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HIGH-TEMPERATURE SENSORS FOR BORAX-V
BOILING FUEL RODS

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I. INTRODUCTION

As part of its design as a flexible reactor facility for testing various combinations of boiling and nuclear superheating cores, BORAX V is being instrumented to measure characteristics of the reactor fuel and coolant systems. One facet of the program has required the development of sensors for measurement of temperatures to 2760°C in the center of the UO_2 -fueled, boiling fuel rods. These high temperatures are expected to occur when the low thermal conductivity of the UO_2 fuel is combined with cases of flux peaking, low coolant flow, and maximum design power.

Thermocouples were proposed for measuring fuel temperature as a function of reactor power; this data later was to be correlated with postirradiation examinations of the fuel. A second use of the thermocouples would be to determine effective power generation rate per fuel rod by comparison of temperatures at various reactor locations. The postirradiation examinations, together with in-pile performance data, will, hopefully, lead to better information regarding in-pile thermal conductivity of UO_2 as a function of temperature and fuel burnup. These same examinations may also help to better understand the physical changes reported in UO_2 after undergoing irradiation. Some researchers have advanced the theory of fuel sublimation and recrystallization to explain the holes found in the center of irradiated UO_2 , whereas others explain the phenomenon by center-melting. Both theories need the support of temperature measurements above the ranges of conventional materials and techniques used in normal pyrometry.

II. SURVEY OF REQUIREMENTS FOR TESTING PROGRAM

A. Range of Temperature Measurement

A maximum temperature of 2760°C was set as the upper limit required for measurement, based on current data for the melting point of UO_2 . A minimum limit of about 260°C was desired to indicate fuel temperature rise above the reactor coolant temperature (254°C nominal).

B. Limitations of Size of the Temperature Sensor

Design of the boiling fuel rods limited the size of any central axial hole to a maximum diameter of 0.073 in. To limit the amount of fuel removed from the rod, it would be desirable to use a hole of smaller diameter, but practical limitations of thermocouple and fuel rod construction ruled this out. Penetrations into the 0.345-in. OD fuel pellets range from 6 to 18 in. in depth.

C. Commercially Available Materials and Temperature Sensors

Consideration was given to several measuring techniques, including resistance thermometry, radiation pyrometry, gas expansion, mechanical expansion, and thermoelectric devices. Primarily because of physical space limitations and the extreme environmental conditions, the last scheme was picked for development.

Generally available metallic-sheathed thermocouples are not suitable for direct application to the problem because of their temperature limitations and questionable radiation stability. When preliminary design was started on the fuel rod thermocouples, platinum/platinum-10% rhodium, platinum/platinum-13% rhodium, and iridium/iridium-40% rhodium were the only well-known thermocouple pairs used in the temperature range from 1649 to 1927°C. These compositions had at least one known area of unsuitability as regards radiation instability because of change of composition through neutron-capture transmutations.

Refractory metal thermo-elements had been used experimentally by various individuals, and the tungsten-molybdenum thermocouple had seen service as a device for steel-making temperature measurements as early as 1933. The latter was not favorably accepted because of "aging effects," nonreproducibility between batches, reversal of emf output polarity at about 1204°C, and susceptibility to contamination by atmospheric gases.⁽¹⁾ These couples, as well as others of compositions reported above, were not useful, if only because of their upper temperature limit of operation.

During this period of investigation, work was being performed by Lachman^(2,3) on the characteristics of various high-temperature thermocouples. Tungsten/tungsten-rhenium couples in various alloy combinations (W/W-26% Re, W/7% Re-W/26% Re, W-Re, etc.) were tested along with rhenium-molybdenum in attempts to establish useful materials having favorable electrical and physical characteristics. Other combinations of materials were being evaluated by other investigators for possible use at this same time. Some findings are reported by Anderson and MacKenzie.⁽⁴⁾

D. Sample Thermocouple Designs

Based on data by Lachman, the choice of tungsten/tungsten-26% rhenium was made for the thermocouple materials. This junction produces a useful emf vs temperature characteristic, but has one disadvantage in that the tungsten wire is subject to failure because of its extreme brittleness after operation at high temperature. An alternative choice for the tungsten wire would have been another alloy of tungsten and rhenium, such as tungsten-3% rhenium, tungsten-5% rhenium, or tungsten-7% rhenium.⁽⁵⁾ All such alloys, used as the positive wire of the couple, reduced the net output and introduced further nonlinearities to the calibration; therefore they were not considered at the time.

Having chosen the thermocouple materials, selection of insulation and sheath design remained. Factors influencing the choice of sheath material included:

1. melting point and practical maximum temperature limitation due to loss of strength;
2. chemical stability with respect to UO_2 fuel, gases in the surrounding atmosphere, and thermocouple insulation;
3. mechanical stability after thermal cycling and irradiation;
4. commercial availability of material; and
5. thermo-electric effects with fuel and possible effect on thermocouple.

The thermocouple insulation presented problems of its own; additional problems were related to the design of the complete thermocouple. These major factors were:

1. melting point or limit of maximum useful temperature;
2. electrical resistivity at elevated temperatures;
3. commercial availability of material;
4. adaptability to thermocouple fabrication;
5. chemical stability with respect to sheath and wires of the couple;
6. mechanical stability and thermal shock resistance; and
7. neutron cross section.

Data on electrical resistivity⁽⁶⁾ pointed to a choice between BeO and MgO for the insulating material. These two materials were available

from vendors in refractory metal sheaths of molybdenum and tantalum built to the required OD of 0.062 in. Tantalum was favored over molybdenum because of its higher melting point and because two investigators reported its compatibility with UO_2 to temperatures approaching 2760°C .^(7,8) Bradshaw and Matthews⁽⁹⁾ reported temperature limits for performance of BeO , MgO , and ThO_2 in oxidizing and reducing atmospheres and in vacuo, and Campbell reported the compatibility of these oxides with tungsten and molybdenum in vacuum.⁽¹⁰⁾

The nuclear cross sections of candidate materials were considered to the extent that none were found to be great absorbers. A detailed analysis of the thermal performance of an instrumented fuel rod was not performed, primarily because of complexity and small scale of the system.

