340
F	50
Na	0.06
Mg	0.6
Al	2
Si	30
Cl	120
K	0.01
Ti	0.2
V	6
Cr	2
Mn	0.9
Fe	20
Ni	20
Cu	7
Y	3
Zr	10
Mo	10
Nb	560
Ta	Balance

TABLE XIII

COMPOSITION OF Ta TUBING TA-AV
Vacuum Annealed to 2073K

Element	PPM By Weight
H	0.1
B	<5
C	30
N	80
O	190
F	10
Na	0.03
Al	0.15
Si	1
Cl	40
K	0.003
Ti	0.2
V	2
Cr	10
Mn	3
Fe	60
Ni	13
Y	10
Zr	5
Mo	6
Nb	500
Ta	Balance

TABLE XIV

Mass Spectrographic, Vacuum Fusion Combustion, and Kjeldahl Analysis of W-22%Re (ppmw)

Element	Sample Designation		Element	Sample Designation	
	WR-VP	WR-AR		WR-VP	WR-AR
H (a)	0.4	0.4	Ru	<0.06	<0.06
Li	0.1	0.005	Rh	<0.02	<0.06
Be	<0.05	<0.2	Pd	<0.2	<0.2
B	0.1	0.1	Ag	≤0.06	<0.1
C (a)	6.	6.	Cd	<0.07	<0.2
N (a)	10.	10.	In	<0.02	<0.02
O (a)	18.	38.	Sn	<0.07	<0.07
F	30.	3.	Sb	<0.05	<0.05
Na	1.	2.	Te	<0.1	<0.1
Mg	0.4	1.	I	<0.02	≤0.02
Al	15.	5.	Cs	<0.02	<0.02
Si	50.	15.	Ba	<0.03	<0.03
P	<2.	<0.6	La	<0.03	<0.03
S	2.	1.	Ce	<0.03	<0.03
Cl	3.	3.	Pr	<0.03	<0.03
K	0.6	2.	Nd	<0.1	<0.1
Ca	1	1	Sm	<0.1	<0.1
Sc	<0.03	<0.03	Eu	<0.06	<0.06
Ti	0.3	0.1	Gd	<0.1	<0.1
V	<0.03	<0.03	Tb	<0.03	<0.03
Cr	1.	1.	Dy	<0.1	<0.1
Mn	0.2	0.2	Ho	<0.03	<0.03
Fe	20.	20.	Er	<0.1	<0.1
Co	0.03	<0.03	Ym	<0.03	<0.03
Ni	0.5	0.5	Yb	<0.1	<0.1
Cu	0.7	0.7	Lu	<0.03	<0.03
Zn	≤0.1	≤0.1	Hf	<0.1	<0.1
Ga	<0.1	<0.1	Ta	2.	2.
Ge	<0.1	<0.1	Re (c)	20.2%	19.0%
As	<0.04	<0.04	Os	<0.1	<0.1
Se	<0.1	<0.1	Ir	<0.05	<0.05
Br	<0.1	<0.1	Pt (d)	<1.	<10.
Rb	<0.02	<0.02	Au (d)	<1.	<2.
Sr	<0.02	<0.02	Hg (d)	<5.	<5.
Y	0.1	<0.1	Tl	<0.4	<0.2
Zr	<3.	<3.	Pb	<1.	≤2.
Nb	(b)	(b)	Bi	<0.3	<1.
Mo	≤0.2	≤0.2	Th	<0.04	<0.04
			U	<0.04	<0.04

(a) Determined by classical methods.
(b) Interference from W^{+n} ions.
(c) See text for description of technique.
(d) Interference from matrix complexes.

Code: VP - Vacuum Processed
AR - As Received

TABLE XV

THERMOCOUPLE SUMMARY

Code No.	Sheath	Wire	Insulation	Environment	Lead Color[1]	Tie Color[2]	Flag Color[3]	O_2 Content[4]
TS-1	Ta	Solid	S-11	Argon	White	Black	Orange	5.8 ppm
TS-2	"	"	"	"	"	"	"	"
TS-3	"	"	"	"	"	"	"	"
TS-4	"	"	"	"	"	"	"	"
TH-1	"	"	CF-1 HIGH	"	"	White	"	1.8 ppm
TH-2	"	"	"	"	"	"	"	"
TH-3	"	"	"	"	"	"	"	"
TH-4	"	"	"	"	"	"	"	"
TL-1	"	"	CF-1 LOW	"	"	Bk-Wt-Bk	"	2.2 ppm
TL-2	"	"	"	"	"	"	"	"
TL-3	"	"	"	"	"	"	"	"
TL-4	"	"	"	"	"	"	"	"
TC-1	"	"	Commercial I	"	Wt-Bk	White	Yellow	7.0 ppm
TC-2	"	"	"	"	"	"	"	"
TC-3	"	"	"	"	"	"	"	"
WL-1	W22-Re	"	CF-1 LOW	"	White	"	Grey	2.2 ppm
WL-2	"	"	"	"	"	"	"	28.0 ppm
TS-1XA	Ta	"	S-11	Air Exposed	"	Black	"	300 ppm
TS-1-XS	"	Stranded	"	Argon	Red	"	Orange	15 ppm
TS-2-XS	"	"	"	"	"	"	"	"
TS-3-XS	"	"	"	"	"	"	"	"
TN-1-XA	"	Solid	Commercial II	Air Exposed	Black	White	Orange	15 ppm
TC-1XA R	"	"	Commercial I	"	White	"	Yellow	7.0 ppm

Notes: (1) Color of spaghetti insulation on T/C wires
(2) Color of plastic over jacket
(3) Color of "Label-on" marker
(4) Glove Box oxygen content at time of making last braze

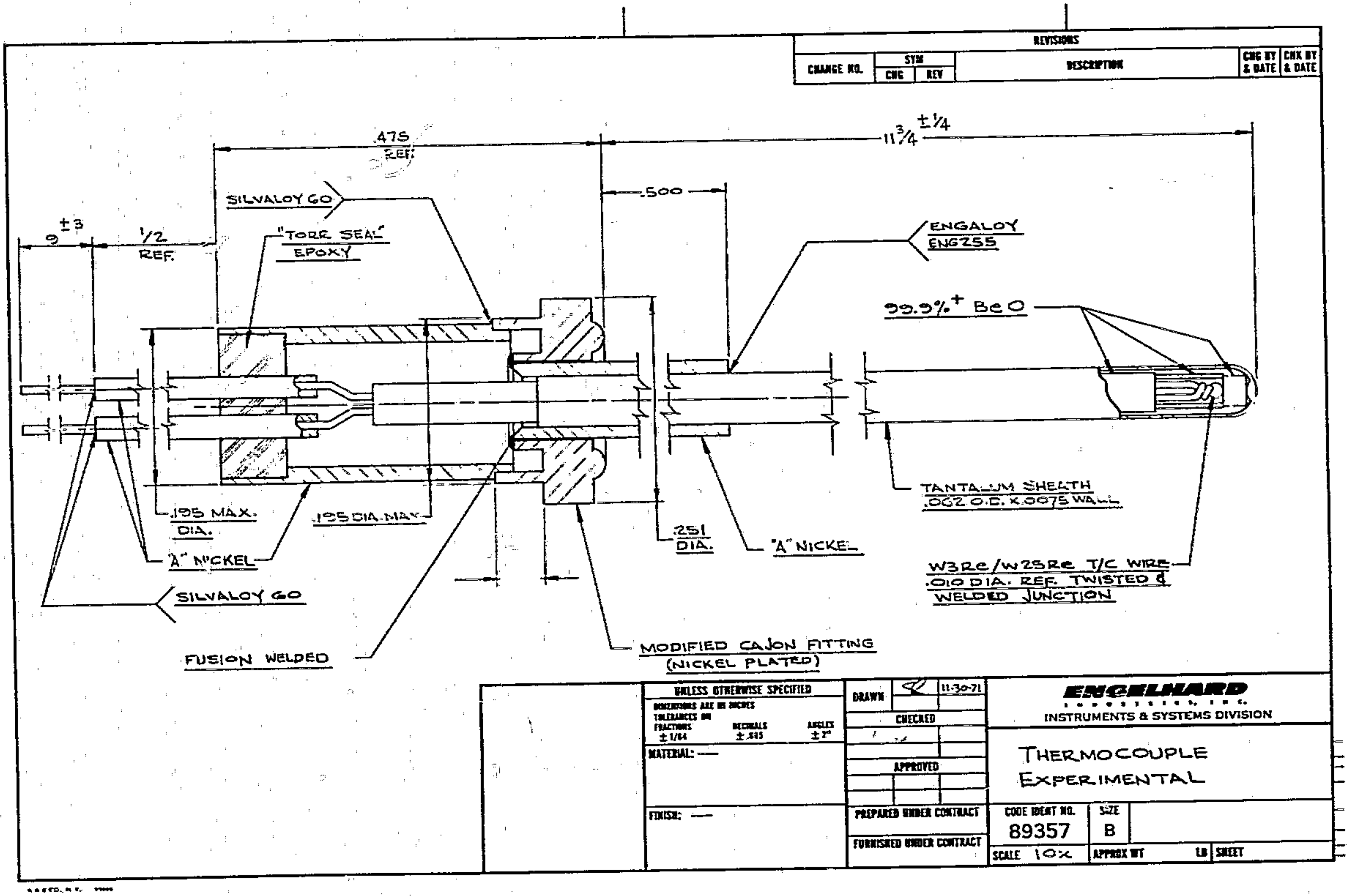

FIGURE 1

Thermocouple Model Drawing

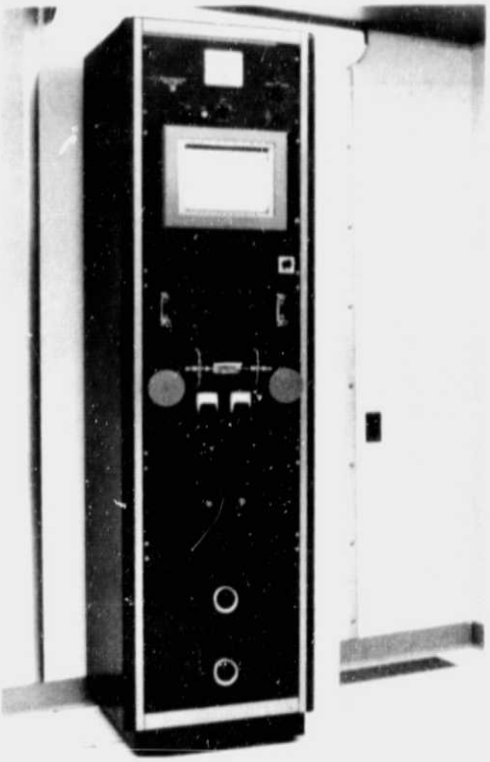

FIGURE 2
Wire Homogeneity Test Facility

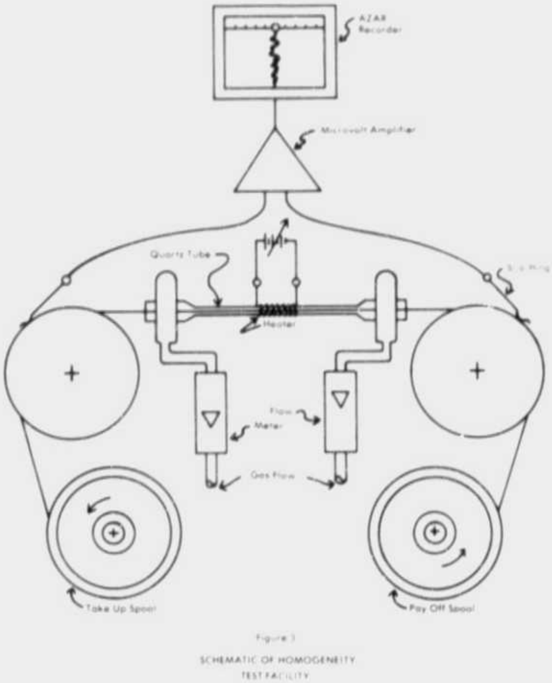

FIGURE 3
Wire Homogeneity Circuit Schematic

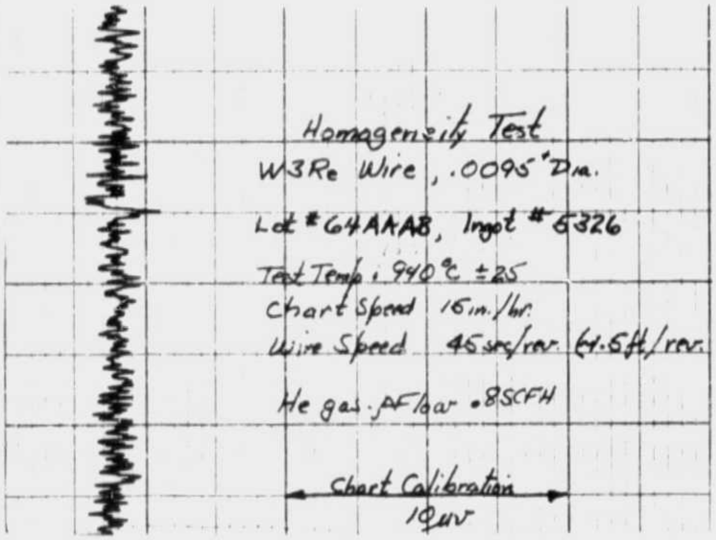

FIGURE 4a
Homogeneity Test Signal, W3Re Wire

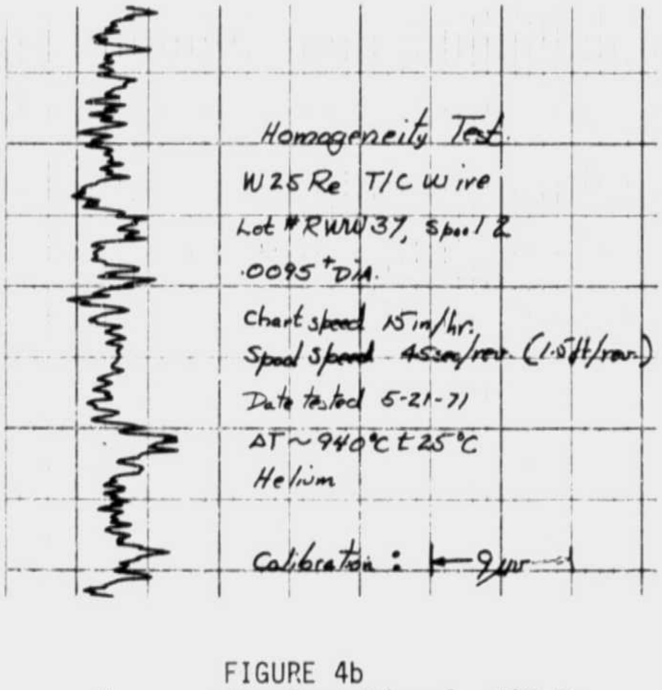

FIGURE 4b
Homogeneity Test Signal, W25 Re Wire

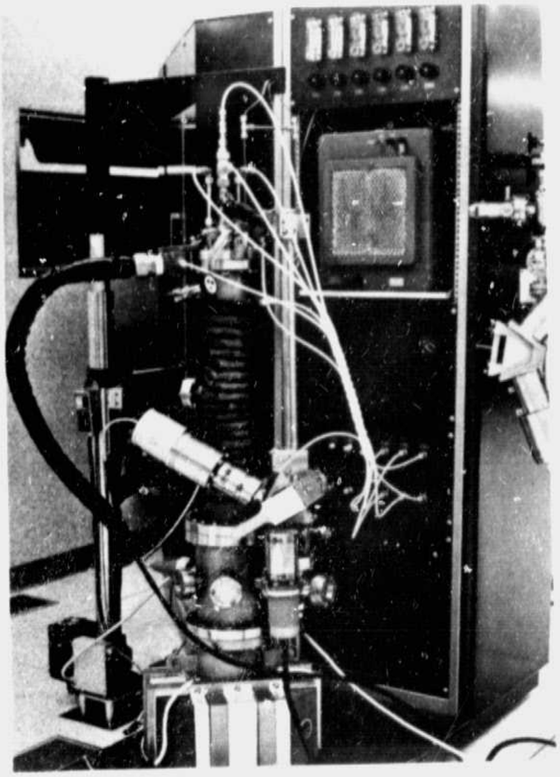

FIGURE 5
Wire and Sheath Vacuum Degassing Chamber

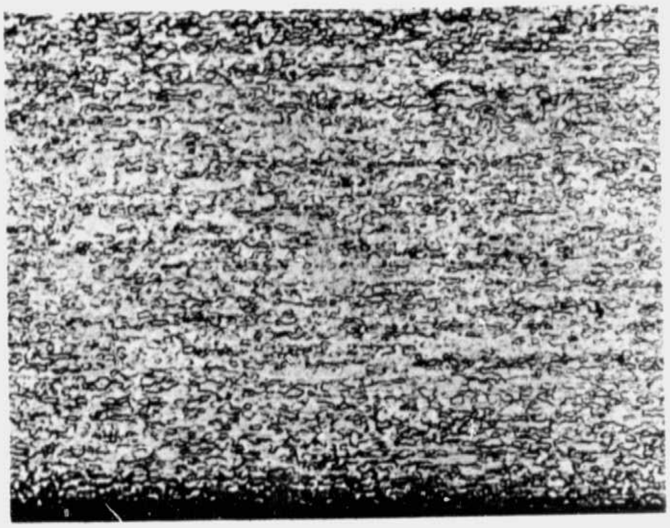

FIGURE 6
W25Re Wire .0254 cm dia.
Longitudinal Section,
As Received Condition
500X