The atmosphere surrounding the thermocouple sheath in a fuel rod has been purposely made as nonreactive as possible through an initial vacuum bake out and back-fill with helium. This should provide a good environment, at least for the initial stages of reactor operation.

III. TESTING PROGRAM

Because of the lack of data on thermocouple performance as a function of sheath and insulation selection, it was decided to obtain samples of tantalum-sheathed thermocouples with BeO and MgO insulation, and test these samples to failure.

A. Selection of Reference Design

Samples for testing were obtained in which 0.062-in.-OD tantalum sheaths and both MgO and BeO for insulation were used in two different groups. Tungsten vs tungsten-26% rhenium was utilized as the thermocouple pair. Some samples were supplied with welded hot junctions and others with open ends.

1. Electrical Characteristics of MgO- and BeO-insulated Samples at High Temperatures

Two types of thermocouples (seven pieces, total) were tested in selecting the reference design. Both types had tantalum sheathing and tungsten/tungsten-26 w/o rhenium wires. The only difference in materials was that MgO was used to insulate the wires from the sheathing in one type and BeO was used as insulating material in the other type.

Of the commercially available insulating materials, BeO and MgO have been reported to maintain a high degree of resistivity at elevated temperatures. Campbell⁽¹¹⁾ reports resistivities at 2100°C of 8×10^2 ohm-cm for BeO and 4.5×10^2 ohm-cm for MgO. For this reason, these two materials were used in combination with commercially available tantalum sheath and tungsten/tungsten-26 w/o rhenium wires as showing promise for high-temperature thermocouples.

The above samples were tested by Hoskins Manufacturing Company, Detroit, Michigan, in an argon-atmosphere furnace at temperatures ranging from 1760 to 2315°C. Thermo-electric characteristics of all "junctioned" thermocouples were determined, and some measurements of insulation resistance were made on open-ended samples. Table I shows the comparative performance of the BeO- and MgO-insulated samples tested.

Table II shows the difference between MgO and BeO in insulating qualities. A relatively high vapor pressure in the MgO-insulated sample was apparently responsible for the fumes which prohibited readings during furnace run No. 3. A large loss of MgO from Sample No. 5 was noted after shutdown.

Table I
THERMOCOUPLE CALIBRATION (FIRST TEST SERIES)

Furnace Run No. 1							
T/C-1		T/C-2		T/C-3		T/C-4	
Temp, °F	EMF, mv	Temp, °F	EMF, mv	Temp, °F	EMF, mv	Temp, °F	EMF, mv
489	1.529	492	1.554	494	1.560	497	1.576
990	5.391	991	5.427	992	5.387	993	5.438
1814	14.506	1814	14.501	1813	14.365	1812	14.377
3202	29.800	3200	29.850	3194	29.480	3190	29.140
4200	-	-	-	-	-	-	-
3207	28.453	3200	29.410	3197	29.066	3190	28.900
1818	14.480	1797	14.300	1798	14.205	1805	14.298
992	5.417	995	5.482	996	5.402	999	5.530
501	1.542	505	1.590	508	1.612	510	1.632
Furnace Run No. 2				Furnace Run No. 3			
T/C-4		T/C-4A		T/C-2A		T/C-4A	
496	1.546	496	1.510	500	1.592	504	1.507
1006	5.533	999	5.408	1006	5.557	1000	5.453
1793	14.025	1798	14.197	1800	14.217	1800	14.171
3198	28.860	3194	29.588	3203	32.135	3200	31.619
4001	33.745	4064	34.870	4200	-	-	-
Furnace Run No. 4							
T/C-1		T/C-2		T/C-3		T/C-2A	
3194	28.900	3196	28.790	3196	29.065	3204	17.575
4212	34.007	4202	34.555	4202	34.437	4202	26.746
3210	27.979	3200	28.380	3198	28.445	3204	17.127
						1800	11.162
						1000	4.510
						500	1.330

Notes: (1) T/C's 1 through 4 were MgO-insulated; T/C's 2A and 4A were BeO-insulated.

(2) A maximum temperature of 4200°F was reached, but data were not taken because of low readings, run 1, and fumes in furnace, run 3.

(3) Manufacturer's wire calibration is shown in Table VII.

Table II
RESISTANCE AND EMF MEASUREMENTS ON UNJUNCTIONED SAMPLES
(FIRST TEST SERIES)

Furnace Run No. 2								
Sample No. 6 (MgO Insulation)					Sample No. 8 (BeO Insulation)			
Temp, °F	Wire-Wire Resistance		Both Wires to Sheath		Wire-Wire Resistance		Both Wires to Sheath	
	Ohms (Fwd)	Ohms (Rev)	Ohms (Fwd)	Ohms (Rev)	Ohms (Fwd)	Ohms (Rev)	Ohms (Fwd)	Ohms (Rev)
500	6.7×10^6	7.2×10^6	4.3×10^6	7.3×10^6	162×10^6	100×10^6	8.3×10^6	23×10^6
1000	0.48×10^6	0.41×10^6	0.46×10^6	0.64×10^6	7.8×10^6	8.3×10^6	1.9×10^6	5.6×10^6
1800	47	139	95	120	52	128	81	138
3200	15.2	33.4	10.5	24	31.5	128	16.5	98
4050	1	-	-	-	-	-	-	-
Furnace Run No. 3								
Sample No. 5 (MgO Insulation)					Sample No. 7 (BeO Insulation)			
500	190×10^6	200×10^6	110×10^6	20×10^6	25.8×10^6	26.4×10^6	27×10^6	5.7×10^6
1000	3.2×10^6	3.1×10^6	5.9×10^6	5.1×10^6	1.4×10^6	1.1×10^6	6.3×10^5	1.2×10^6
1800	1.05×10^4	1.11×10^4	8.4×10^3	8.9×10^3	146	138	49	48
3200	15.7	13.3	11.4	10.3	23.8	23.9	13.6	12.9
Developed EMF - Furnace Run No. 2								
		Temp, °F*	Sample No. 8 EMF, mv	T/C-4A EMF, mv				
		3440	20.93	31.14				
		3840	31.14	33.65				
		3920	32.64	34.06				
		3960	33.21	34.21				
		4000	34.14	34.53				
		4050	34.94	34.72				
		4060	35.32	34.79				
		4080	35.44	34.87				