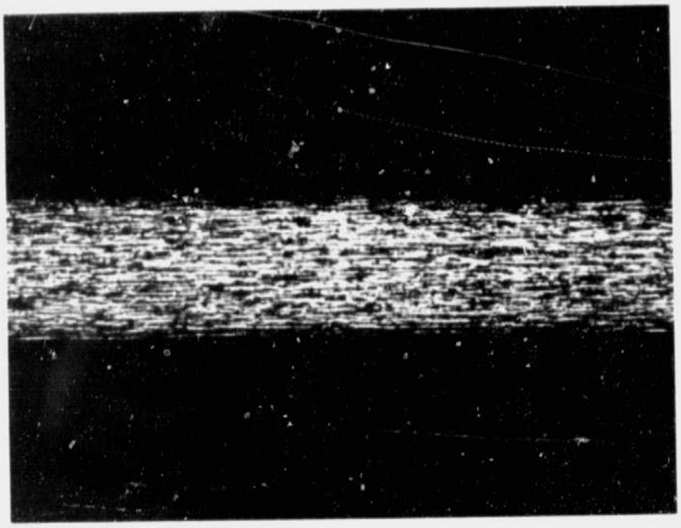

FIGURE 7
W25Re Wire .0076 cm dia.
Longitudinal Section,
As Received Condition
500X

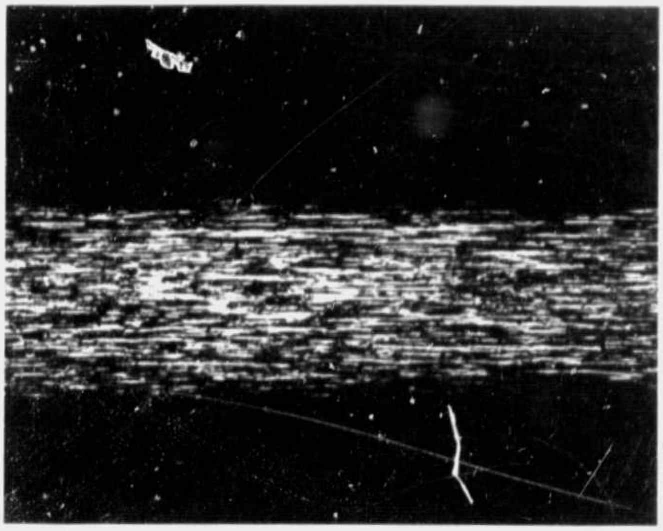

FIGURE 8
W3Re Wire .0076 cm dia.
Longitudinal Section
As Received Condition
500X

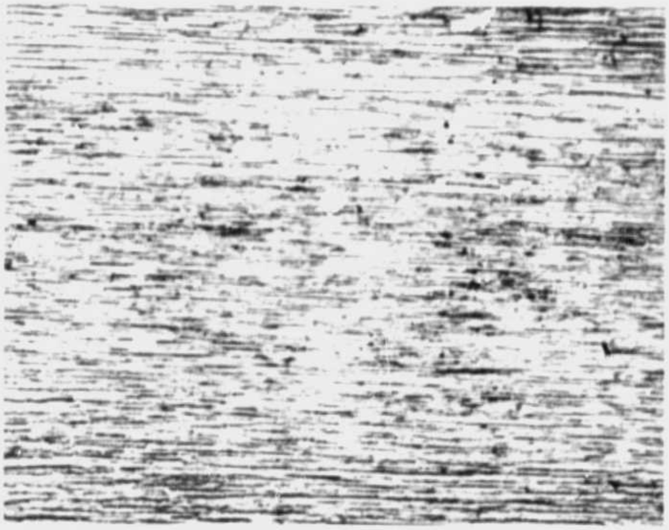

FIGURE 9
W3Re Wire .0254 cm dia.
Longitudinal Section
As REceived Condition
500X

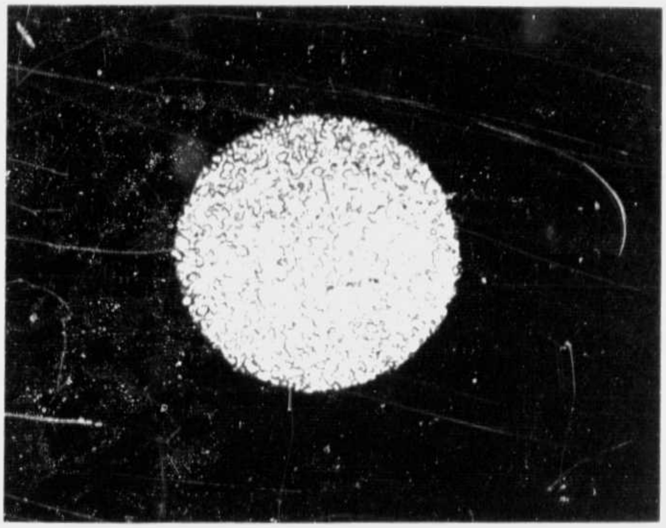

FIGURE 10
W3Re Wire .0254 cm dia.
Transverse Section
Annealed Condition
200X

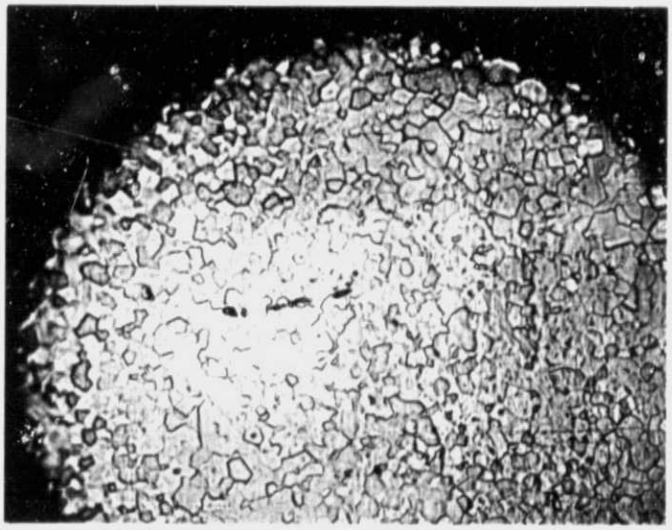

FIGURE 11
W3Re Wire .0254 cm dia.
Transverse Section
Annealed Condition
500X

FIGURE 12
W3Re Wire .0254 cm dia.
Longitudinal Section
Annealed Condition
200X

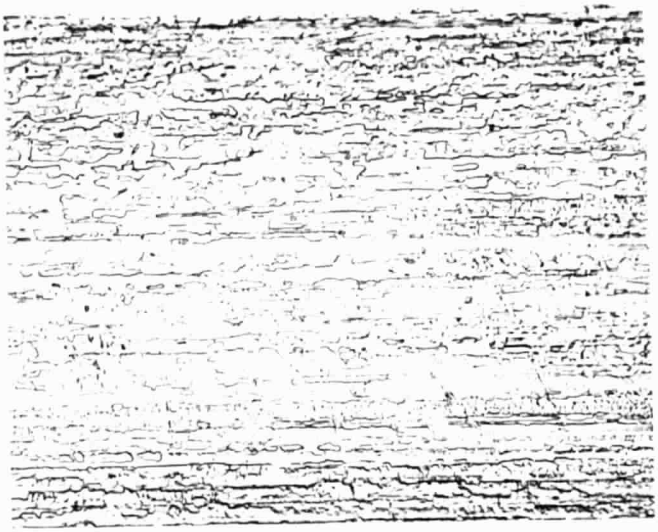

FIGURE 13
W3Re Wire .0254 cm dia.
Longitudinal Section
Annealed Condition
500X

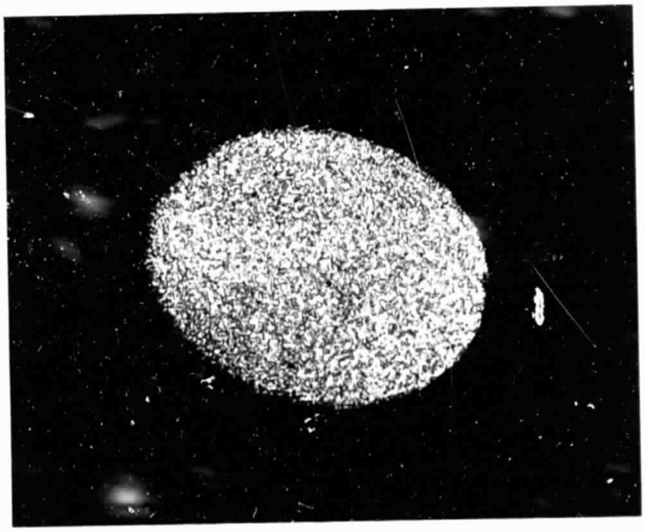

FIGURE 14
W25Re Wire .0254 cm dia.
Transverse Section
Annealed Condition
200X
(Ovality due to sample mounting)

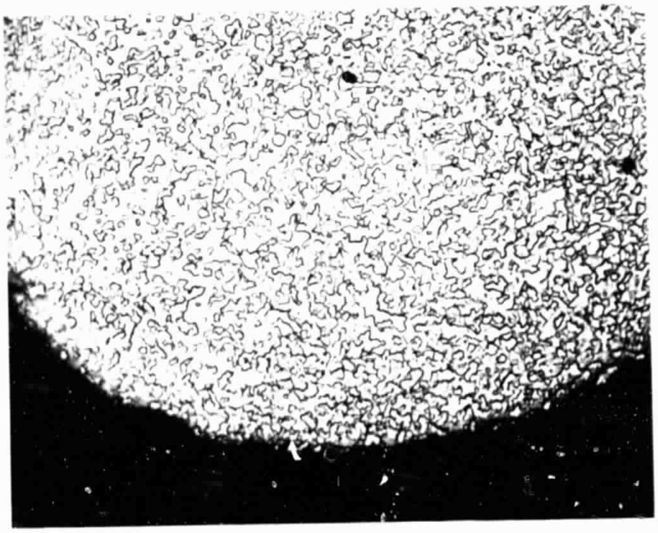

FIGURE 15
W25 Re Wire .0254 cm dia.
Transverse Section
Annealed Condition
500X

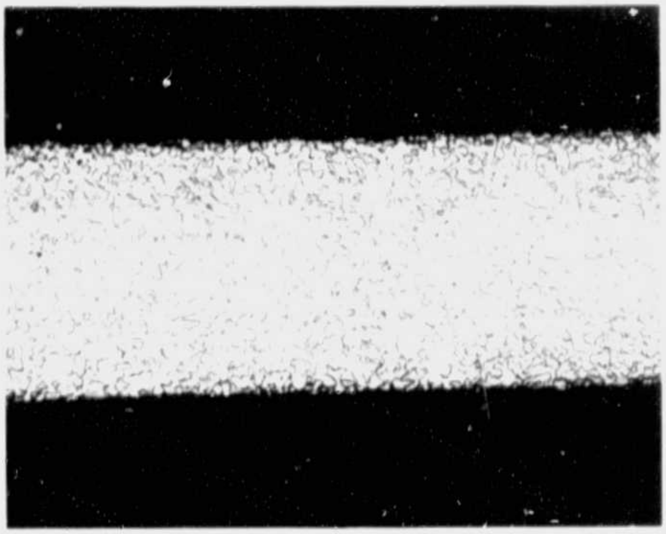

FIGURE 16
W25Re Wire .0254 cm dia.
Longitudinal Section
Annealed Condition
200X

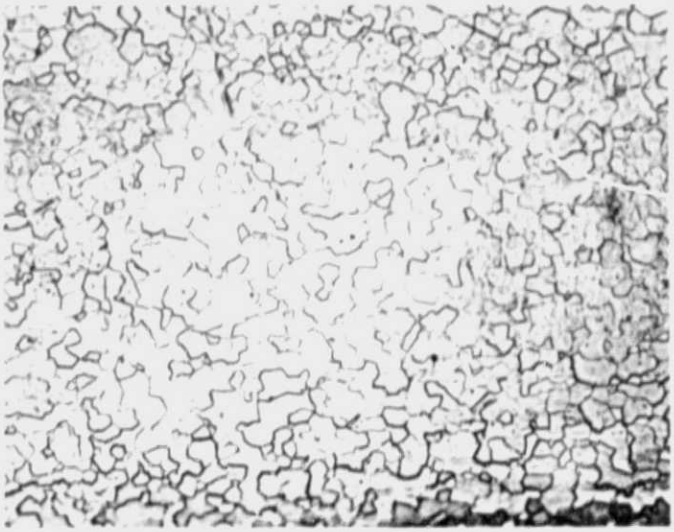

FIGURE 17
W25Re Wire .0254 cm dia.
Longitudinal Section
Annealed Condition
500X

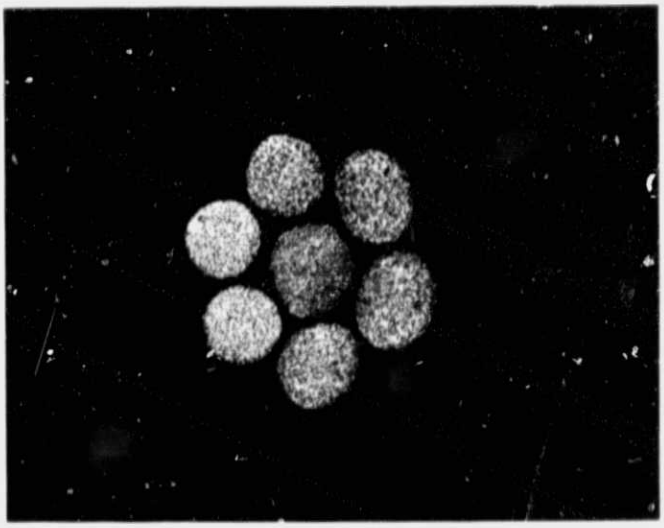

FIGURE 18
W3Re 7-Strand Wire .0254 cm nominal dia.
Transverse Section
Annealed Condition
200X

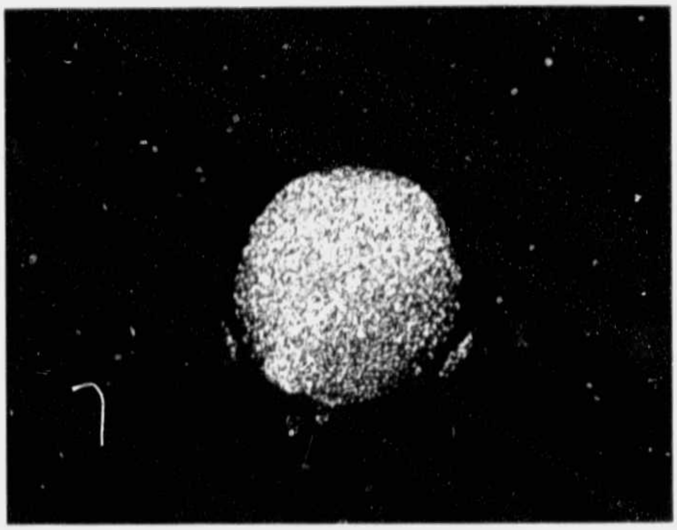

FIGURE 19
W3Re 1-Strand Wire .0254 cm nominal dia.
Transverse Section
Annealed Condition
500X

FIGURE 20
W3Re 7-Strand Wire .0254 cm nominal dia.
Longitudinal Section
Annealed Condition
200X

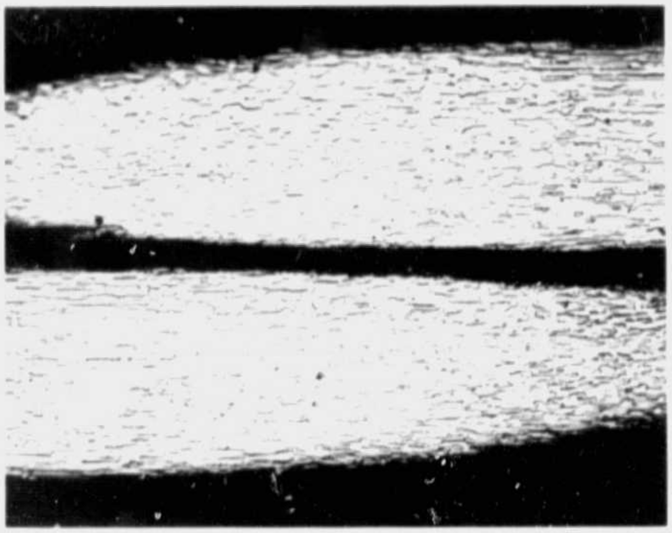

FIGURE 21
W3Re 7-Strand Wire .0254 cm nominal dia.
Longitudinal Section
Annealed Condition
500X

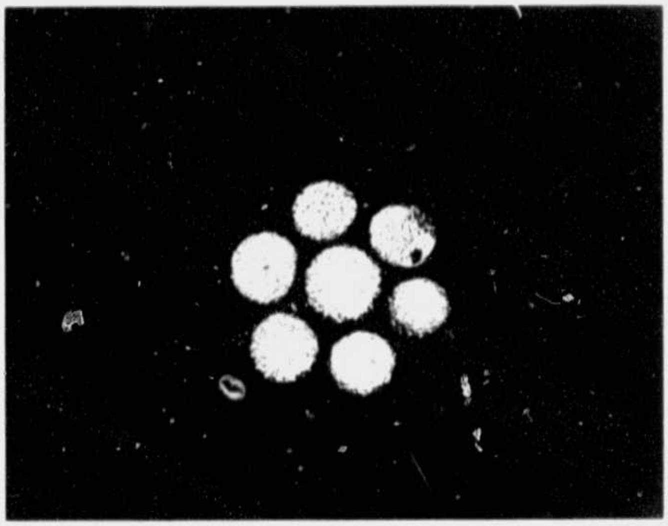

FIGURE 22
W25Re 7-Strand Wire .0254 cm nominal dia.
Transverse Section
Annealed Condition
200X

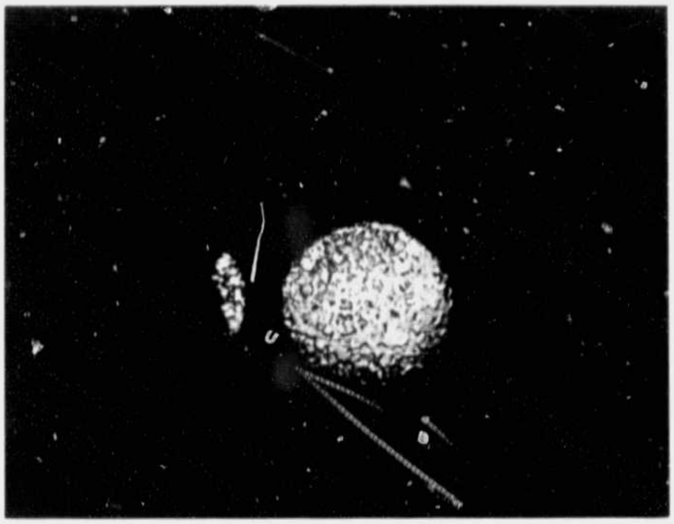

FIGURE 23
W25 Re 7-Strand Wire .0254 cm nominal dia.
Transverse Section
Annealed Condition
500X

FIGURE 24
W25Re 7-Strand Wire .0254 cm nominal dia.
Longitudinal Section
Annealed Condition
200X

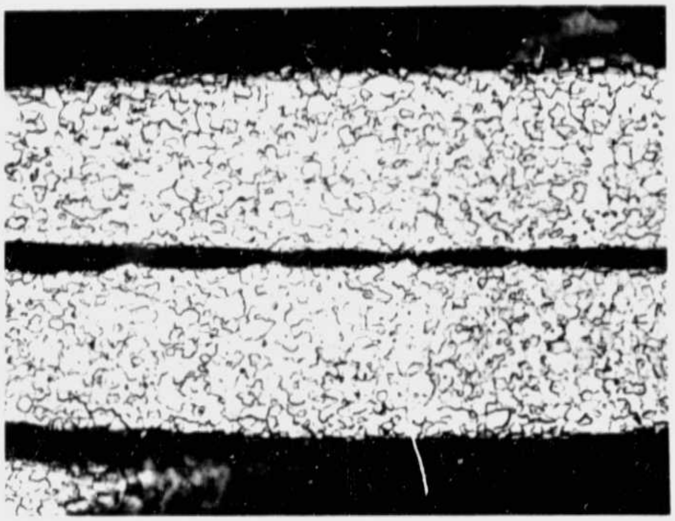

FIGURE 25
W25Re 7-Strand Wire .0[illegible]4 cm nominal dia.
Longitudinal Section
Annealed Condition
500X

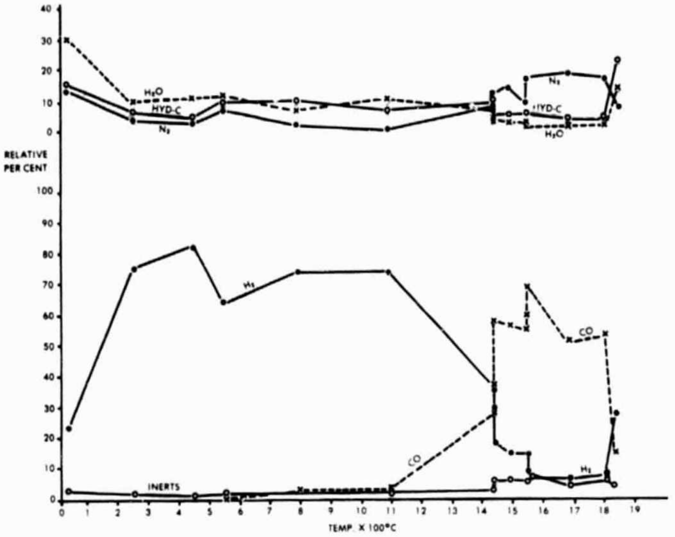

FIGURE 26
Outgassing Constituents of Tantalum Sheath
Processed at 2110K (~1835°C)

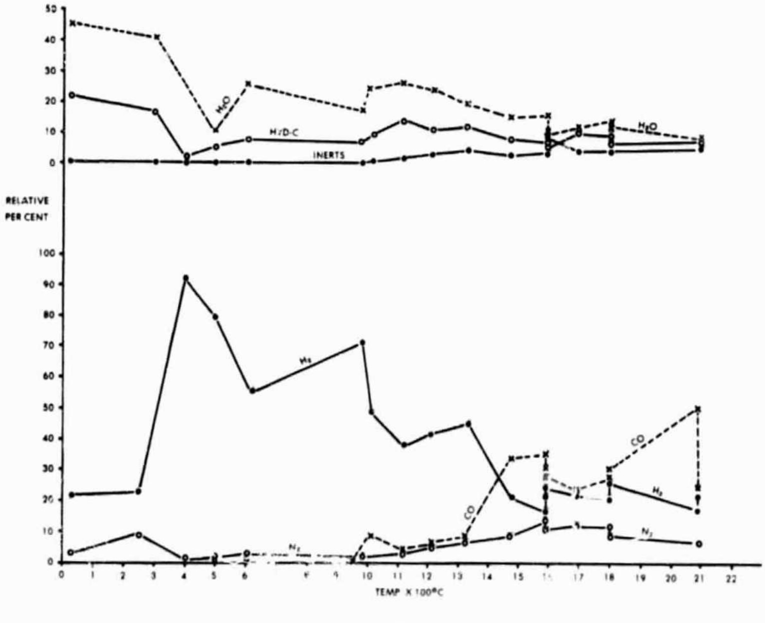

FIGURE 27
Outgassing Constituents of Tantalum Sheath
Processed at 2360K (~2090°C)

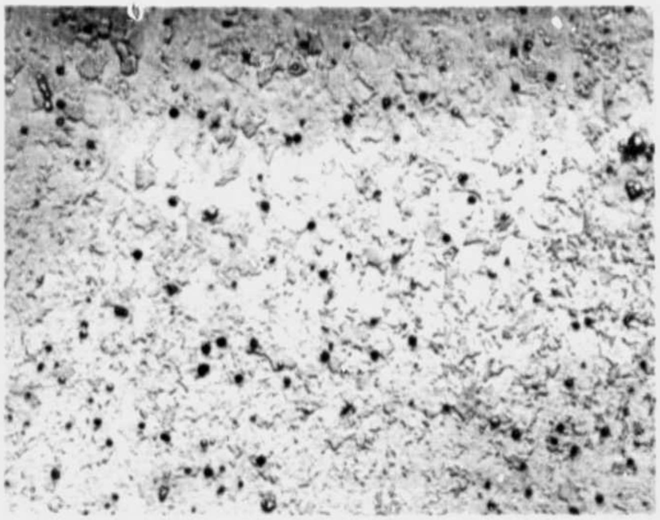

FIGURE 28
Tantalum Tubing
As Received Condition
Transverse Section
500 X

FIGURE 29
Tantalum Tubing
As Received Condition
Longitudinal Section
500X

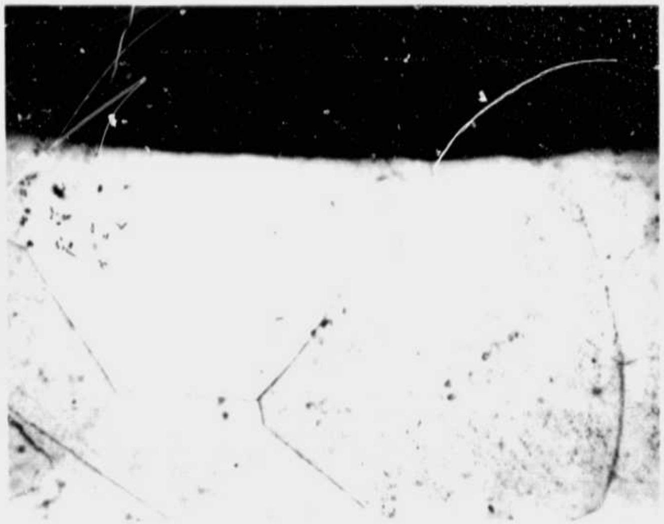

FIGURE 30
Tantalum Tubing
Vacuum Processed Condition at 2110K
Transverse Section
ASTM Grain Size #2 DPH 101
500X

FIGURE 31
Tantalum Tubing
Vacuum Processed Condition at 2110K
Longitudinal Section
ASTM Grain Size #2 DPH 101
500X

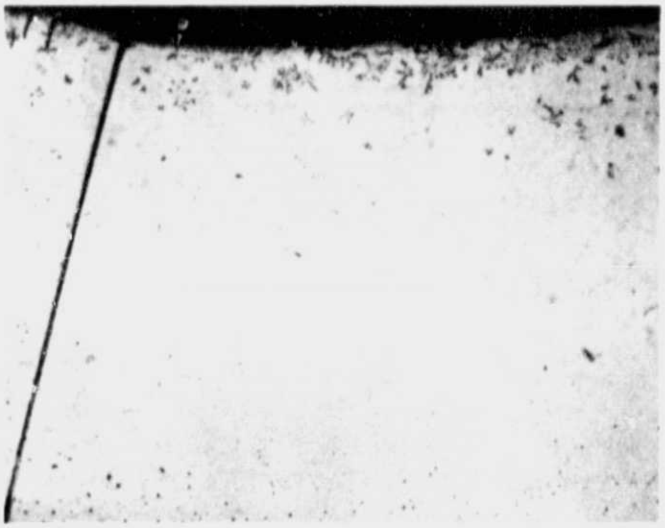

FIGURE 32
Tantalum Tubing
Vacuum Processed Condition at 2360K
Transverse Section
ASTM Grain Size #1 DPH 82
500X

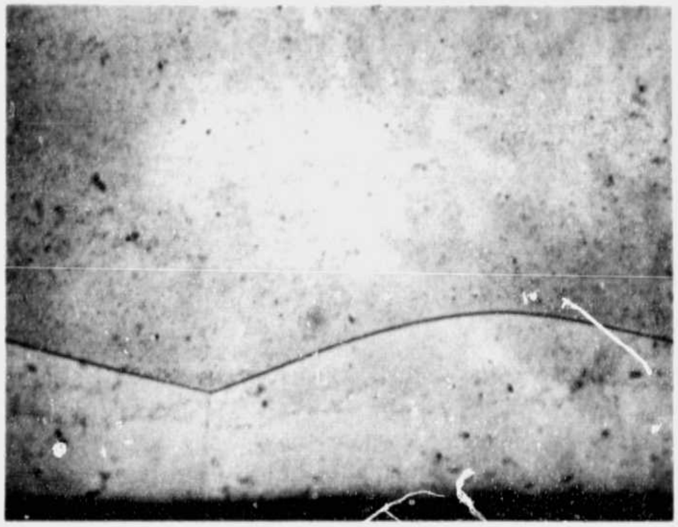

FIGURE 33
Tantalum Tubing
Vacuum Processed Condition at 2360K
Longitudinal SEction
ASTM Grain Size #1 DPH 82
500X

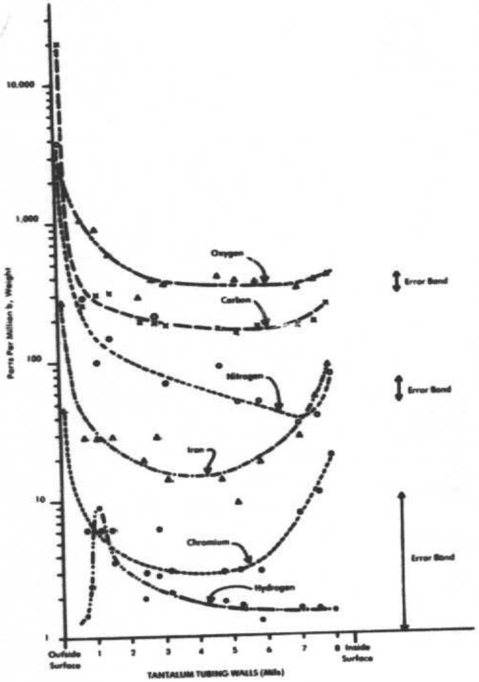

FIGURE 34
Impurity Distribution, Tantalum Tubing
Surface Cleaned Condition

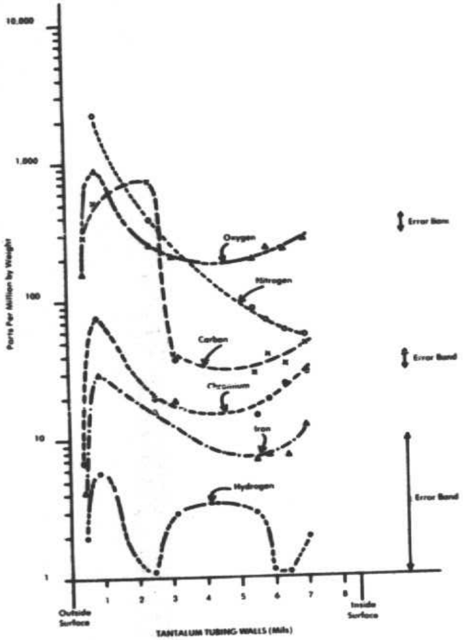

FIGURE 35
Impurity Distribution, Tantalum Tubing
Vacuum Degassed Condition

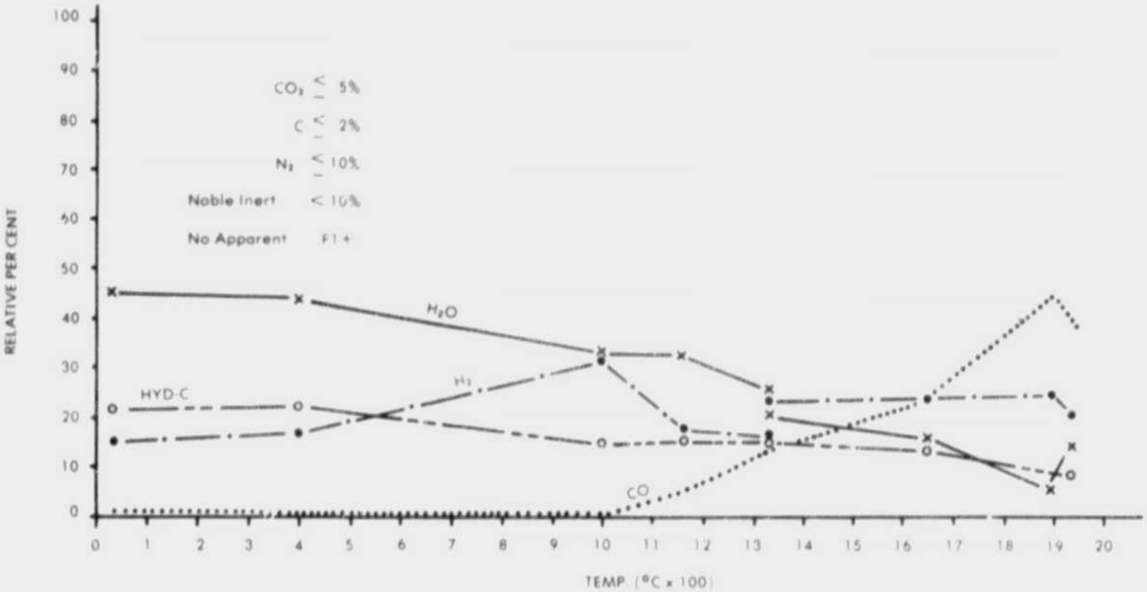

FIGURE 36
Outgassing Constituents of W22%Re Tubing

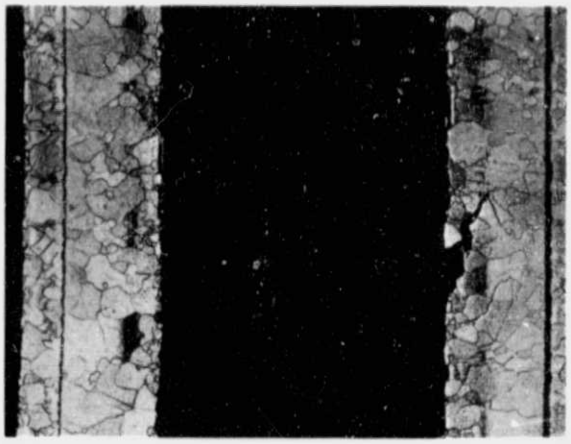

FIGURE 37
W22Re Tubing
As Received Condition
Longitudinal Section
100X

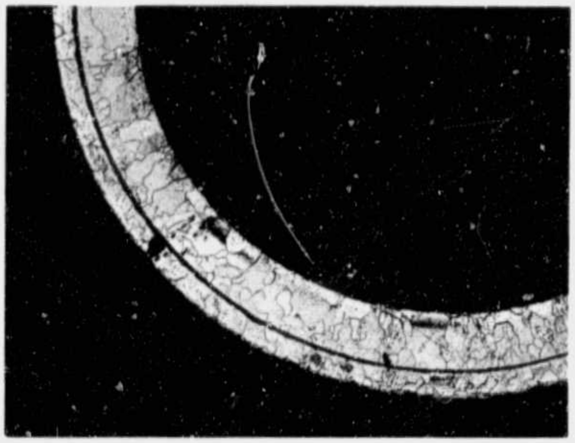

FIGURE 38
W22Re Tubing
As Received Condition
Transverse Section
100X

FIGURE 39
W22Re Tubing
Vacuum Processed at 2200K
Transverse Section
100X

FIGURE 40
W22Re Tubing
Vacuum Processed at 2200K
Longitudinal Section
ASTM Grain Size 5, 6 & 7