* These temperatures taken during heat-up and are accurate to approximately $\pm 50^\circ\text{F}$.

One unjunctioned sample was monitored for emf as well as resistance, and was found to develop a measurable emf at temperatures below 2800°F. The output of this sample was recorded at the higher temperatures and was shown to eventually overtake that of thermocouple No. 4A. This fact is of value as an indication that an open-circuited thermocouple is not completely useless at ultra-high temperatures.

Figure 1. Thermocouple Equivalent Circuit

The above performance also points to an important fact, usually neglected, and rightly so, in describing the performance of sheathed thermocouples at much-reduced temperatures. The simplified equivalent circuit of the thermocouple appears in Fig. 1. It can be seen that the couple consists, not only of a primary "hot junction" whose output is shunted by the low-resistance insulation, but also of other secondary junctions made between the wires of the couple and the sheath through the same insulation. A complex network results, whose final output voltage is dependent on hot-junction temperature, insulation material, sheath material, and, to some extent, wire diameter (because of its effect on resistivity and the corresponding variations in the network).

Because of all the above-mentioned variables, it is fairly obvious that calibrations of thermocouples made to the user's design specifications are necessary if any reliance is to be placed in data obtained from similar couples in actual service.

2. Post-high-temperature Metallurgical Examinations

Examination of the thermocouple specimens after testing consisted basically in noting physical appearance, metallographic examination of transverse and longitudinal sections, and comparison of results of the examination with what might be expected based on previously reported work.

External appearance of the thermocouples showed that reactions of some sort had occurred. It was also apparent that thermocouples containing MgO had undergone reaction at considerably lower temperatures than those containing BeO.

A transverse section through a thermocouple containing MgO and tested at 1760°C showed that the insulating material had undergone some reaction with the tantalum. In Fig. 2, evidence of a reaction between the oxide and sheath materials is clearly seen. Thermocouples containing MgO which were tested at higher temperatures also exhibited physical change. In one sample, the insulation had changed from the typical white oxide to a black, sintered reaction product. Thermocouple samples containing BeO exhibited little reaction at the lower testing temperatures, but noticeably greater reaction at the higher temperatures.

Micro 31329

Bright Field

250X

Figure 2. Transverse Section through Tantalum Sheath Tested at 1760°C Showing Apparent Reaction between MgO and Tantalum. In this thermocouple sample, a wire had been in contact with, and had adhered to, the sheath. At this point the wire, which is no longer present, was seated in the "saddle" formed by the oxide.

Sheathing of all samples was quite brittle; however, this brittleness was more pronounced in samples exhibiting greatest reaction tendencies. The thermocouple wires did not seem to be adversely affected by the tests performed at various temperatures. Typically, one wire was quite brittle and the other noticeably more ductile.

Aside from the effects of high-temperature testing, two types of defects were noted which were most likely introduced during fabrication. Examples were found of cracks emanating from the outside diameter of the sheathing. The most extensive crack found, shown in Fig. 3, points out the potential weakening of the tantalum sheath because of fabrication defects.

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Figure 3. Longitudinal Section through Tantalum Sheath Tested at 2315°C Showing Extensive Cracking Probably Introduced during Fabrication.

Another example of a defect probably introduced during fabrication can be found in Fig. 2. At this point, the oxide in contact with the sheath forms a curved "saddle" in which a thermocouple wire had been seated. Although the wire was pulled out during polishing operations, it had been in contact with, and had adhered to, the sheath at this point. It is obvious that contact between wires and sheath will cause erroneous temperature measurements.

3. Relative Merit of the Two Designs Tested, and Recommendations for Final Selection

a. Metallurgical Aspects. A knowledge of the expected properties of the thermocouple materials at elevated temperatures is necessary to establish a basis for performance evaluation. Consequently, a correlation has been made between observations during examination and claims made in several literature references.

b. Embrittlement of Tantalum. Miller⁽¹²⁾ states that the interatomic distance in tantalum is large enough to allow some interstitial solution of the small atoms hydrogen, carbon, nitrogen, and oxygen. Contamination of tantalum from atmospheres occurs readily and is not always detectable by simple microscopic examination unless very severe. Specimens from each of the seven thermocouple samples were metallographically prepared and examined. All of the samples exhibited contamination to some extent. Based on comparisons with Miller's conclusions, the contaminants

were mainly oxygen and nitrogen. Figure 4 is an example of what appears to be oxide precipitation from tantalum-oxygen solid solution. Figures 5 and 6 illustrate platelet-type oxide precipitation from solid solution. The presence of this type of oxide precipitate causes a large loss in ductility. The light-colored grain boundary precipitate shown in Figs. 6 and 7 is most likely nitride. Commercially pure argon gas contains small amounts of nitrogen, oxygen, and hydrogen and is therefore a potential source of impurities; however, contamination could have been introduced during fabrication of the sheathing.

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Figure 4. Longitudinal Section through Tantalum Sheath Tested at 2235°C Showing (Oxide) Precipitation from Solid Solution.