FIGURE 41
W22Re Tubing
Vacuum Processed at 2200K
2000X, Oblique Lighting
To Show Rhenium Rich Band

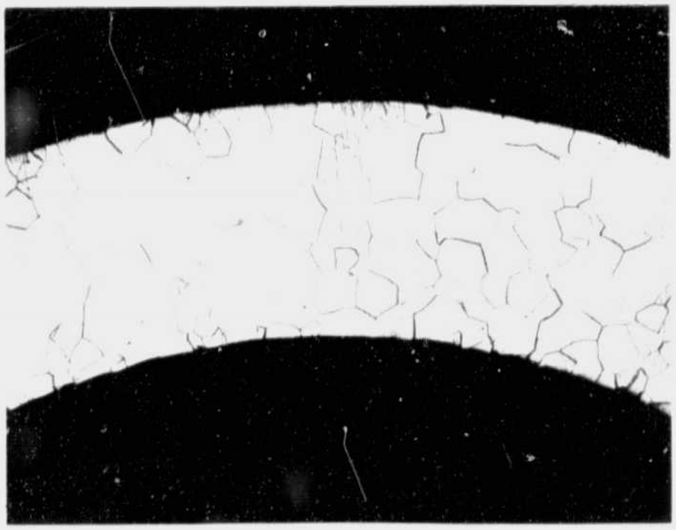

FIGURE 42
W22Re Tubing Used in
Probe WL-1
Transverse Section
200X

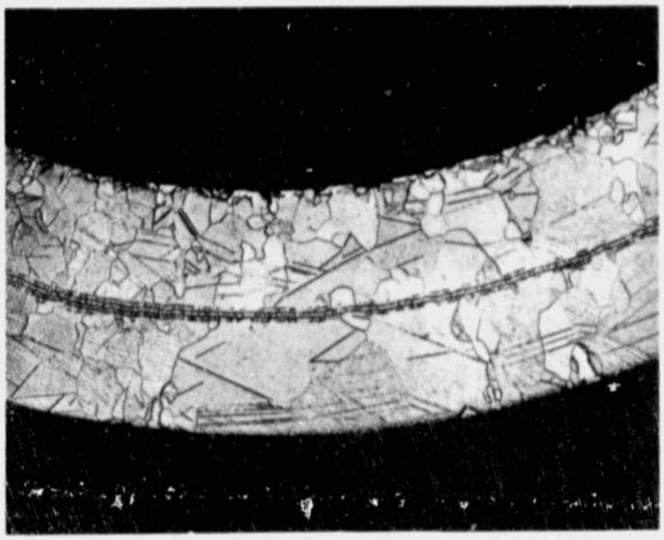

FIGURE 43
W22Re Tubing Used in Probe
WL-2
Transverse Section
200X

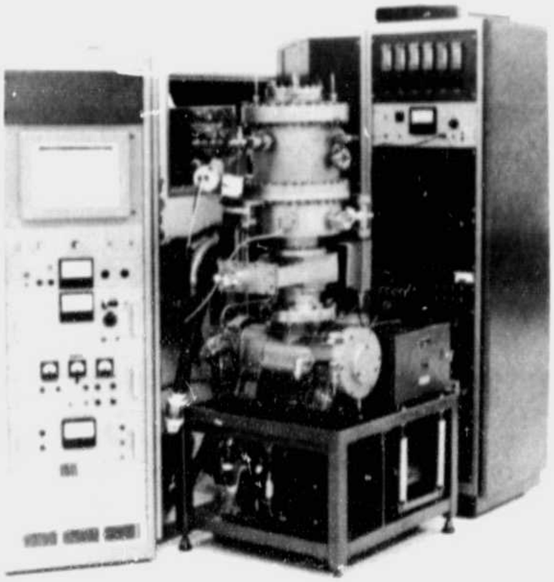

FIGURE 44
Main Vacuum Process Chamber

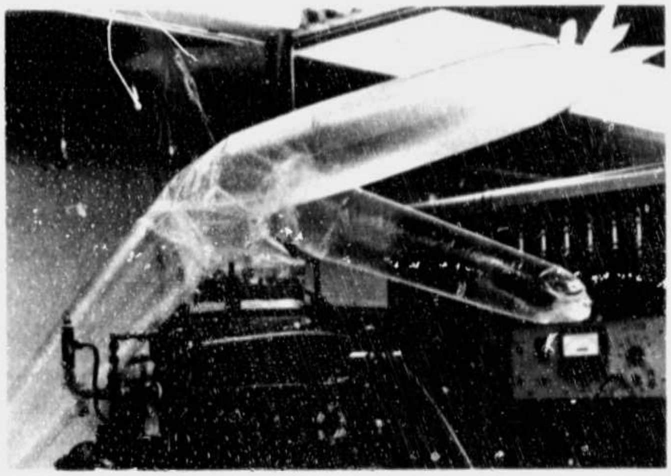

FIGURE 45
Polyethylene Bag Attached to
Process Chamber and Inflated In
Preparation for Component Transport

FIGURE 46
Thermocouple Assembly
Glove Box

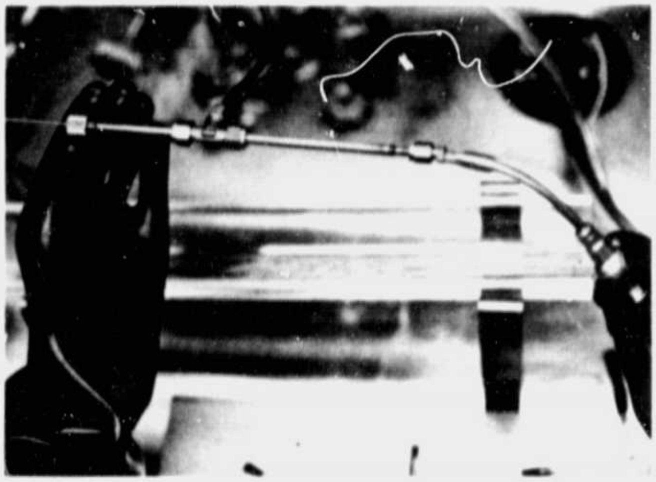

FIGURE 47
Helium Leak Testing Inside
Glove Box

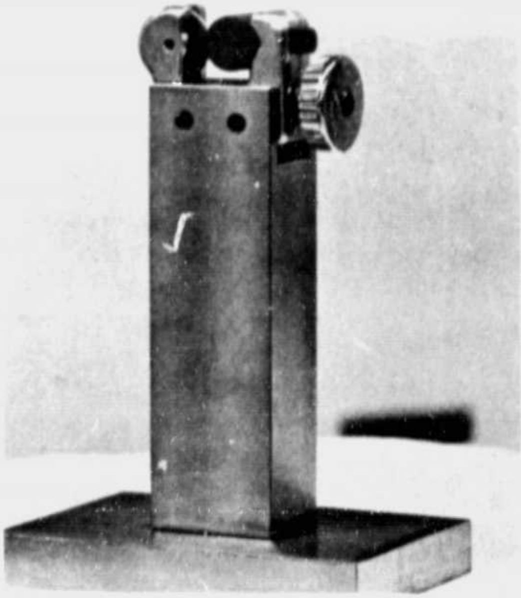

FIGURE 48
Modified Tubing Cutter for
Tantalum Sheaths

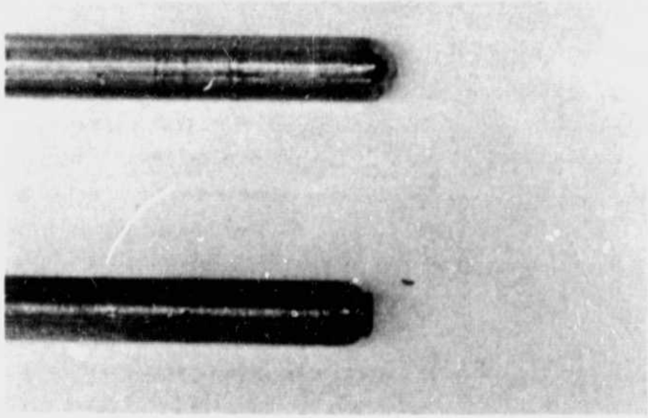

FIGURE 49
Tantalum Tubing as Cut and
as Fusion Welded

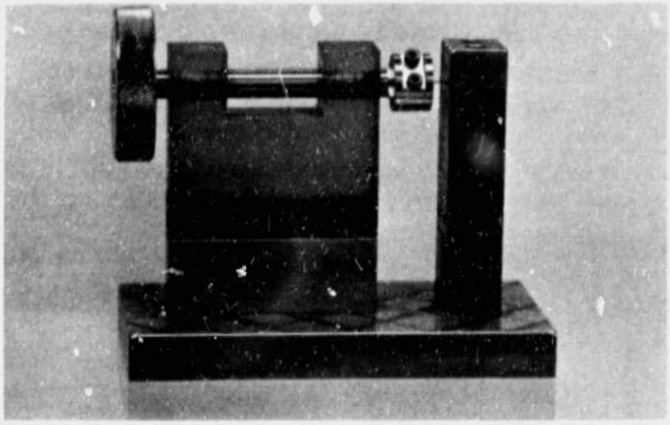

FIGURE 50
Jig for Forming Twisted
Wire Junctions

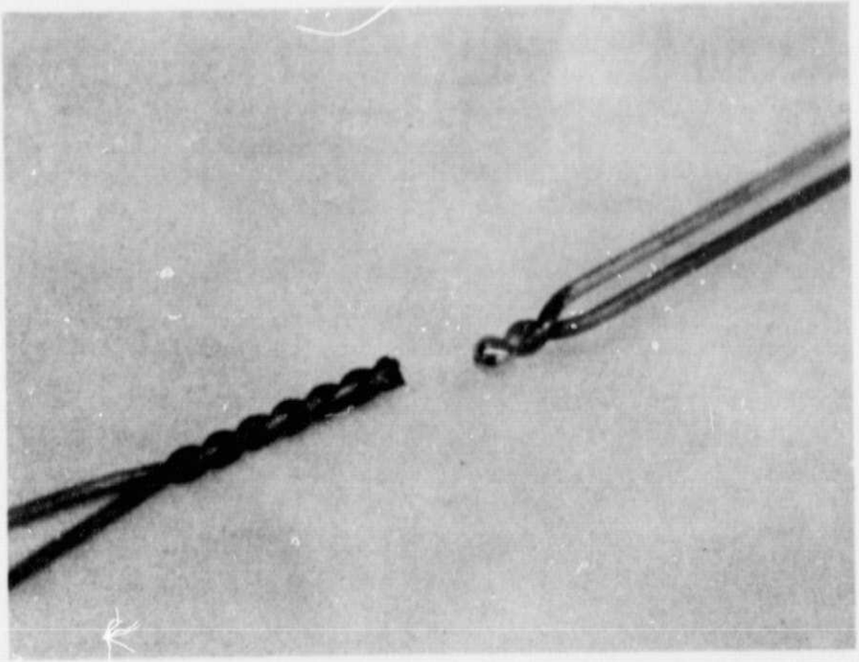

FIGURE 51
Twisted Wire and Junctions

PART B

DEVELOPMENT OF ULTRA HIGH PURITY BERYLLIUM OXIDE THERMOCOUPLE INSULATORS

NATIONAL BERYLLIA CORPORATION

ON SUBCONTRACT TO

ENGELHARD INDUSTRIES

UNDER NASA CONTRACT NAS 3-10950

INTRODUCTION

A ceramic insulator for thermocouple application is required to be electrically and chemically stable at elevated use temperatures. Beryllium oxide, by virtue of strong ionic bonding and a tightly packed lattice structure, has proven to be an excellent ceramic material for this application. Many thermocouple programs have shown that of all insulating materials, beryllia creates the least high temperature electrical drift and is also the most compatible material in contact with metallic thermocouple elements.

Failure modes related to the usage of beryllia as high temperature thermocouple insulation have been attributed to the detrimental effects of impurity ions. Impurity ions may diffuse through the beryllia structure at high temperatures and can cause EMF drifting and preferential chemical attack upon the metallic thermocouple wires. The nature and extent of these deleterious effects are strongly dependent upon the character of the migrating ion. The more active smaller ions can lead to failure while the larger impurity ions may become entrapped within the structure and cause little concern.

Prior to this study, attention was not directed toward identifying the amount or character of the impurities present. Since the present state-of-the-art high purity beryllia was only 99.5% pure, a wide spectrum of impurity elements could be found within the structure. Likewise, the reliability of this insulation was highly dependent upon its containing low levels of active impurity ions.

The objective of this effort was the development of a fabrication technique for preparing ultra high purity beryllium oxide thermocouple insulation for usage in improved, reliable thermocouples capable of operating at extremely elevated temperatures. To satisfy this objective, insulators must be prepared that contain less than 500 parts per million total impurities, exhibit a density in excess of 95% theoretical value, possess high strength, and be capable of being formed to exacting dimensional tolerances.

This research program was divided into four major areas: a raw material characterization study to determine the impurity content and physical characteristics of the beryllium oxide powder utilized in the program; a processing and fabrication study to examine selective milling conditions, binder systems, mixing techniques, extrusion parameters and drying methods that are effective in producing the desired end results yet do not introduce high impurity levels; a firing study to determine optimum firing temperatures, atmospheres, and times that yield high density, high purity, beryllia insulators; and finally, the actual fabrication of the insulators to be supplied to Engelhard Industries.

EXPERIMENTAL PROGRAM

Raw Material Characterization

A. Chemical Analysis

Kawecki-Beryllco High Purity
S-11 Beryllia Powder
Lot No. 521-68-22

A quantitative spectrographic analysis was performed by Ledoux and Co., Teaneck, N. J., utilizing standards developed on an Air Force Standards program (AF33 (6615(-2408). Ledoux and Co. has determined from standards that there is a ±15% accuracy associated with this type analysis. The analytical results are reported in Table I. As can be seen, only 36 ppm metallic impurities were detected in two test samples of this raw material. The limits of detection for the non-detected elements are presented in Table IV.

The anionic impurity analyses, reported in Table II, was performed by the Kawecki-Beryllco Corporation in their analytical laboratory. These anionic impurities are volatile at temperature and atmospheric conditions of firing; thus, the total anionic impurity content should be significantly reduced when analyzed in the fired ceramic.

This lot of beryllia powder was considered to be of sufficiently high purity to be utilized in this program. Insulators prepared using this raw material will be identified by the Code S-11.

NKG Insulators, Ltd. High Purity CF-1 Grade
Beryllia Powder, Lot Number 44-18

Quantitative spectrographic and wet chemical analyses were performed by Ledoux and Co. on a representative sample taken from the total lot utilizing Air Force developed standards. The impurity analysis of the CF-1 powder is reported in Table III. The limits of detection for the non-detected elements are presented in Table IV. As can be seen, 198 ppm metallic impurities were detected. The anionic impurities, while of relatively high value, are considered to be volatile during firing and the value should be significantly reduced in the fired ceramic.

This lot of beryllia powder was considered to be of sufficiently high purity to be utilized in this program. Insulators prepared using this raw material will be identified by the code CF-1.

B. Detection Limits

The detection limits for the quantitative spectrographic analysis performed by Ledoux and Co. are presented in Table IV. These limits will be utilized for determining the assumed state impurity levels.

C. Surface Area

Surface area measurements were performed by Coors Spectro-Chemical Laboratory, Golden, Colorado, on a representative sample taken from each lot. Surface area was determined by Brunauer, Emmet and Teiller gas absorption techniques. The samples were degassed at 833K for sixteen hours under vacuum to prepare the surface for analysis.

The Kawecki-Beryllco S-11 beryllia powder (Lot Number 521-68-1-22) possessed a mean specific surface of 9.2 m^2/gm. The NGK-CF-1 beryllia powder (Lot Number 44-18) possessed a mean specific surface of 19.8 m^2/gm. The surface area measurements were stated to be ± 10% accurate.

D. Average Particle Size

An average particle size determination was performed on a representative sample of the beryllia powders using sedimentation techniques and standard MSA* equipment. Dried powder samples were dispersed in a carbon tetrachloride/ mineral oil/sodium petro-sulfonate liquid solution. A sample of dispersed powder was sedimentated in a carbon tetrachloride/sodium petro-sulfonate settling liquid by centrifical means. Standardized centrifute speeds and times were incorporated to obtain particle size fractions.

The average measured particle size for the Kawecki-Beryllco beryllia powder (Lot Number 521-68-1-22) was 1.89 microns. The average particle size for the NGK-CF-1 powder (Lot 44-18) was measured to be 1.0[illegible] microns. There was no sedimentation noted for particles in excess of 4 microns. The MSA particle size determinzations possess an accuracy of ± 10%.

Since the powders used in this program are extremely fine, the measured values of average particle size are in reality a measure of average agglomerate size. This number then would be related to electrostatic surface charges and particle packing rather than ultimate particle size.

D. Loss on Drying

A loss on drying test was performed on a representative powder sample to determine the percentage of surface attached water associated with the beryllia powders. The test consisted of heating .1 kilograms of powder in a porcelain crucible to 368 K in a laboratory dryer for twelve hours and measuring the weight loss on an analytical balance.

The amount of surface attached water for the Kawecki-Beryllco S-11 beryllia powder was measured to be 0.16 percent. Lot Number 44-18 of the CF-1 powder possessed 0.13 percent moisture. The test is determined to possess an accuracy of ± 5%.

E. Bulk Density

Bulk density measurements were performed on a representative sample of the beryllia powders by weighing 1 X $10^{-4}m^3$ of powder placed in a graduated cylinder. The S-11 powder possessed a bulk density of 130 Kg/m^3 and CF-1 Lot 44-18 powder had a bulk density of 210 Kg/m^3. The test was determined to posses an accuracy of ± 10%.

F. Electron Microscopy

The electron microscopic examination was performed by the Instrumental Analysis Laboratory of Engelhard Industries.

a. Sample Preparation - The beryllia powder sample was ultrasonically mixed into etyl alcohol. A drop of the beryllia-alcohol mixture was then placed on an electron microscope grid and the alcohol was allowed to evaporate. The

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*Mine Safety Appliance Company

powder was carbon shadowed by vacuum evaporation and introduced into the electron microscope.

b. Kawecki-Beryllco S-11 Beryllia Powder
Lot Number 521-68-22

Figures 1 and 2 are electron micrographis of the S-11 beryllia powder magnified 12,960 and 108,000 times. The sample appeared to consist of small beryllia particles which measured from 0.05 microns to 0.3 microns in diameter. Many different shaped particles are seen and no generalizations can be made concerning the shape.

These small particles clumped together form agglomerates 1.0 to 2.0 microns in diameter. This number was verified by particle size analysis. From the electron micrographs, it can readily be seen that these are loosely packed agglomerates. This would explain the low bulk density values obtained.

c. NGK Insulators CF-1 Beryllia Powder
Lot Number 44-18

Figures 3 and 4 are electron micrographs of the CF-1 powder magnified 12,100 and 112,320 times. The smaller particles in this sample are generally hexagonal in shape and are very thin. The size of the platelets ranged from 0.2 microns to 0.5 microns in diameter. Agglomeration in loosely packed clusters of 1.0 to 2.0 microns in diameter is also observed for this powder.

PROCESSING STUDIES

Introduction

The intent of this processing study is to prepare ultra-high purity beryllia insulators exhibiting high fired densities. This necessitates utilizing an effective forming process that minimizes impurity introduction. To maintain high purity during processing, a reverse flow clean air work station was purchased from Clean Room Products, Inc., Farmingdale, New York, for this program. This unit was specified to meet or exceed requirements described in Sections 40.3, 50.3, 70.4.1 of Federal Standard 209. The continuous duty ball bearing centrifugal blower contained is capable of generating a maximum air flow of 30.05 meters per minute. A 99.97% HEPA filter was incorporated in the station to entrap toxic particles.

The simplest and most straight forward approach to high purity fabrication is the elimination of as many impurity producing processing steps as possible. With this philosophy, the initial fabrication tests in this program entailed the hand mixing of a Methocel* binder solution into the S-11 beryllia powder and then extruding the resultant mixture.

A 3% Methocel solution was hand mixed into the S-11 powder in a polyethylene container using plastic tools. The solution was added in quantities to realize a 45% moisture level. The extrusion mix was extruded at 140.6 Kg/cm^2 through a .00152 m diameter orifice in a stainless steel laboratory extruder using carbide tooling. The extruded rods were rolled on a flat plexiglas plate and then covered with spectrographically pure graphite to control the

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*Methocel HG. Hydroxypropyl Methylcellulose. Dow Chemical Company

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drying rate. The dried rods were then hung in a beryllia sagger using the high purity S-11 powder as a cement. The sagger was sealed and transferred to the high purity laboratory furnace. Dry air was introduced into the furnace such that a 261 K dewpoint was maintained during the firing cycle. The rods were fired to 1833 K, in 12 hours, held at that temperature for two hours, and allowed to cool uncontrolled back to room temperature in 24 hours.

The first series of test extrusions resulted in extremely high purities (150 ppm detectable impurities) and very low densities (49% of theoretical density). It was quite clear that this fabrication approach would yield high purities; however, high density was also a progress requirement.

To attain high fired densities, the forming process must place ceramic particulates into intimate contact. A measure of this intimate contact is the green, or unfired fabricated, density. Experience with extruding high purity beryllia had shown that a minimum green density of 1700 Kg/m^3 (56.5% theoretical density) was required to attain high levels of densification. The green density of these initial extrusions was measured to be 1130 Kg/m^3 (37.3% theoretical density), a value far below that required. The green densities were measured by determining the volumes by mercury immersion and weighing on an analytical balance. The accuracy of this technique is estimated to be ± 5%.

The following sections will describe the processing studies undertaken to realize a forming process that produces high green density extrusions possessing high purity levels.

Processing Tests

a. Moisture Content Studies - An effective method of increasing the green density is to reduce the moisture content of the extrusion mix and then to extrude at higher pressures. Thus, a series of extrusion mixes were prepared containing 35, 40 and 50% moisture by hand mixing in appropriate amounts of a 3% Methocel solution. The insulators were processed and fired in an identical manner to those described in the initial extrusion test.

The results are shown in Table V. As can be seen, the green density increases from 1130 Kg/m^3 (37.3% theoretical density) with a decrease in moisture content and an increase in forming pressure. In a similar fashion, the final fired density increases from 1.48 X 10^3 Kg/m^3 (49.1% theoretical density) to 1.72 X 10^3 Kg/m^3 (57.1% theoretical density). The final fired density was measured on five samples and the results averaged. Liquid immersion techniques in accordance with ASTM test C373-56[5]. The accuracy of this technique is estimated to be ± .2%.

This experiment indicated that decreased moisture contents increase green and final densities. However, the large increases in forming pressure required for extrusion with the lowest moisture content would not, for practical purposes, allow this approach to attain the green densities required.

b. Binder Studies - The second approach utilized to attain higher green densities was an investigation of other binder systems. At this juncture of the program, it was felt that harder binders and a lubricant would result in higher green density values.

A series of experiments were performed using as binder ingredients: a 3% Methocel solution(a), a 5% Floc-gel solution(b), a 10% Polyvinyl Alcohol solution (c), a 2% Carbowax solution(d), and Glycerine(e). The following binder combinations were prepared from these solutions: 1) 100% Methocel solution; 2) 50% by weight Methocel solution-50% Polyvinyl Alcohol solution; 3) 60% by weight Methocel solution-20% Glycerine; 4) 100% Floc-gel solution and 5) 80% by weight Floc-gel solution-20% Glycerine. The binder mixtures were hand mixed in polyethylene containers into the S-11 beryllia powder in quantities to yield the moisture levels shown in Table VI. The extruded methods, drying methods and firing cycles were identical to those described in the initial extrusion tests.

Table VI presents the results of this test. As can be seen, the test indicated that a different binder system would not significantly increase green or fired densities.

c. Mixing Studies - A microscopic examination of the unfired insulators revealed that the binder was not being homogeneously mixed into the beryllia powder. Unmixed islands of binder were noticed, and these would result in larger void pockets after firning. Also, significantly, more binder content was required to attain plasticity for extrusion and this resulted in a greater separation of the beryllia particles. It became apparent that hand mixing was not an adequate method of incorporating the binder if a high green density was to be attained.

Hand mixing, using plastic tools, was initially incorporated into this program to eliminate an impurity producing mechanical mixing step. Since this approach did not produce the desired end results, it was necessary to incorporate a high shear mixing action for binder incorporation that did not contaminate the powder. A high shear Braebender mixer (650 X $10^{-6}m^3$ capacity, twin sigma blades) was purchased for this program. The stainless steel interior and the stainless steel blades were then coated with Teflon S,* an abrasion resistant organic compound.

An experimental test series was performed to evaluate the high shear mixer as a means of improving green density. Extrusion mixes were formulated with a

*Du Pont de Nemours, Inc.

(a) Methocel HG. Hydrozypropyl Methylcellulose. Dow Chemical Company.
(b) Floc-gel. S. K. Perine Company
(c) Polyvinyl Alcohol. EVANOL. Grade 51-056. Du Pont DeNemours & Co.
(d) Carbowax 1540. Polyethylene Glycol. Union Carbide Corporation.
(e) Glycerol. Reagent Grade. Matheson Coleman and Bell Corporation

3% Methocel solution binder prepared both by hand mixing and by using the high shear mixer. Several moisture levels were incorporated by adjusting the binder/powder weight ratios. The extrusion methods, drying procedure and firing cycle were identical to that described in the initial extrusions.

The results of this study are shown in Table VII As can be seen, there were increases in green and fired densities. The significance of the test was in the reduced binder contents and much reduced pressures required for extrusion. The test proved rather conclusively that the high shear mixing was necessary for homogeneously mixing the binder into the beryllia powder.

A spectrographic analysis was performed by Ledoux and Co. to determine the metallic impurities introduced by the mechanical mixing operation. The results are shown in Table VIII. The semi-quantitative analysis (± 30%) indicated very slight impurity pickup using the Braebender mixer. There is an increase of 20 ppm in iron impurity; however, this increase was so slight that it must be considered insignificant. This analysis indicated that the Braebender mixer could be utilized in this program.

d. Milling Studies - An analysis of the green densities from the preceding tests indicated that factors other than poor mixing of the binder were operative in retarding densification. The low bulk density of the powder led to a reexamination of the electron photomicrographs of the raw powder. These photographs, presented in Figures 1 to 4, showed loose agglomeration of the powder particles. These agglomerates are held together by strong electrostatic forces and probably were not de-agglomerated by the macroscopic action of the high shear mixer. Also, the pressure of the extrusion was not sufficiently high to force the particles into intimate contact to enhance densification. Thus, it was deemed necessary to incorporate a high energy milling operation in order to break down these agglomerates.

To minimize impurity contamination, a two gallon rubber lined mill, containing 99.5% beryllia grinding media, was incorporated into the processing operation. Test extrusions were prepared from unprocessed S-11 beryllia powder, wet milled beryllia powder and dry milled beryllia powder. The wet milled powder was milled for 24 hours in a mill containing 1.0 Kg beryllia powder, 5.0 Kg beryllia grinding media and 2000 cc distilled water. The dry milled powder was milled for 24 hours in a mill containing 1.0 Kg beryllia powder, a proprietary dry grinding aid and 5.0 Kg beryllia grinding media. The two gallon mill was rotated at 55 RPM.

The wet milled powder was pan dried in a plastic container at 398 K for 24 hours. The dried cake was then crushed with a plastic utensil and passed through a 40 mesh nylon screen prior to adding the binder.

The dry milled powder was placed in a beryllia sagger and heated in a dry air atmosphere to 923 K to burn out the dry grinding aid. This powder was then passed through a 40 mesh nylon screen prior to the binder addition stage.

A 3% Methocel solution was mixed into the powder for 20 minutes in the Braebender mixer at a 28% moisture level. The extrusion methods, drying procedure and firing cycles were identical that described in the initial extrusions.

The test results are shown in Table IX. As can be seen, milling resulted in a significant improvement in final fired density. This density rose from 1.79 X 10^3 Kg/m^3 (59.5% theoretical density) for unmilled, to 2.39 X 10^3 Kg/m^3 (79.4% theoretical density) for wet milled to 2.52 X 10^3 Kg/m^3 (83.7% theoretical density) for dry milled.

A semi-quantitative analysis was performed by Ledoux and Co. on the fired extruded samples to determine if the milling operation introduced significant impurities. The results are shown in Table X. As can be seen, there is no significant increase in major impurity content related to the milling operation.

Figure 5a and 5b show the electron micrographs of the dry milled S-11 powder. When compared with Figures 1 and 2, electron micrographs of as received S-11 powder, one can immediately notice a compaction of the agglomerates. This would result in more intimate particle contact and enhance densification.

e. Raw Materials Studies - In the course of the program, there was a serious question as to the sinterability of the Kawecki-Berylco S-11 powder. The low surface area, 9.2 m^2/gm was only considered marginal in regard to obtaining high densities in the absence of a sintering aid. As a parallel approach, a high purity, high surface area (19.8 m^2/gm), NGK CF-1 beryllia powder was introduced into the program.

Figures 3 and 4, the electron micrographs of the as received CF-1 powder, show similar agglomerates as was evidenced with the as received S-11 powder. Since beneficial results were obtained in compacting the S-11 agglomerates by dry milling, the CF-1 powder was dry milled in an identical manner. Figure 6 is an electron photomicrograph of the dry milled CF-1 powder. A significant compaction of the agglomerates is noted.

The dry milled CF-1 power was used to fabricate test specimens in a manner identical to that used in preparing rods from the dry milled S-11 powder. An extrusion pressure of 42.2 Kg/m^2 realized a green density of 1.78 gms/cc (59.1% theoretical density). These rods, when fired to 1833 K in dry air, exhibited a fired density of 2.86 gms/cc (95.9% theoretical density) and less than 200 ppm detectable metallic impurities. Thus, the higher surface area of the CF-1 powder was beneficial in realizing higher final fired densities.

f. Drying Studies - The extrusions required a covering of spectrographically pure graphite powder during the drying operation. This graphite covering was required to minimize the warpage caused by uneven drying. An analysis supplied by Union Carbide Corporation, the vendor, indicated only 2 ppm total detectable impurities. During this program, there was some concern as to the total removal of the graphite powder covering during firing.

Three test drying methods were studied in this program to determine if the graphite powder was necessary:

1) Drying using spectrographically pure graphite.
2) Drying using a microcrystalline wax powder.
3) Drying without the aid of a covering powder.

A carbon analysis showed that all three methods yield less than 50 ppm carbon impurity after firing. Figure 7 presents a photograph of the fired extrusions. As can be seen, the uncovered extrusions (101-21-2) warped considerably, the microcrystalline wax covered extrusions (101-21-4) warped slightly, and the graphite covered extrusions (101-21-3) showed almost no warpage. This study would indicate that the graphite covering for drying is necessary and is not detrimental.

Firing Studies

a. Introduction - Firing studies were undertaken to determine conditions whereby beryllia insulators can be fired to achieve high levels of densification and yet maintain the purity requirements set forth in this program. The effort involved firing in four atmospheres (hydrogen, oxygen/propane, vacuum and dry air) and analyzing the density and impurity levels of the beryllia insulators fired under each condition. From this study, firing methods would be developed that satisfied all program requirements. The following sections describe the efforts undertaken in achieving the required end objectives.

b. Hydrogen Firing Study- A cold wall Harrop elevator furnace with a cylindrical heating chamber 20.3 cm in diameter, 30.5 cm high, was used in the hydrogen firing study. This furnace was reconstructed for this program by relining with new high alumina refractories and by replacing the molybdenum heating elements. In addition, a concentric molybdenum radiation shield was introduced adjacent to the new refractory liner.