Micro 31331

Bright Field

250X

Figure 5. Longitudinal Section through Tantalum Sheath Tested at 1760°C Showing Platelet-type (Oxide) Precipitate.

Micro 31332

Bright Field

250X

Figure 6. Transverse Section through Tantalum Sheath Tested at 1760°C Showing Platelet-type (Oxide) Precipitate and Light-colored (Nitride) Precipitate.

Micro 31333

Bright Field

250X

Figure 7. Longitudinal Section through Tantalum Sheath Tested at 1760°C Showing Light-colored (Nitride) Precipitate.

c. Embrittlement of Tungsten. Due to the growth of extremely large grains, full annealing or recrystallization of tungsten embrittles the metal to a point at which it is difficult to use or handle. An explanation which has been offered for this phenomenon is that a film of foreign material, possibly absorbed gas, exists between the grains, even in the purest metal obtainable, and is the cause of weak intercrystalline cohesion.⁽¹³⁾ In addition, as explained by Schwartzberg *et al.*,⁽¹⁴⁾ ductile-brittle transition behavior characteristically occurs in the body-centered-cubic refractory metals. This transition results in greatly reduced low-temperature ductility and is a vital consideration in fabrication and handling of refractory metals at ambient temperatures. The transition is very pronounced in tungsten; however, it has not been observed in tantalum.

Cottrell's theory of dislocation locking by interstitial atoms⁽¹⁵⁾ is generally used to explain the yield-strength rise at low temperatures.

The effect of rhenium in improving the fabricability and ductility of tungsten is well-known.⁽¹⁶⁾ Recently reported work^(17,18) has shown that rhenium has two major effects when alloyed with tungsten; first is the formation of an oxide phase which does not wet the grain boundaries, and, second, an improvement in low-temperature ductility. The latter is a result of mechanical twinning which permits plastic deformation at low stresses, thus avoiding increased locking of dislocations at low-temperature and high-strain rates. Twinning has been observed at room temperature in alloys containing 22-30% Re, but decreases in quantity with increasing temperature.

A cross section of the brittle tungsten wire from one thermocouple specimen (see Fig. 8a) is seen to contain very large grains. On the other hand, the more ductile tungsten-26 w/o rhenium wire (see Fig. 8b) has many small grains per cross section.

8a. Wire exhibiting extreme brittleness typical of large-grained, fully annealed tungsten.

8b. More ductile wire showing much smaller grains typical of tungsten containing alloying addition.

Micro 31957

Bright Field

250X

Micro 31958

Bright Field

250X

Figure 8. Transverse Sections through Thermocouple Wires Tested at 1760°C.

d. Interaction between Ceramic and Metallic Materials.

Kerr⁽¹⁹⁾ has reported results of a limited study to obtain information regarding the compatibility of various refractory metals and oxides.

Although it is emphasized that the temperatures of the various reactions reported are only approximate, they are reproduced here to indicate relative orders of magnitude. The data in Table III were collected by resistance-heating metal strips in contact with the oxides in vacuo.

According to Campbell, for general stability with metals at very high temperatures, some of the most refractory of the oxides may be listed in the following order of increasing reactivity: ThO_2 , BeO , ZrO_2 , Al_2O_3 , and MgO .

A review of the observations and literature findings leads to the conclusion that BeO is a more suitable insulating material than MgO for the intended BORAX V application. The most important metallurgical advantage that BeO has is stability in contact with tantalum at higher temperatures. First reaction of MgO with tantalum, as reported by Kerr in Table III, occurs at approximately 1790°C , whereas no reaction was noted between BeO and tantalum until a temperature of approximately 2245°C was attained. Samples of thermocouples containing MgO which were tested up to 2315°C exhibited extreme brittleness and spalled sheathing. Greater stability of specimens containing BeO was apparent at the lowest and the highest testing temperatures.

Table III

APPROXIMATE TEMPERATURES ($^\circ\text{C}$) FOR INITIAL AND FAST REACTIONS BETWEEN OXIDES AND METALS*

Oxide	Metal			
	Tungsten		Tantalum	
	First	Fast	First	Fast
Al_2O_3	Melted	Melted	2045	Melted
BeO	2140	2310	2245	2355
MgO	2030	2495	1790	2000
ThO_2	No reaction up to 2645	No reaction up to 2645	No reaction up to 2795	No reaction up to 2795
TiO_2	1775	1780	1785	1785
UO_2	1785	2600	2295	2420
Y_2O_3	1865	2165	Very slight, 1705	Very fast, 2410
ZrO_2	2385	2390	1955	2125

*All temperatures shown are $\pm 50^\circ\text{C}$.

Interaction between either MgO or BeO, and tungsten, or W-26 w/o Re, wires does not appear to be a problem. Kerr reports first approximately 2030 and 2140°C, respectively. The reaction is apparently very slow, since none of the wires from the tested samples was significantly attacked. It is possible, however, that the tantalum oxide reactions proceed more readily than the tungsten or W-26 w/o Re-oxide reactions. In this event, once the reaction between tantalum and either of these insulating materials begins, any interaction involving the wires would be greatly reduced.

It can be expected that, at best, the tantalum sheath and tungsten wire will exhibit brittleness. This has nothing to do with the type of insulation used, but is due, rather, to the nature of these materials, as explained earlier.

e. Electrical Aspects. Data obtained from testing the above sample pieces showed the better electrical characteristics to be obtained through the use of BeO as an insulator, with the known limitation on maximum operating temperature imposed by metallurgical considerations.