The furnace was heated to 2073 K for 72 hours prior to usage to burn out volatiles associated with the new refractory liner.

The hydrogen source was bottled high purity hydrogen with a dewpoint of 227 K supplied by Air Products Corporation. A flow of 4.72 liters/sec hydrogen was maintained during the firing cycle.

The extrusion mix was prepared by hand mixing a 3% Methocel binder solution with the S-11 powder to a 40% moisture level. The mix was extruded through a 0.15 cm diameter orifice at 140.6 Kg/cm^2, dried with spectrographic graphite covering, and hung in a high purity beryllia sagger. All operations with the exception of the extrusion were carried out in the clean air station.

The sagger was sealed and then transferred to the hydrogen furnace. Two firings, one to 1923 K in 20 hours and one to 2073 K in 23 hours, were performed. A density of 1.47×10^3 Kg/m^3 (48.8% theoretical density) as measured using ASTM methods was recorded for the 1923 K fire and 1.70×10^3 Kg/m^3 (56.5% theoretical density) was obtained with the 2073 K temperature. Table XI presents the spectrographic analysis for the 2073 K fire. As can be seen, significant contamination of the insulators occurred during the hydrogen firing.

The low densities obtained were more likely associated with the processing of the insulators than with the hydrogen atmosphere. The hydrogen firing tests occurred prior to the incorporation of high shear mixing and milling into the forming operation. It was assumed that this non-optimum processing resulted in insulators possessing such low green density values that densification was retarded.

The hydrogen furnace did not have a provision for introducing a separate hydrogen line directly into the sagger. To accomplish this would have required major furnace modifications and no assurance of a safe operation. Thus, the hydrogen atmosphere surrounding the insulators was the hydrogen atmosphere of the total furnace. At the high temperatures utilized, impurities were introduced into the insulators at levels higher than allowed by the requirements of the program. For this reason, the hydrogen firing portion of the program was terminated.

c. Oxygen Propane Firing Study - A circular pot furnace with a cylindrical heating chamber 30.5 cm in diameter, 45.7 cm high was relined with high purity calcia stabilized zirconia refractories for this program. The furnace was heated to 2273 K for 72 hours prior to usage in order to burn out the volatiles associated with the new refractory liner.

The fuel source was bottled high purity oxygen and propane supplied by Air Products Corporation. The gas flows were regulated to control the temperature cycle and, at maximum temperature, flows of 905.6 liters/hr. oxygen and 3396 liters/hr. propane were recorded.

The test samples were prepared in an identical manner to those used in the hydrogen firing study. A sealed high purity beryllia sagger was used to house the insulators during the firing.

Two firings, one to 2223 K in seven hours and one to 2343 K in eight hours, were performed. A density of 2.40 X 10^3 Kg/m^3 (86.0% theoretical density) was measured for the 2343 K temperature. Table XII presents the spectrographic analysis of the insulators fired to 2343 K temperature. As can be seen, considerable contamination was observed.

In the oxygen-propane firing, it was not possible to introduce the fuel directly into the sagger. The atmosphere of the total furnace was the atmosphere surrounding the insulators. At these elevated firing temperatures, there is significant volatility associated with the refractories. This led to an extremely high level of impurity introduction within the insulators. Since the contamination was far in excess of tolerable program limits, and since there appeared to be no way in which to control the atmosphere within the closed sagger, the oxygen-propane firing portion of the program was terminated.

Once again, the low densities obtained were more likely associated with the processing of the insulators rather than the oxygen-propane atmosphere. The higher density values obtained, as compared to the hydrogen firing, were related to the impurities. The impurity levels were so high that the impurities could now act as sintering aids to promote densification.

d. Vacuum Firing Study - In the vacuum firing study, test extrusion samples were prepared utilizing six distinct processing combinations. Table XIII presents a summary of the combinations used for the individual batches. These differences were introduced to further define the effects of raw materials, drying aids and milling.

The processing steps summarized in Table XIII used to prepare these insulators for the vacuum firing have been described in detail in prior sections of this report. After fabrication and drying, the extrusions were hung on a high purity beryllia plate and attached with a beryllia cement prepared from the high purity S-11 powder. The plate was inserted into a sealed beryllia sagger that possessed an inlet tube for introducing high purity air (see Figure 8). The sealed sagger was placed in the high purity laboratory electric furnace constructed for this program and heated to 1573 K for eight hours with dry clean air blowing into the sagger at a rate of 1.42 liters/sec. After firing, the sealed sagger was returned to the clean air station where the bisque fired insulators were placed in sealed polyethylene bags with a positive pressure of clean dry air. The packaged insulators were then sent to Engelhard Industries for the vacuum firing.

At Engelhard, the insulators were fired in a beryllia crucible under a vacuum of greater than 2.6×10^{-4} N/m^2 to 1983K with a three hour hold at maximum temperature. It was reported by Engelhard that there was considerable outgassing of the ceramic insulators during heating, and this heavy gas load for long periods of time degraded their ion [illegible]

Table XIV presents the impurity analysis and density determinations of the vacuum fired insulators. As can be seen, the purity levels are within the limits set by the program. However, the densities are quire low. Since the densities were low and since the cost of repairing the vacuum equipment after each firing was prohibitive, the vacuum firing trials were terminated. A major factor in this decision was the simultaneous obtaining of excellent purity and density results from the dry air firing tests. These tests will be discussed in the next section.

e. Dry Air Studies - An electric resistance heated Glo-Bar* furnace was relined with high purity alumina refractories for this program. The furnace was heated to 1873 K for 72 hours prior to usage to burn out the volatiles associated with the new refractories. This furnace was constructed by laboratory personnel and has a .61 m X .61 m X .457 m interior. Eight .1016 m long Super Glo-Bars* were spaced, four to each side, 101.6 mm apart along the vertical side walls. A platinum-13%rhodium/platinum thermocouple placed adjacent to the sagger was used for temperature measurement. A Minneapolis Honeywell temperature controller, Model 152C33PS-21K1-11,was used to regulate the firing cycles. Optical temperature measurements were taken at two hour intervals using a calibrated Leeds and Northrup Optical Pyrometer Model No. 8622-C to verify the thermocouple readings.

The dry air was supplied by Air Products Company, and a chemical analysis is shown in Table XV.

f. Dew Point Studies - With reactive beryllia powder, the dew point, or water vapor content, of the air atmosphere plays an influential role in the

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*Norton Corporation

densification of beryllia powder. Test firings at selected dew points were performed using insulators prepared from the highly reactive CF-1 beryllia powder.

Extrusions were prepared by hand mixing in a 3% Methocel binder solution to 40% moisture, extruding at 140.6 Kg/cm^2 through a .0015 m diameter orifice, and drying the extrusions under a covering of spectrographically pure graphite. All operations, with the exception of the extrusion, were carried out in the clean air station. The extrusions were then hung vertically in a high purity beryllia sagger 30.5 cm high, 12.7 cm outside diameter and 11.4 cm inside diameter that was sealed prior to firing. High purity dry air was introduced into the sagger by means of 0.64 cm inside diameter high purity beryllia tubes. Figure 8 shows the sagger placed within the furnace.

The dew point was measured with a Model 700 Dew Pointer, Alnor Instrument Company. The dew point was lowered by increasing the flow of the 199 K dew point air into the sagger. The results of this test are shown in Table XVI. As can be seen, the fired density increases dramatically from $1.75 X 10^3 Kg/m^3$ (58.1% theoretical density) at a 258 K dew point to $2.70 X 10^3 Kg/m^3$ (89.7% theoretical density) with a 244 K dew point. This is significant when it is considered that all other factors of the firing were held constant.

Furnace Atmosphere Analysis

A gas analysis was performed to determine the atmosphere within the sagger at selected temperatures during the firing cycle. The gas samples were collected in stainless steel gas analysis cylinders. A beryllia extension tube was cemented onto one of the two beryllia tubes entering the sagger. Tygon tubing was attached between the extension tube and the gas analysis cylinder. A vacuum within the collection cylinder was used as a means of drawing the furnace atmosphere into the cylinder.

The atmospheric samples were taken during a dry air firing. The analyses of these samples determined by mass spectroscopy are shown in Table XVII. The analysis was performed by Hollob Analytical Services, Berkeley Heights, New Jersey. The analysis indicates that carbon dioxide, water and hydrogen are generated during the binder burnout stages of firing.

One sample, that taken at 973 K, is in suspect because of the argon content. It is assumed that room air had leaked into the sample cylinder.

Since this was a one sample analysis and since the atmosphere generated by the binder burnout would be highly dependent upon the amount of insulators in the sagger, these analytical results must be looked on only as a trend and not in quantitative terms.

Draw Trials

Because there was a time slippage in the program, an abbreviated draw trial was performed to determine the role of time and temperature upon the densification level. Rods of the six extrusion batches used in the vacuum firing studies were also utilized in the dry air draw trials. These extrusion batches were summarized in Table XIII. Three firings were performed at 244 K dew point:

(1) 1773 K with a 330 minute soak.
(2) 1843 K with a 80 minute soak.
(3) 1873 K with a 600 minute soak.

This time-temperature grid would give good indication as to the effect of the variables on density and impurity pick-up. Table XVIII presents the impurity analysis and density determinations of the insulators fired under the selected densifying conditions.

As seen from Table XVIII, the density of the double bore extrusions increases with time and temperature. The density values are shown also to significantly change with processing methods. The values range from 1.74 X 10^3 Kg/m^3 (57.8% theoretical density) for the lowest firing temperature and no raw material processing to 2.94 X 10^3 Kg/m^3 (97.7% theoretical density) for the longest time, highest temperature and milling the raw material.

The results obtained in the draw trial regarding purity are also relatively conclusive. Increased temperatures and soaking times resulted in an increased impurity level. The major impurities: aluminum, silicon, iron and magnesium were found to increase with temperature and soaking time. Since the fluorine and sulfur must be determined by wet chemical analysis on a larger sample than was used in the draw trial, these two were not determined in this series. In the entire draw trial, these two were not determined in this series. In the entire draw trial study, only three sets of conditions resulted in purities below 99.95% beryllia.

g. Summary of Firing Studies - These firing studies have resulted in methods of obtaining ultra high purity, high density, beryllia insulators. The firing procedures utilized in the preparation of the double bore insulators supplied to Engelhard Industries are described in the following section of this report.

FABRICATION PROCEDURES AND ANALYSIS OF HIGH PURITY BERYLLIA PARTS

Since its inception, National Beryllia Corporation has devoted a continuing effort toward improving the processing techniques employed in the fabrication of beryllium oxide. In proposing this program, it was decided not to incorporate any of the National Beryllia's proprietary processing methods in the fabrication of the thermocouple insulators. It was felt that the purity could be maintained only by using non-mechanical processing with the purest form of binder. As the program progressed, it became apparent that high densities could not be obtained with non-mechanical processing. As time became a consideration of the program, it was decided to incorporate proprietary binder systems, milling methods and extrusion techniques in order that the highest density, highest strength insulators would be realized. Certain proprietary processing techniques were utilized with success and the end objectives of the program were met. In the following sections of this report, exact details associated with the proprietary techniques are omitted.

Fabrication of Insulators

This section of the report describes the procedures used in fabricating the beryllia thermocouple components supplied to Engelhard Industries. Included in this section are the results of analytical tests performed on the particular components.

1. Raw Material Handling

The beryllium oxide used in this program was received and stored in the Research and Development area. The powder was stored in double sealed polyethylene bags contained in closed steel drums. The bags were opened only within the clean air station and were sealed immediately after the required amount of material had been removed. The powder was handled only research technicians trained in methods of high purity material handling.

2. Raw Materials

Three lots of beryllium oxide powder were utilized in the fabrication of the insulators. Kawecki-Beryllco S-11 powder (Lot No. 521-68-1-22) and NGK Insulators CF-1 Powder (Lot No. 44-18) were used to fabricate the double bore insulators. NGK Insulators, Ltd. Powder (Lot No. 43-10) was used to fabricate the insulating end caps.

3. Milling Operation

The weighed charge of beryllia was loaded into the mill in the clean air station and the mill was sealed prior to the removal. The milling operation utilized rubber lined mills with high purity (99.5% pure) beryllia grinding media. The speed of rotation and time of the dry milling operation are considered proprietary to National Beryllia Corporation.

After milling, the mill was returned sealed to the clean air station. The powder was removed from the mill, free screened through a 60 mesh stainless steel screen, and then sealed in double wrapped polyethylene bags for storage.

In the dry milling operation, a proprietary organic grinding aid was added to the mill. The following procedure was used to remove this organic compound after the milling operation. The milled powder was placed in the high purity beryllia sagger (Figure 8) within the clean air station. The sagger was sealed and placed within the high purity electric furnace used in this program. The powder was heated to 873 K for five hours with a 0.609 meters/sec flow of clean dry air. After the burn-out was completed, the powder was removed from the sagger within the clean air station and then sealed in double polyethylene bags for storage.

4. Mixing Operation

The mixing operation was carried out in the clean air station with a Teflon S lined Braebender sigma blade mixer. A proprietary binder solution was added to the powder and a fifteen minute mixing operation was employed. The powder was then removed from the mixing chamber with a plastic scoop and placed in a poltethylene bag. The powder was allowed to age for twenty-four hours in the sealed bag prior to extrusion.

5. Extrusion

The extrusion gun used in this program was a small National Beryllia Corporation designed and constructed laboratory model that allowed loading in the clean air station. The extrusion gun was constructed of stainless steel 61 centimeters long with an inside barrel diameter of 7.6 centimeters. The orifice die and pins were constructed of cemented carbide. The diameter of the orifice was 0.122 cm and the configuration and the die lubricant are considered to be proprietary National Beryllia process information.

This extrusion gun, shown in Figures 9 and 10, required a large hydraulic press that operated in a vertical fashion. Thus, the extrusion operation was carried out immediately adjacent to the clean air station, and the extruded rod was quickly transferred into the station after extrusion. Figure 9 shows a technician extruding the double bore insulators.

The extrusion process was carried out at 703 Kg/cm^2 in an intermittent manner. As shown in Figure 9, approximately a three foot length was extruded and then transferred to the clean air station. No measurements were taken for linear extrusion rate.

The extrusions were rolled on a plexiglas plate to insure straightness and then were covered with spectrographically pure graphite to allow uniform drying. This is shown in Figures 10 and 11. The extruded rods were stored in sealed drying racks within the clean air station while awaiting firing.

6. Furnace

An electrical resistance heated Glo-Bar furnace was relined with high purity alumina refractories for this program. This furnace was previously described within this report.

7. Sagger

A cylindrical high purity (99.5% pure) beryllia sagger, 30.48 cm high, 12.7 cm outside diameter, 11.43 cm inside diameter, was used to house the beryllia insulators during the firing operation. The ends of the cylindrical sagger were capped with high purity beryllia plates. A groove was cut in the interior of the sagger to support the high purity beryllia rod to which the insulators were attached. Two high purity beryllia tubes were inserted through holes in the wall of the sagger. Figure 8 shows the sagger placed within the furnace.

8. Dry Air

Dry air was introduced into the sagger through the high purity beryllia tubes. The flow rate of air was adjusted between 1.83 and 3.05 meters/min. during firing to produce the 244 K dew point required for the program. The dry air was supplied by Air Products Company and a chemical analysis of the air was shown in Table XV.

9. Sagger Loading

The extrusions were cemented to a high purity beryllia rod in the clean air station. The cement consisted of the high purity S-11 beryllia powder mixed with Methocel solution. The hung extrusions are shown in Figure 11. The rod was placed in the grooves of the sagger with the extrusions hanging in a vertical fashion. The sagger was sealed in the clean air station and transported to the furnace.

10. Firing

From the results of the draw trial, Engelhard Industries requested three groups of insulators:

1) Insulators prepared from CF-1 powder fired to 1873 K with a 600 minute soak
2) Insulators prepared from S-11 powder fired to 1873 K with a 600 minute soak
3) Insulators prepared from CF-1 powder fired to 1843 K with an 80 minute soak.

These groups of insulators were fired in the laboratory Glo-Bar furnace with a dry clean air atmosphere, 244 K dew point.

In all firings, the Minneapolis Honeywell Controller was employed to achieve the following heating and cooling schedule:

a. 150 K per hour from room temperature to 923 K.
b. Hold at 923 K for four hours to insure binder burn-out.
c. 150 K per hour from 923 K to 1423 K.
d. 75 K per hour from 1423 K to soak temperature.
e. Soak temperature hold.
f. Cool at 200 K per hour to 1593 K.
g. Cool at 95 K per hour to 593 K.
h. Controller off, furnace opened and sagger removed to clean air station.

Table XIX presents the impurity analysis and density determinations of the different groups. It is noted that the fired density of the S-11 insulators increased from 2.74 X 10^3 Kg/m^3 (91.0% theoretical density) in the draw trial to 2.97 X 10^3 Kg/m^3 (98.7% theoretical density) in the final firing of insulators. This is attributed to the lower green density obtained in the extrusion of the insulators prepared for the draw trials. The moisture content of the S-11 extrusion mix was reduced to correct for shrinkage as the S-11 insulators fired in the draw trial did not meet dimensional tolerances.

The fired shrinkage of the insulators was found to be 13% measured across the diameter. The camber for the bulk of the insulators supplied to Engelhard was less than 0.01 cm/cm. The outside diameter of the insulator was measured

.0.009 ± .005 cm and the inside diameter of the double bore hole was measured to be 0.033 ± .002 cm. The double bore holes were separated by webbing of .013 ± .005 cm.

As can be seen, the insulators are of very high purity and high density. These insulators were acceptable for usage in thermocouple assembly and were transmitted to Engelhard Industries in sealed polyethylene bags.

11. Grain Size Determinations of Double Bore Industries

Polished and etched specimens were prepared of the three insulator batches. The specimens were etched in concentrated hydrofluoric acid at 368 K for 60 seconds, and the grain size was measured by linear intercept method using the Lennon technique.[6] The Photomicrographs are presented in Figures 12, 13 and 14. The grain size of: the CF-1 insulators fired to 1873 K was measured to be 30 microns average; the CF-1 insulators fired to 1843 K was measured to be 6.5 microns average; and the S-11 insulators fired to 1923 K was measured to be 9 microns average.

12. Flexural Strength Measurements

Flexural strength measurements were performed on a sample size of 15 test rods with 1.9 cm span and a head travel of .105 cm/sec on a Dillon Dynamometer using a low poundage head. Strength measurements of 260 Kg/m^2 were obtained for the S-11 insulators fired to 1873 K, and 1406 Kg/m^2 for the CF-1 insulators fired to 1873 K. The measurements were calculated assuming a solid rod configuration; thus, the strength values are well in excess of measured values because the insulators possessed two holes in the interior. The strength values with regard to the different groups of insulators is consistent in that the finer grained ceramic bodies possess higher strength values.

SUMMARY AND CONCLUSIONS

1. Beryllium oxide thermocouple insulators have been fabricated in high density form (over 95% theoretical density) and possessing less than 500 parts per million total impurities.

2. To attain high purity beryllium oxide shapes, it is necessary to obtain ultra high purity raw materials, process and fabricate under clean room type conditions, fire in clean controlled atmospheres, and use protective handling techniques.

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TABLE I

Cation Impurity Analysis

Kawecki-Beryllco S-11 Powder

Element	Sample #1	Sample #2
Aluminum	7 ppm	7 ppm
Copper	2 ppm	2 ppm
Iron	10 ppm	10 ppm
Magnesium	2 ppm	2 ppm
Silicon	15 ppm	14 ppm

TABLE II

Anion Impurity Analysis

Kawecki-Beryllco S-11 Powder

Fluorine	50 ppm
Sulfur	630 ppm
Phosphorous	Less than 50 ppm
Carbon	140 ppm

TABLE III

Impurity Analysis

NGK CF-1 Powder, Lot 44-18

Detected Cationic Impurities

Aluminum	40 ppm
Boron	2 ppm
Calcium	50 ppm
Iron	25 ppm
Lithium	1 ppm
Magnesium	30 ppm
Potassium	10 ppm
Silicon	20 ppm
Sodium	20 ppm

Anionic Impurities

Sulfur	1790 ppm
Carbon	410 ppm
Chlorine	10 ppm
Phosphorous	5 ppm
Fluorine	0.5 ppm

Limits of Detection Presented in Table IV.

TABLE IV

Limits of Detection
For
Analysis Shown in Tables I, II & III

Aluminum	1 ppm	Magnesium	1 ppm
Antimony	10 ppm	Mercury	500 ppm
Arsenic	50 ppm	Molybdenum	2 ppm
Boron	2 ppm	Nickel	2 ppm
Barium	2 ppm	Osmium	70 ppm
Bismuth	1 ppm	Palladium	5 ppm
Calcium	2 ppm	Potassium	2 ppm
Cadmium	5 ppm	Rhodium	10 ppm
Chromium	2 ppm	Ruthenium	30 ppm
Cobalt	2 ppm	Silicon	1 ppm
Columbium	30 ppm	Sodium	2 ppm
Copper	1 ppm	Silver	1 ppm
Gallium	5 ppm	Strontium	5 ppm
Germanium	5 ppm	Tantalum	500 ppm
Hafnium	200 ppm	Titanium	5 ppm
Indium	5 ppm	Tungsten	500 ppm
Iridium	50 ppm	Vanadium	5 ppm
Iron	1 ppm	Zinc	10 ppm
Lead	2 ppm	Zirconium	10 ppm
Lithium	1 ppm		

TABLE V

MOISTURE CONTENT STUDIES

Moisture	Pressure Required for Extrusion	Green Density	Firing Temperature	Fired Density
50%	140.6 Kg/cm^2	1130 Kg/M^3	1830K	1480 Kg/M^2
40%	703.0 Kg/cm^2	1150 Kg/M^2	1830K	1630 Kg/M^2
35%	1,406.0 Kg/cm^2	1210 Kg/M^2	1830K	1720 Kg/M^2

TABLE VI

Binder Studies

Binder	Moisture	Pressure Required for Extrusion	Green Density	Firing Temperature	Fired Density
Methocel	50%	140.6 Kg/cm^2	1.13 X 10^3 Kg/M^3	1833K	1.48 X 10^3 Kg/M^3
Methocel/PVA	50%	14.1 Kg/cm^2	1.14 X 10^3 Kg/M^3	1833K	1.47 X 10^3 Kg/M^3
Methocel/PVA/Glycerine	50%	126.5 Kg/cm^2	1.51 X 10^3 Kg/M^3	1833K	1.51 X 10^3 Kg/M^3
Floc-gel	50%	14.1 Kg/cm^2	1.19 X 10^3 Kg/M^3	1833K	1.53 X 10^3 Kg/M^3
Methocel	40%	703.0 Kg/cm^2	1.15 X 10^3 Kg/M^3	1833K	1.63 X 10^3 Kg/M^3
Methocel/PVA	40%	703.0 Kg/cm^2	1.20 X 10^3 Kg/M^3	1833K	1.61 X 10^3 Kg/M^3
Methocel/PVA/Glycerine	40%	534.3 Kg/cm^2	1.18 X 10^3 Kg/M^3	1833K	1.59 X 10^3 Kg/M^3
Floc-gel/Carbowax	40%	562.4 Kg/cm^2	1.19 X 10^3 Kg/M^3	1833K	1.57 X 10^3 Kg/M^3
Floc-gel/Glycerine	40%	406.2 Kg/cm^2	1.21 X 10^3 Kg/M^3	1833K	1.66 X 10^3 Kg/M^3
Methocel	35%	1406.0 Kg/cm^2	1.21 X 10^3 Kg/M^3	1833K	1.72 X 10^3 Kg/M^3
Methocel/PVA	35%	1265.4 Kg/cm^2	1.26 X 10^3 Kg/M^3	1833K	1.70 X 10^3 Kg/M^3
Methocel/PVA/Glycerine	35%	1124.8 Kg/cm^2	1.20 X 10^3 Kg/M^3	1833K	1.65 X 10^3 Kg/M^3

TABLE VII

Mixing Studies

Mixing	Binder	Moisture	Pressure Required for Extrusion	Green Density	Firing Temperature	Fired Density
Hand	Methocel	35%	1406.0 Kg/cm^2	1.21 gms./cc.	1833K	1.72 gms./cc.
Braebender	Methocel	33%	35.2 Kg/cm^2	1.36 gms./cc.	1833K	1.79 gms./cc.
Braebender	Methocel	30%	70.3 Kg/cm^2	1.39 gms./cc.	1833K	1.82 gms./cc.
Braebender	Methocel	30%	63.3 Kg/cm^2	1.41 gms./cc.	1833K	1.84 gms./cc.

TABLE VIII

Impurity Analysis of Mixing Study

Impurities Detected

	Hand Mixing	Braebender Mixing
Aluminum	25 ppm	20 ppm
Iron	20 ppm	40 ppm
Silicon	50 ppm	60 ppm
Magnesium	30 ppm	20 ppm
Sodium	10 ppm	10 ppm

TABLE IX

Variations in Green & Fired Density as a Function of Milling

Conditions:
BeO Powder - S-11
Binder - Methocel
Mixing - Braebender
Moisture - 28%
Extrusion Pressure - 42.2 kg/cm^2
Firing Temperature - 1830K

Process	Green Density	Fired Density
As Received	1.24 X 10^3 Kg/m^3	1.79 X 10^3 Kg/m^3
Wet Milled	1.61 X 10^3 Kg/m^3	2.39 X 10^3 Kg/m^3
Dry Milled	1.77 X 10^3 Kg/m^3	2.75 X 10^3 Kg/m^3

TABLE X

Impurity Analysis of Milling Operation

Impurities Detected

	No Milling	Wet Milling	Dry Milling
Silicon	20 ppm	20 ppm	20 ppm
Magnesium	20 ppm	20 ppm	20 ppm
Iron	10 ppm	10 ppm	20 ppm

TABLE XI

Impurity Analysis for Hydrogen Firing

Aluminum	200 ppm
Copper	10 ppm
Iron	80 ppm
Lithium	10 ppm
Magnesium	200 ppm
Nickel	80 ppm
Potassium	10 ppm
Silicon	120 ppm
Sodium	20 ppm

TABLE XII

Impurity Analysis for Oxygen-Propane Firing

Aluminum	1000 ppm
Calcium	600 ppm
Iron	200 ppm
Magnesium	1500 ppm
Silicon	2000 ppm
Titanium	30 ppm
Zirconium	5000 ppm

TABLE XIII

Extrusion Batches for Vacuum Firing Study

Batch N001	Raw Material	S-11
	Powder Preparation	None
	Binder	3% Methocel Solution
	Mixing	Braebender
	Drying Agent	Spectrographically pure graphite
	Moisture	30%
	Extrusion	70.3 Kg./cm.^{2}
Batch N002	Raw Material	S-11
	Powder Preparation	None
	Binder	3% Methocel Solution
	Mixing	Braebender
	Drying Agent	Microcrystalline Wax
	Moisture	30%
	Extrusion	70.3 Kg./cm.^{2}
Batch N003	Raw Material	S-11
	Powder Preparation	Wet Milling
	Binder	3% Methocel Solution
	Mixing	Braebender
	Drying Agent	Spectrographically pure graphite
	Moisture	30%
	Extrusion Pressure	70.3 Kg./cm.^{2}
Batch N004	Raw Material	S-11
	Powder Preparation	Wet Milling
	Binder	3% Methocel Solution
	Mixing	Braebender
	Drying Agent	Microcrystalline Wax
	Moisture	30%
	Extrusion Pressure	70.3 Kg./cm.^{2}
Batch N005	Raw Material	CF-1
	Powder Preparation	Dry Ball Milling
	Binder	3% Methocel Solution
	Mixing	Braebender
	Drying Agent	Spectrographically pure graphite
	Moisture	30%
	Extrusion Pressure	70.3 Kg./cm.^{2}
Batch N006	Raw Material	S011
	Powder Preparation	Dry Ball Milling
	Binder	3% Methocel Solution
	Mixing	Braebender
	Drying Agent	Spectrographically pure graphite
	Moisture	30%
	Extrusion Pressure	70.3 Kg./cm.^{2}

TABLE XIV

Impurity Analysis and Density Determinations of Vacuum Fired Insulators

	Extrusion Batches					
	N001	N002	N003	N004	N005	N006
Aluminum	10 ppm	80 ppm	80 ppm	10 ppm	80 ppm	20 ppm
Silicon	50 ppm	70 ppm	70 ppm	60 ppm	60 ppm	70 ppm
Magnesium	8 ppm	30 ppm	30 ppm	5 ppm	30 ppm	30 ppm
Iron	40 ppm	40 ppm	40 ppm	40 ppm	40 ppm	40 ppm
Manganese	1 ppm	1 ppm	1 ppm	1 ppm	2 ppm	1 ppm
Density(gms./cc.)	1.87	1.90	1.70	2.41	2.41	2.28
% Theoretical Density	62.3	63.3	56.7	80.3	80.3	76.0

TABLE XV

Chemical Analysis of Dry Air

Oxygen	20.90%
Nitrogen	79.09%
Argon	58 ppm
Hydrogen	1 ppm
Carbon Dioxide	1 ppm
Carbon Monoxide	1 ppm
Nitrous Oxide	0.5 ppm
Methane	3.5 ppm
Acetylene	0.05 ppm
Krypton	2 ppm
Hydrocarbons	4 ppm
Dew Point	199K

TABLE XVI

Dew Point Studies

Dew Point	Firing Temperature	Density of Insulator
258K	1833K	1.75 gms./cc.
253K	1833K	2.40 gms./cc.
244K	1833K	2.70 gms./cc.

TABLE XVII

Gas Analysis During Dry Air Firing

	Molar Percent Measured					
	373K	573K	773K	973K*	1373K	1773K
Nitrogen	79+	79+	79+	82+	79+	79+
Oxygen	19.5	18.9	18.4	17.5	18.5	19.5
Carbon Dioxide	.001	.007	.041	.098	.036	.001
Hydrogen	ND	.003	.007	.004	.001	ND
Water	1.0	1.6	1.3	1.6	.40	.10
Argon	ND	ND	ND	.098	ND	ND

*Sample value is suspect. Probable leak when sample was taken.

TABLE XVIII

Draw Trial Study

Impurity Analysis & Density Determinations

	1770K 330 Min.	1840K 80 Min.	1870K 600 Min.	1770K 330 Min.	1840K 80 Min.	1870K 600 Min.
	Extrusion Batch N001			Extrusion Batch N002		
Aluminum	ND	ND	20	40	ND	80
Iron	20	10	20	10	10	20
Lithium	ND	5	ND	ND	ND	ND
Magnesium	ND	5	ND	20	20	80
Silicon	20	20	80	30	20	160
Sodium	ND	ND	80	ND	ND	80
Carbon	200	50	50	50	300	50
Density (gms./cc.)	1.74	2.06	2.58	1.99	2.14	2.73
% Theoretical Density	58.1	68.7	85.3	66.2	71.3	91.0
Green Density (gms./cc.)	1.49	1.49	1.49	1.50	1.50	1.50
	Extrusion Batch N003			Extrusion Batch N004		
Aluminum	40	ND	80	30	ND	ND
Iron	10	10	40	10	20	40
Lithium	ND	ND	ND	ND	ND	ND
Magnesium	20	20	100	20	15	20
Silicon	30	20	200	20	20	60
Sodium	ND	ND	80	ND	ND	ND
Carbon	50	50	50	50	200	50
Density (gms./cc.)	1.97	1.98	2.63	1.85	2.03	2.42
% Theoretical Density	65.7	66.0	87.0	61.7	67.7	80.7
Green Density (gms./cc.)	1.61	1.61	1.61	1.60	1.60	1.60
	Extrusion Batch N005			Extrusion Batch N006		
Aluminum	29	ND	20	20	ND	40
Iron	20	20	80	10	20	200
Lithium	ND	ND	ND	ND	ND	ND
Magnesium	20	20	80	15	20	80
Silicon	20	20	80	20	20	200
Sodium	ND	ND	ND	ND	ND	ND
Carbon	50	50	300	50	50	50
Density (gms./cc.)	2.15	2.70	2.94	2.50	2.52	2.74
% Theoretical Density	71.7	90.0	98.0	83.3	84.0	91.3
Green Density (gms./cc.)	1.71	1.71	1.71	1.65	1.65	1.65

TABLE XIX

Impurity Analysis and Density

Double Bore Insulators

		CF-1		S-11		CF-1	
Element	Assumed State	Amount Detected	Assumed Purity Level	Amount Detected	Assumed Purity Level	Amount Detected	Assumed Purity Level
Aluminum	Al_2O_3	20 ppm	37.8 ppm	--	18.9 ppm	40 ppm	75.6 ppm
Silicon	SiO_2	50 ppm	107.0 ppm	20 ppm	42.8 ppm	30 ppm	62.4 ppm
Fluorine	F	--	0.2 ppm	--	0.2 ppm	--	0.2 ppm
Carbon	C	42 ppm	42.0 ppm	18 ppm	18.0 ppm	75 ppm	75.0 ppm
Sulfur	SO_3	--	25.0 ppm	--	25.0 ppm	--	25.0 ppm
Magnesium	MgO	50 ppm	90.0 ppm	30 ppm	48.0 ppm	50 ppm	90.0 ppm
Chlorine	Cl	40 ppm	40.0 ppm	--	10.0 ppm	--	10.0 ppm
Calcium	CaO	--	28.0 ppm	--	28.0 ppm	--	28.0 ppm
Sodium	Na_2O	--	13.5 ppm	--	13.5 ppm	10 ppm	13.5 ppm
Potassium	K_2O	--	12.1 ppm	--	12.1 ppm	--	12.1 ppm
Boron	B_2O_3	--	95.4 ppm	--	95.4 ppm	--	95.4 ppm
Zinc	ZnO	--	375.0 ppm	--	375.0 ppm	--	375.0 ppm
Copper	CuO	--	12.5 ppm	--	12.5 ppm	--	12.5 ppm
Manganese	Mn_3O_4	--	13.9 ppm	--	13.9 ppm	--	13.9 ppm
Molybdenum	MoO_3	--	15.0 ppm	--	15.0 ppm	--	15.0 ppm
Nickel	NiO	--	12.7 ppm	--	12.7 ppm	--	12.7 ppm
Lead	PbO	--	32.4 ppm	--	32.4 ppm	--	32.4 ppm
Iron	Fe_2O_3	--	14.3 ppm	20 ppm	28.6 ppm	40 ppm	57.2 ppm
Lot No.		44-18		521-68-1-21		44-18	
Firing Temperature		1870K		1870K		1840K	
Soaking Time		600 min.		600 min.		80 min.	
Density		2.95 gm./cc.		2.97 gm./cc.		2.80 gm./cc.	
% Theoretical Density		98.3		99.0		93.3	
Green Extrusion Density		1.70 gm./cc.		1.70 gm./cc.		1.70 gm./cc.	