4. Testing and Evaluation of Production Thermocouples

The full lot of thermocouples necessary for instrumentation of special fuel assemblies was ordered with BeO selected as the insulating material. From the same production run of material, the vendor, Continental Sensing Company, also furnished eight pieces, approximately 4 ft long, for destructive test purposes. These samples were then tested to determine the average performance of the production run of thermocouples.

a. Test Schedule. A total of eight production thermocouple samples, each approximately 4 ft long, was tested. The thermocouple wires were 0.010 in. in diameter and were fabricated from tungsten and a tungsten-26 w/o rhenium alloy. The sheath consisted of a seamless tantalum tube, 0.065 in.-OD with a 0.010-in. wall. A fine powder of BeO filled the annulus of the tube and served to insulate the wires from each other and from the tantalum sheath electrically.

Calibration tests to determine the temperature-millivolt equivalents for the thermocouples were performed by Thermatest Laboratories, Inc., Sunnyvale, Calif. The thermocouples were divided into two groups, and calibration tests were performed simultaneously on each of the four thermocouples within a group. Figure 9 illustrates the arrangement of test equipment.

Figure 9. Arrangement of Equipment for High-temperature Testing

appeared to be cracks ran along the length of the sheath to a distance of approximately 2 in. away from the hot junction (see Fig. 11). This end was very brittle and easily snapped in two during handling. By contrast, the opposite ends of the samples were ductile and no visible indication of any reaction could be seen. Metallographic samples were taken from both ends to compare the microstructures and to determine the extent of physical damage.

Examination of the test results and the calibration curves for thermocouples No. 1 through 4 revealed that an unexpected departure from linearity began to occur at approximately 1650°C (see Table IV and Fig. 10). Therefore, before the calibration tests on the second group were made, the initial group was returned to Argonne for metallographic inspection and evaluation.

(1) Metallurgical Tests.

The four thermocouples as received were 6 in. long, including the end which served as the hot junction. The samples were fused together at this end for a distance of 1 in. along the length. In addition, the surface of the tantalum was rough, and what

Table IV

TEMPERATURE-MILLIVOLT EQUIVALENTS FOR TUNGSTEN/TUNGSTEN-26% RHENIUM THERMOCOUPLES NOS. 1, 2, 3, AND 4

Temperature, °C			Millivolts*			
Chromel-Alumel Thermocouples	Uncorrected Optical Pyrometer	Corrected Optical Pyrometer	W/W-Re No. 1	W/W-Re No. 2	W/W-Re No. 3	W/W-Re No. 4
668			7.95	8.00	8.10	8.19
810	836	804	10.74	10.88	10.75	10.88
910	924	893	12.44	12.54	12.46	12.60
963	972	938	13.67	13.85	13.73	13.86
1049	1049	1015	15.33	15.44	15.35	15.45
1221	1224	1182	20.20	25.24	19.15	19.25
1304**	1296	1249	21.03	21.81	21.15	21.23
	1288	1260	20.37	16.60	20.38	20.31
	1588	1549	28.53	25.78	28.11	27.14
	1904	1860	29.97	30.49	30.28	29.73
	2124	2071	31.60	30.75	31.86	30.14
	2415†	2354	30.92	30.85	30.90	30.37

*73°F reference junction for W/W-Re thermocouples

**Chromel-Alumel thermocouples removed

†Calibration halted. Due to apparent failure of W/W-Re thermocouples Nos. 1, 2, 3, and 4, readings were not taken on the cooling cycle.

Figure 10

Temperature-Millivolt Equivalent of Tungsten/
Tungsten-26% Rhenium Thermocouples

Macro 33201

14X

Figure 11. Surface of Tantalum Sheathing after Testing
at 4600°F in an Argon Atmosphere

A transverse section through the fused area is shown in Figs. 12 and 13. These pictures illustrate that there definitely was a reaction between BeO and the tantalum sheath. Portions of the sheath wall were totally penetrated by the BeO. The oxide almost completely filled what was originally a void area formed where three thermocouples were in contact with each other. In Fig. 13, the gray areas correspond to BeO, the light areas to tantalum, and the dark areas are those void of any material. Considering the circular shape of the BeO particles, it is thought that this material was molten at some time during the test cycle. The highest temperature reached during testing was 2350°C. Kerr reports a fast reaction between BeO and tantalum at this temperature. The damage to the sheath was caused by the formation of a low-melting alloy or compound of BeO and tantalum at the interface. As the reaction continued, sections of the wall were destroyed and BeO particles escaped from the tubing. The presence of BeO outside the sheathing accounts for the fused section of the thermocouples.

Macro 33307

34X

Figure 12. Cross Section through Fused Tantalum Sheath Showing the Extent of Reaction between BeO and Ta.

Micro 33380

Bright Field

150X

Figure 13. Section through the Fused Sheathing Showing the Reaction that Occurred and the Presence of BeO Outside the Sheath.

In Figs. 14 and 15, transverse and longitudinal sections of the sheath from the unfused end are shown in comparison with similar sections from the fused end. The transverse section of the unfused end shows that a slight reaction between BeO and tantalum had occurred; however, the reaction did not progress much further than one-tenth of the wall thickness. This difference in reaction depth between the two samples indicates the presence of a considerable temperature gradient along the length of the thermocouples within the furnace. This theory is supported by the fact that the microstructures shown in the longitudinal sections are directionally oriented at the unfused end and recrystallized at the fused end.

A reaction also occurred between the BeO and the thermocouple wires. Figure 16 shows one of the wires at a point near the hot junction. The measured depth of reaction is 0.0007 in. Information reported by Kerr states that a fast reaction between tungsten and BeO begins at 2310°C, lower than that for a fast reaction of BeO with tantalum. Probably the main reason that a severe reaction has not occurred is due to the movement of BeO particles away from the wires toward and through the sheath wall.

Micro 33323

B.F.

250X

Micro 33321

B.F.

250X

Figure 14. Transverse Sections through the Unfused End (left) and the Fused End Illustrating the Original Structure of the Sheathing and the Porous, Recrystallized Structure of the Heated End.

Micro 33325

B.F.

250X

Micro 33324

B.F.

250X

Figure 15. Longitudinal Sections of Sheathing from Both Ends of Thermocouple. Unfused End is at Left.

Micro 33320

Bright Field

250X

Figure 16. Transverse Section through One of the Thermocouple Wires Showing Reaction between BeO and W.

The main temperature effect upon the wires was on the grain size (see Fig. 17). The wire with the smaller grains is the tungsten alloy. At 2350°C, the process of recrystallization and grain growth had begun within the wires. Although the large grains result in a brittle structure, this has little effect upon the material for use in a thermocouple. Figure 17 also shows the reaction layer within the two wires. There is little difference, if any, in the depths of penetration in the two wires. This indicates that alloying did not appreciably change the temperature at which a fast reaction between BeO and tungsten takes place.

Based on results of the metallographic evaluation of thermocouples Nos. 1 through 4, it was decided to limit the maximum calibration temperature on the second group to 2150°C. Still unknown is the reason for the lack of continuity in the curves beginning at 1650°C. This temperature is well below that temperature (2140°C) at which the first reaction between BeO and tungsten occurs. It is most probable that the difficulty arose in the test procedure or equipment, as it is not likely that all four thermocouples were defective. This seems especially true after the calibration curves were obtained on the second group, in which it was observed that the curves were essentially linear.

Micro 33326

Bright Field

150X

Figure 17. Transverse Section of the Two Thermocouple Wires from the Heated End.
BeO reaction with W (top) and W-26 w/o Re is essentially identical.

The second group of thermocouples was tested in a manner identical with that for the initial group, with the exception of the previously mentioned temperature limitation. The data obtained and the derived calibration curves are shown in Table V and Fig. 18. With the exception of thermocouple No. 5, the curves were linear. X-ray radiographs taken of these four samples after testing revealed a parting of the wires at the hot junction within thermocouple No. 5. This fact could account for the erratic data obtained on this specimen.

As with the first group, this latter batch was returned to Argonne for inspection and evaluation. The external appearances of the samples showed no evidence of any reaction.

Metallography was performed on thermocouples Nos. 5 and 8. These two were chosen because both had cracks at the tip of the hot junction. Figure 19 shows the cracks as they appeared in thermocouple No. 8. The cracks in No. 5 were more severe; however, this specimen was damaged in mounting, and a true indication of the nature of these defects could not be obtained. It is not known what caused the defect. The crack may have developed during the swaging operation, and thermal expansion could have caused propagation and widening of the defect. No other defects were found within the samples.

Table V

TEMPERATURE-MILLIVOLT EQUIVALENTS FOR TUNGSTEN/TUNGSTEN-26% RHENIUM
THERMOCOUPLES NOS. 5, 6, 7, AND 8

Temperature, °C			Millivolts*			
Chromel-Alumel Thermocouples	Uncorrected Optical Pyrometer	Corrected Optical Pyrometer	W/W-Re No. 5	W/W-Re No. 6	W/W-Re No. 7	W/W-Re No. 8
250			1.49	1.51	1.51	1.50
473			4.51	4.59	4.58	4.56
510			5.16	5.24	5.23	5.22
571			6.29	6.35	6.33	6.33
671			8.11	8.21	8.13	8.13
793	843	810	10.81	10.94	10.77	10.81
938	988	949	13.35	13.45	13.38	13.35
1021**	1060	1027	15.20	15.30	15.20	15.20
	1288	1260	20.28	20.37	20.38	20.34
	1538	1504	21.54	25.46	25.59	25.41
	1660	1621	23.75	27.73	27.93	27.63
	1746	1704	25.60	29.40	29.61	29.33
	1893	1849	28.40	32.06	32.20	31.89
	1993	1949	29.77	33.63	33.78	33.46
	2093	2043	35.38	35.35	35.50	35.29
	2204	2149	34.85	36.62	36.93	36.66
	2093	2043	33.56	35.30	35.64	35.18
	1982	1993	30.68	33.55	33.79	33.28
	1871	1826	28.55	31.77	31.95	31.40
	1760	1718	26.35	29.57	29.77	29.18
	1649	1610	24.25	27.29	27.46	26.78
	1538	1504	22.53	24.91	25.11	24.39
	996	971		11.54	12.34	11.06

*72°F reference junction for W/W-Re thermocouples

**Chromel-Alumel thermocouples removed for all settings after this temperature. They were not replaced for the settings below 2000°F on the cooling cycle.

Figure 18

Temperature-Millivolt Equivalent of Tungsten/
Tungsten-26% Rhenium Thermocouples.

Micro 33942

Bright Field

75X

Figure 19. Cracks in the Sheath of Thermocouple No. 8 after Calibration Tests Performed at Temperatures up to 2150°C.

Figure 20 is a photomicrograph of a transverse section through thermocouple No. 8 at a point $\frac{1}{4}$ in. away from the hot junction. No visible reaction zone between the sheath and BeO or between the wires and BeO was observed. The BeO was powdery and had not been sintered as were the samples from the other group.

(2) Electrical Tests. As mentioned previously, tests on these eight samples were run in two groups of four each because of the erratic performance exhibited by the first four. Figures 10 and 18 show the individual thermo-electric performance curves of the two sample groups. The second group of thermocouples more nearly matches the calibration curve for the wire supplied by Hoskins Manufacturing Company, although all samples were made from the same materials throughout.

Micro 33966

Bright Field

75X

Figure 20. Transverse Section of Thermocouple No. 5 at a Point 1/4 in. Away from the Hot Junction. This sample was tested at temperatures up to 2150°C with no visible reaction occurring between BeO and tantalum or tungsten.

Only one explanation seems to account for the performance exhibited, even though the possibility is remote. The extreme hygroscopic action of most swaged ceramic materials is well known, and it was believed that a short exposure to humid air at room temperature during the test connection installation may have admitted sufficient moisture to initiate insulation breakdown at elevated temperatures. (The test lead connections had been sealed to the sample sheaths with epoxy resin, making them watertight.)