FIGURE 1

Electron Micrograph of S-11
Beryllia Powder as Received
Magnified 12,960 Times

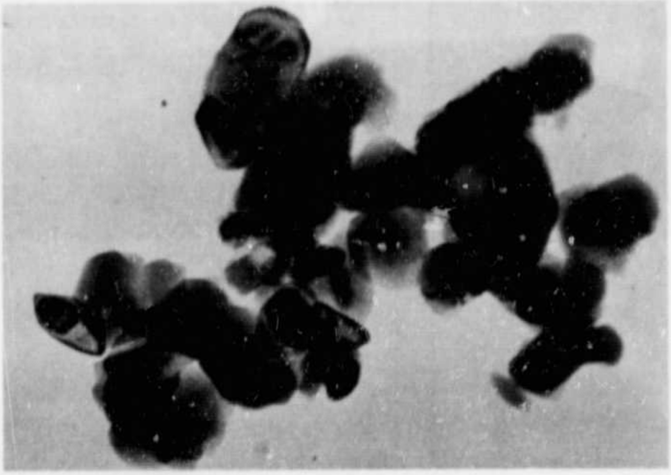

FIGURE 2

Electron Micrograph of S-11
Beryllia Powder as Received
Magnified 108,000 Times

FIGURE 3

Electron Micrograph of CF-1
Powder Magnified 12,100 Times

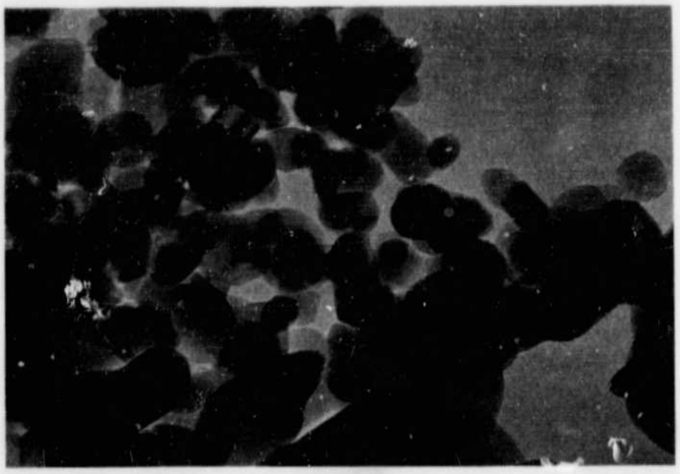

FIGURE 4

Electron Micrograph of CF-1
Powder Magnified 113,320 Times

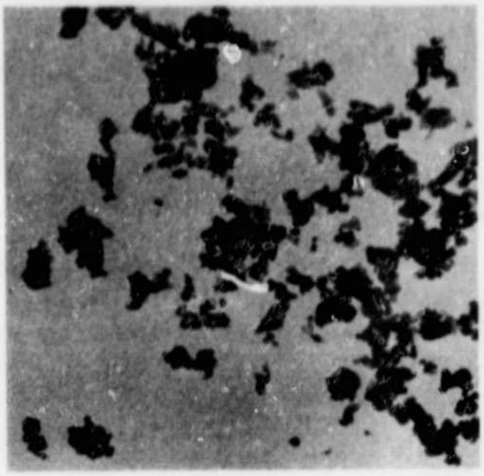

FIGURE 5a

Electron Micrographs of Dry Ball
Milled S-11 Beryllia Powder
Magnified 12,000 Times

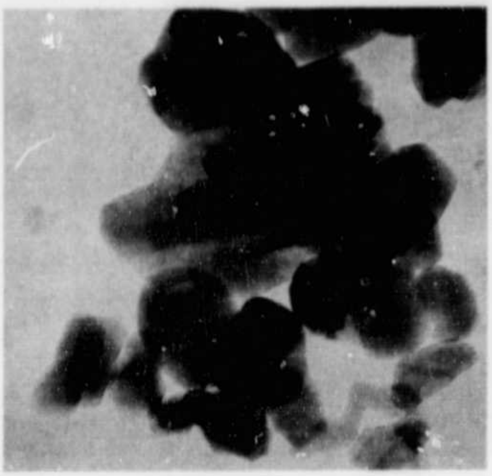

FIGURE 5b

Electron Micrographs of Dry Ball
Milled S-11 Beryllia Powder
Magnified 108,000 Times

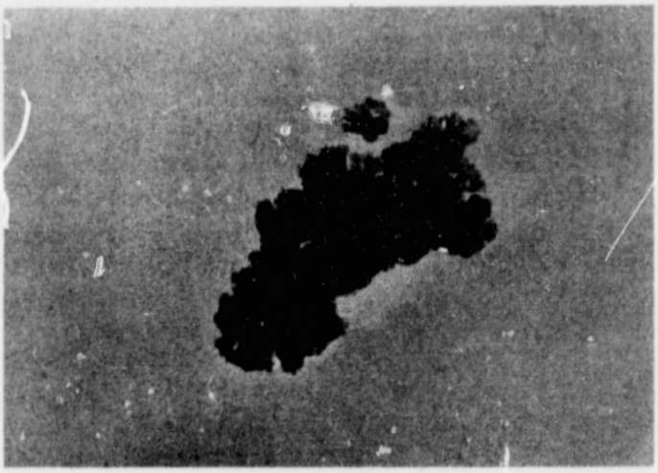

FIGURE 6a

Electron Micrographs of Dry Ball
Milled CF-1 Beryllia Powder
Magnified 12,000 Times

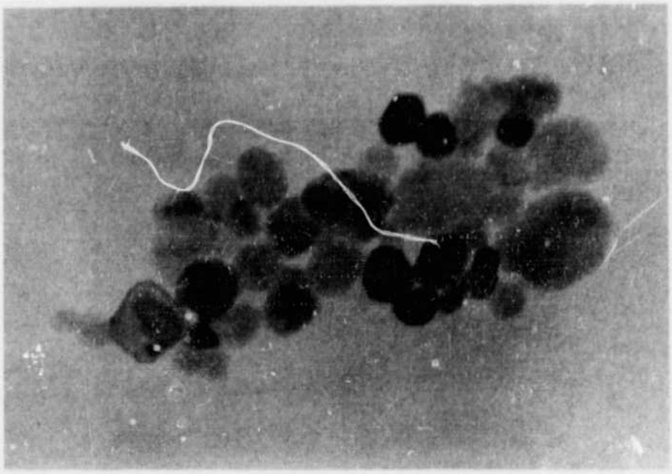

FIGURE 6b

Electron Micrographs of Dry Ball
Milled CF-1 Beryllia Powder
Magnified 108,000 Times

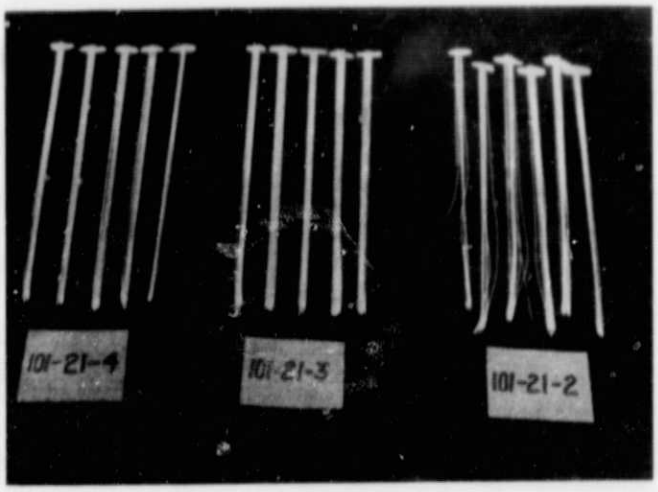

FIGURE 7

Dried Extrusions with Various
Drying Aids
Showing Warpage

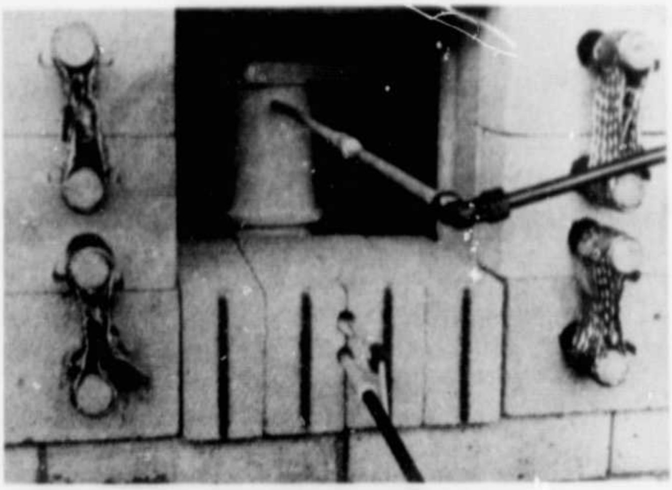

FIGURE 8

High Purity BeO Swager
With Gas Line Installed
in Sintering Furnace

FIGURE 9

Extrusion of Material

FIGURE 10

"Laying Out" of Extruded
Material in Clean Air Work
Station

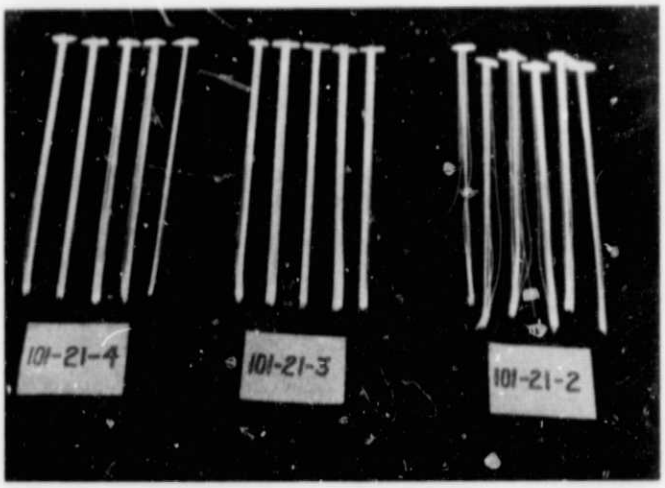

FIGURE 7

Dried Extrusions with Various Drying Aids Showing Warpage

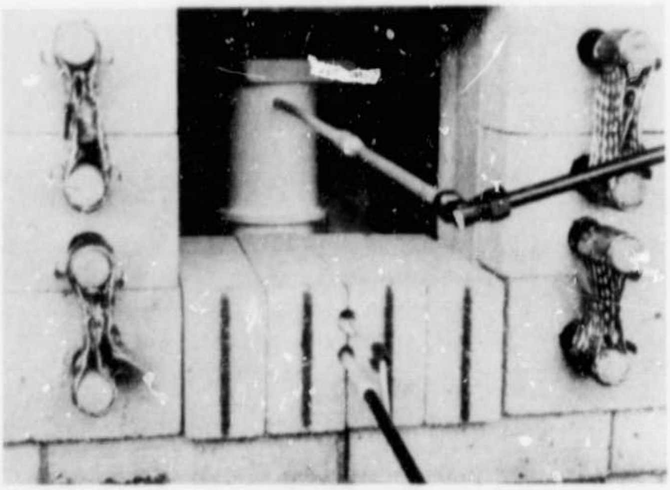

FIGURE 8

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"Laying Out" of Extruded Material in Clean Air Work Station

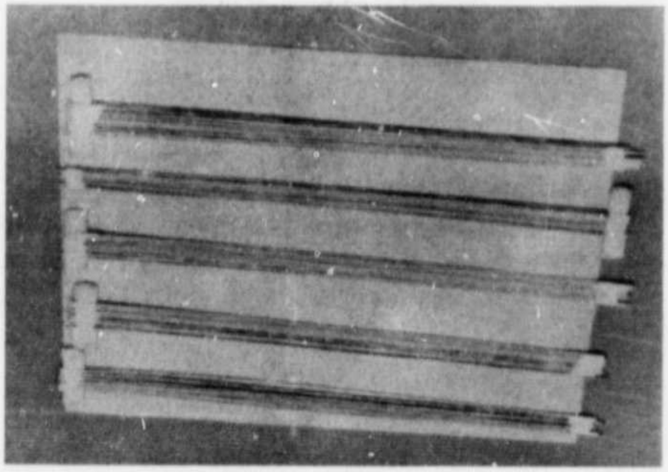

FIGURE 11

Insulators Prepared for Mounting
Within Sagger and Sintering

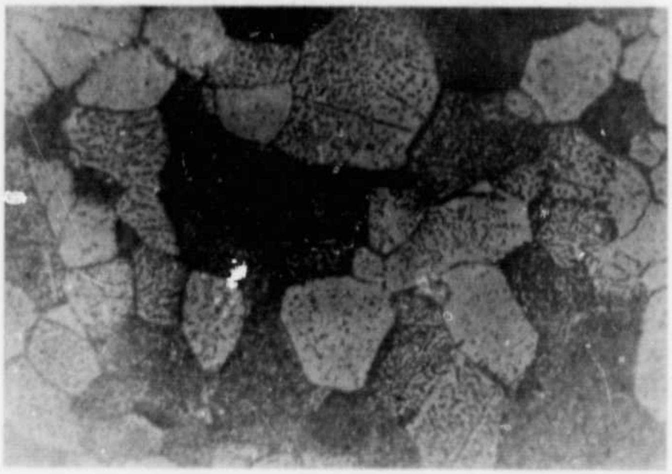

FIGURE 12

Photomicrographs of Final
Insulators CF-1, Fired to 1870K

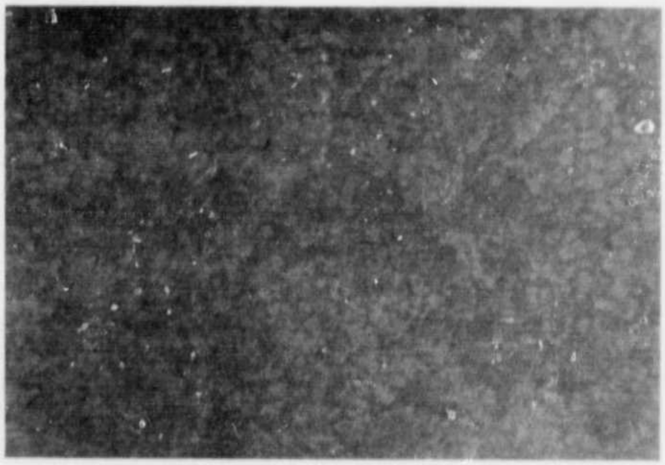

FIGURE 13

Photomicrographs of Final
Insulators CF-1, Fired to 1840K

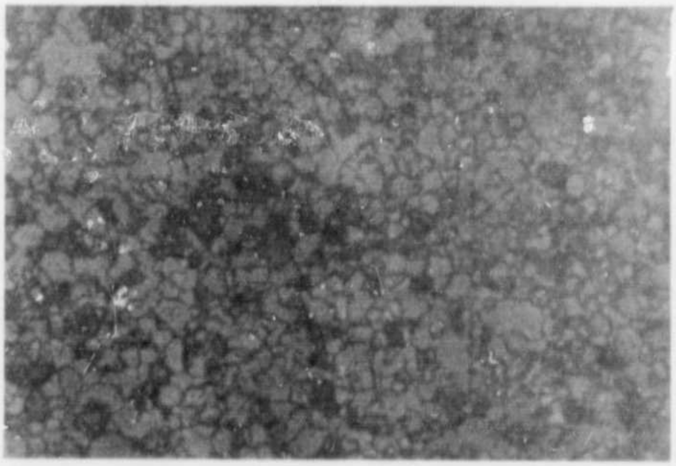

FIGURE 14

Photomicrographs of Final
Insulators S-11, Fired to 1870K