To help avoid the same occurrence during testing of the second group of four samples, the extra precaution was taken of oven baking all samples for about 4 hr at 149°C, cutting off a short length of sample, meggering same at 500 v dc (100 megohms wire-to-wire resistance),

connecting test leads to samples, and then sealing connections with epoxy resin. Since the second group of four appeared to behave more in line with expectations, the above reasoning may have been correct.

A composite curve showing data points for all eight samples against the curve plotted from data furnished on the W/W-26 w/o Re wire is shown in Fig. 21. Note that the curve shown is not applicable to the material later furnished by Hoskins Manufacturing Company, which is identified by their designation of "Sept. 11, 1961" standardized calibration for W/W-26 w/o Re thermocouple materials.

Figure 21. Standard Calibration Curve and Test Data Points for Thermocouples Nos. 1 through 8.

IV. CONCLUSIONS

The exact reason for the failure of the first group of thermocouples at 1650°C remains unknown. However, the agreement between results of testing on the second group with available literature reports indicates that anomalies existed in the testing procedures for the first group.

Evaluation of eight production thermocouples has shown that the maximum temperature which these thermocouples can measure accurately is approximately 2200°C. The limiting factor is the temperature at which a reaction between BeO and tantalum begins.

From the series of samples tested, it was decided to utilize the standard calibration curve described by Fig. 21 and Table VI. A potentiometer-type recorder was fitted out with a balancing slidewire designed to best match this curve and will be used for recording data obtained from the in-core thermocouples.

Table VI

TEMPERATURE-MILLIVOLT CALIBRATION DATA FOR
TUNGSTEN/TUNGSTEN-26% RHENIUM THERMO-
COUPLES (PRE-"1961 STANDARD")

Calibration Applicable to One 97-Foot Wire Lot Used in
Manufacture of Thermocouples Nos. 1 through 8

Temperature, °F	EMF, Millivolts	Temperature, °F	EMF, Millivolts
200	0.290	2200	18.85
400	1.02	2400	21.18
600	2.19	2600	23.42
800	3.66	2800	25.59
1000	5.40	3000	27.68
1200	7.40	3200	29.60
1400	9.54	3400	31.49
1600	11.77	3600	33.25
1800	15.08	3800	34.89
2000	16.41	4000	36.45
		4200	37.92

V. RECOMMENDATIONS FOR FUTURE WORK

A. Improvement of Material

1. Metallurgical Aspects

The maximum temperature to which the reference thermocouple can be expected to perform dependably is approximately 2200°C. It has been shown that the factor which prevents a higher effective temperature is the interaction which occurs between BeO and tantalum above 2200°C. An approach to the development of a dependable thermocouple design for measurement of temperatures above 2200°C is to find an insulating material which will have greater stability in contact with tantalum at higher temperatures. Selected properties of some of the most promising refractory oxides for high-temperature use have been presented by Campbell and are compiled in Table VII.

Table VII
PROPERTIES OF REFRACTORY OXIDES

Material	Melting Point °C	Limit of Usefulness in Oxidizing Atmospheres °C	Coefficient of Expansion		Thermal Shock Resistance	Stability		Resistivity		Temp of Appreciable Volatility in Vacuum, °C
			Temp Range °C	E x 10 ⁻⁷		Reducing Atmosphere	Metals	Temp °C	Ohm-cm	
Al ₂ O ₃	2015	1950	20-1580	80	Good	Good	Good	1100	1 x 10 ⁶	
BeO	2550	2400	20-1400	95	Excellent	Excellent	Good	1100 2100	5 x 10 ⁶ 8 x 10 ²	2100
MgO	2800	2400	20-1400	140	Fair	Poor	Fair	2100	4.5 x 10 ²	1600
ThO ₂	3300	2700	20-1400	95	Poor	Good	Excellent	1200 2050	1.5 x 10 ⁴ 1.0 x 10 ⁴	2300
ZrO ₂	2600	2500	20-1200	55	Fair	Good	Good	1200 2000	3.6 x 10 ² 1 x 10 ⁰	2300
HfO ₂ *	2777	-	-	-	-	-	-	1500 (lower at higher temp)	1 x 10 ³	-

* Similar to ZrO₂ in most properties.

Courtesy of John Wiley and Sons, Inc., New York

Aluminum oxide is chemically one of the most stable and mechanically one of the strongest of the refractory oxides. Its principal limitation is a relatively low melting point. Alumina is very stable in the presence of both oxidizing and highly reducing atmospheres, and can be used in either type of atmosphere at temperatures up to about 1900°C.

Beryllium oxide has great thermal stability and particularly high resistance to reduction. It has unusually high thermal conductivity and very low electrical conductivity. At high temperatures, it has higher electrical resistivity than all the oxides listed in Table VII except ThO₂.

The high thermal conductivity coupled with a moderate and uniform thermal expansion makes it very resistant to thermal shock. Beryllia has relatively low vapor pressure and can be used in vacuum at temperatures up to about 2000°C. It is readily volatilized by water vapor at temperatures above 1650°C.

Hafnium oxide and zirconium oxide have similar properties. Both exhibit high chemical inertness and relatively low vapor pressures at high temperatures. They are stable in oxidizing and moderately reducing atmospheres, and in contact with many metals. They have low thermal conductivity and fair resistance to thermal shock. Although these oxides are classed as nonconductors at room temperature, they lose most of their resistivity at elevated temperatures and therefore, are not suitable as high-temperature insulators.

Magnesium oxide has very high thermal expansion, but in oxidizing atmosphere it can be used at a higher temperature than alumina. It is easily reduced at high temperatures and volatilizes at temperatures much above 2300-2400°C. In reducing atmospheres, it is limited to about 1700°C, and because of its high vapor pressure it cannot be used above 1600-1700°C in vacuum. MgO has a relatively high electrical resistivity, even at high temperatures.

Thorium oxide has very low vapor pressures at high temperatures and is the least attacked of the refractory oxides by most metals. ThO₂ has somewhat lower thermal conductivity than Al₂O₃, but slightly greater thermal expansion, both properties contributing to rather poor resistance to thermal shock. Thoria has high thermal resistivity at high temperatures. The greatest drawback with thoria is its very low strength above 1000°C. However, for use as a thermocouple insulator this is not an important factor.

Of the refractory materials presented here, ThO₂ has the greatest stability in contact with metals in general. A reference thermocouple consisting of W-W/26 w/o Re wires, tantalum sheathing, and ThO₂ insulation would have greater inherent chemical inertness than designs using any of the other oxides investigated. The only obvious limitations on service of a thermocouple with this reference design is the melting point of tantalum (2996°C), since the melting points of the other materials (W-W/26 w/o Re wires and ThO₂) are higher, and the fact that thorium is a source fissionable material. This latter factor might affect the reaction within the fuel rod or result in erroneous temperature readings due to fission within the thermocouple. Because of the small scale involved, the removal of enriched U²³⁵, and substitution of a thorium compound along with the other elements, makes an exact analysis of errors of temperature measurement too complex.

Another approach to a higher-temperature design is to use sheathing which has greater stability in contact with BeO than tantalum. Although the tungsten or W/26 w/o Re wires were not as strongly attacked by BeO in the samples tested, it is not definitely known whether the presence of tantalum tended to reduce the reactions involving the wires, or whether the wires are actually highly stable in association with the oxide at the temperatures of testing. According to Kerr, however, a fast reaction between tungsten and BeO occurs above 2300°C.

In considering possible combinations of the materials investigated, a tungsten-sheathed thermocouple with ThO₂ insulation and W-W/26 w/o Re wires cannot be overlooked. However, the lack of ductility of tungsten presents a problem of sheath fabrication and would greatly increase the inherent brittleness of the thermocouple. The fabrication of a thermocouple sheath from W-26 w/o Re is more feasible. Although this alloy does undergo a ductile-brittleness transition, it can be readily fabricated at 1000°C because of the redistribution of oxygen as a new phase. As mentioned previously, because the alloy is subject to mechanical twinning, its low-temperature ductility is also much greater than that of tungsten.

Another approach to the problem of avoiding a brittle junction is explained by Driesner *et al.*,⁽²⁰⁾ and consists of making the hot junction by mechanical means only, to avoid the initially recrystallized metal which is formed by the common technique of welding the hot junction.

Brittleness is, perhaps, not an important consideration in selecting a thermocouple for this particular reactor application. It should be mentioned in passing that, if more ductile metal components could be used in high-temperature thermocouples, the tendency toward cracking of the sheath or wires would be reduced, and the overall dependability and versatility of the thermocouple would be increased.

2. Electrical Aspects

The improvement of insulator resistivity at high temperatures can best be accomplished by reduction of impurities which provide free charge carriers at temperature extremes. Ryshkewitch⁽²¹⁾ indicates that thorium can take other oxides into solution in appreciable concentrations without changing its lattice structure, but with serious increase in electrical conductivity. Materials mentioned, which are to be avoided, include oxides of cerium, zirconium, calcium, and lanthanum. Copper, magnesium, and aluminum are also to be avoided, since thorium oxide is reducible in their presence at high temperatures.

3. Additional Developmental Work

Based on the above test results, recommendations for better materials, and the recent availability of same, a new group of test samples is now being procured and testing is arranged for.

The latest samples will be fabricated with W/W-26 w/o Re as the thermocouple, W-26 w/o Re as the sheath material, and thorium oxide insulation meeting the following chemical analysis:

Fe - 50 ppm maximum	La - 5 ppm maximum
Ca - 50 ppm maximum	Ce - 5 ppm maximum
*Mg - 300 ppm maximum	Zr - 20 ppm maximum
Na - 10 ppm maximum	Ti - 50 ppm maximum
Li - 5 ppm maximum	C - 50 ppm maximum
*Si - 500 ppm maximum	H - 20 ppm maximum
B - 10 ppm maximum	N - 50 ppm maximum
*Al - 500 ppm maximum	ThO ₂ - Balance

*Best capabilities of ceramic supplier

The hot junction is to be formed by swaging of the sheath onto the thermocouple wires which will be backed up by a tungsten pin. The pin and sheath will be welded for a backup seal only. The six samples will be tested in two groups of three each to a maximum proposed temperature of 2760°C. Metallurgical examinations will follow the tests in the same way as previously.

B. Suggestion of a New Measuring Device

Another technique, investigated only on a theoretical basis, might apply to other systems not so restricted in size but still limited in the application of more conventional optical techniques. Application of a thermionic diode is proposed as another solution to the problem of high-temperature measurement.

Each specific application would again have its problems of materials; however, many materials are available which would at least have suitable emission characteristics for use in vacuum or gas-filled envelopes. The logarithmic emission characteristics and small sizes of most useful devices would probably limit their application to measurement of temperatures above 1500°C. Insulation, in high-temperature regions, for a sensor of this type would again be a serious problem, since the diode would be a high-impedance device, and would also need structural strength and stability to maintain critical electrode spacing.

A simplified diagram of a theoretical diode and circuit is shown along with a calculated performance curve in Fig. 22. Such a probe might prove possible in applications where depths of insertion in hot zones are less than

those of BORAX V and where diameter is not such a problem. The choice of vacuum or gas-filled envelopes should consider the contribution to current output by any radiation fields present at the detector.

Figure 22

Thermionic Diode
and Theoretical
Performance Curve

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