9. FAST BREEDER REACTOR THERMOCOUPLE DEVELOPMENT

(1414)

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The objective of this program is to identify and establish the properties of reliable high-temperature thermocouple, electrical, and electronic materials to provide instrumentation and electrical components for use in fast breeder reactors.

9.1 W VERSUS W - 25Re THERMOCOUPLE CHARACTERISTICS AT HIGH TEMPERATURE

Determining the centerline fuel temperature of LMFBR fuel elements requires temperature measurements to approximately 2500°C. Thermocouple systems used to measure this temperature must be constructed of materials that are metallurgically and chemically compatible with each other and with the anticipated environment. Although these materials may be compatible, the electrical properties (resistivity and thermoelectric power) of the sheath, insulators, and environmental gas may still influence the thermoelectric signal, making validity of indicated temperatures uncertain. Loss of effective electrical insulating properties of ceramic oxides when used in conjunction with a high resistance of thermoelements has been observed at high temperatures by several investigators,^{1,2} and this effect was measured as a function of temperature.

Investigations during the past year have been primarily concerned with the many factors influencing the thermoelectric output generated in a thermocouple system. The various parameters that have received attention are: effects of gaseous environments, size of thermocouple wires, electrical insulation, and sheathing materials. By varying materials combinations and gaseous environments, and measuring the thermoelectric output as a function of temperature against calibrated standards, abnormal thermoelectric responses could be easily detected. Thermocouples using wire of 0.125-mm and 0.25-mm diameter were made and tested to determine whether optimization of wire diameters would be necessary. Electrical insulating characteristics of thorium and hafnia were compared at temperatures ranging from 1600° to 2600°C. Research on different sheathing materials has been limited to the Mo - 50Re alloy tubing and pure molybdenum tubing. The effects of high-temperature gaseous environments on the thermoelectric response from W versus W - 25Re thermocouples were determined in hydrogen and helium. An in-pile nuclear irradiation program was performed to determine the reactor stability of W versus W - 25Re thermocouple systems. Data were obtained showing thermoelectric deviations as a function of temperature and neutron dosage. Each parameter investigated and significant results and conclusions of the individual experiments are discussed and illustrated.

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‡All compositions are in weight percent unless otherwise noted.

¹E. A. Brown, B. G. Goodier, J. E. Perry, Jr., R. L. Petty, W. R. Prince, and C. R. Tallman, "Thermocouple Development for Project Rover," High Temperature Thermometry Seminar, Washington, D.C., February 24-26, 1965, WASH-1067.

²G. F. Popper and T. Z. Zeren, "Refractory Oxide Insulated Thermocouple Analysis and Design," High Temperature Thermometry Seminar, Washington, D.C., February 24-26, 1965.

ELECTRICAL INSULATION EVALUATION

Comparative tests were made at temperatures ranging from 1600° to 2600°C to determine the electrical insulating properties of the hafnia and thoria insulators. The construction of each thermocouple used was essentially identical for these experiments, except for insulating materials and the web thickness between the two thermocouple holes separating the thermocouple legs. The web thickness of the HfO_2 insulator measured 0.3 mm; the ThO_2 insulator had a web thickness of 0.75 mm. No sheathing was used, and tests were performed in an electrical heat-resistant furnace (Figure 9.1). Both helium and hydrogen atmospheres were used as test environments. The differences in thermocouple response during the experimental testing for electrical insulating characteristics are shown in Figure 9.2. The thermoelectric signals measured are shown by two curves which reveal that the thermocouple insulated with HfO_2 had the strongest thermoelectric response, even though the web thickness separating the W and W - 25Re thermoelements was less than one-half the thickness of the ThO_2 insulator.

EFFECT OF GASEOUS ENVIRONMENT

The next series of tests were primarily to establish effects on the thermoelectric response from thermocouples insulated with HfO_2 and ThO_2 when used in hydrogen or helium environments. The thermocouples were made of 0.25-mm stranded W and W - 25Re alloy wire. The stranded wires were separated with HfO_2 and ThO_2 electrical insulators. The

Fig. 9.1 — Test equipment to measure thermoelectric and thermionic anomalies in thermocouple wires

Fig. 9.2 — Comparative curves showing measured thermoelectric signals as a function of temperature in helium atmosphere from W versus W — 25Re thermocouples insulated with thoria and hafnia

HfO₂ insulator measured 2.1-mm OD with two 0.6-mm holes. The ThO₂ insulator measured 3-mm OD with two 0.3-mm diameter holes. The thermoelectric output as a function of temperature was determined using a direct-current electrical heat-resistant furnace (Figure 9.1). Initially the thermoelectric response of HfO₂-insulated thermoelements was measured in a hydrogen environment. After data had been compiled, the system was purged with helium and electrical measurements were taken in helium. The experiments were repeated using thermocouples insulated with thoria. The changes measured are graphically illustrated in Figure 9.3. The two sets of curves show that the response was lowered considerably for the ThO₂-insulated thermocouple in hydrogen. The helium atmosphere shifted the thermoelectric output downward, but its overall effect was far less than hydrogen on the thoria insulator. The data show that hafnia as an electrical insulator is much less affected by hydrogen or helium atmosphere. All measurements in this series of tests were referenced against black-body measurements using an optical pyrometer calibrated against a NBS calibrated instrument.

SHEATHING STUDIES

Concurrent with the tests on thermocouple evaluation, test thermocouples were sheathed in molybdenum and Mo — 50Re alloy seamless tubing. Measuring the voltage output as a function of temperature for thermoelements insulated with HfO₂ or ThO₂ in either hydrogen or helium gas showed only relatively small changes from calibrated values. The direction of the small shift in voltage output was similar to those previously determined for unsheathed thermocouples.

EFFECT OF UNMATCHED THERMOCOUPLE WIRE DIAMETERS

To determine the effect of unmatched wire sizes in the construction of a thermocouple probe, a series of tests was initiated studying the effects of unmatched pairs on the emf signal. Wire sizes chosen were 0.25-mm- and 0.125-mm-diameter W and W — 25Re. Unmatched systems were made using 0.25-mm W versus 0.125-mm W — 25Re wire; the matched thermocouples had only 0.25-mm-diameter wire. The wires comprising the two thermoelements of the couple were separated physically by HfO₂ ceramic insulation. The thermoelements and electric ceramic insulator were sheathed in Mo — 50Re and unalloyed molybdenum tubing.

Fig. 9.3 — Comparative curves showing measured thermoelectric signals as a function of temperature in hydrogen and helium from W versus W — 25Re thermocouples insulated with thoria and hafnia

The insulation and sheathing materials were selected for their maximum reliability in high-temperature thermocouple measurements, as shown by previous studies. The major variable in the thermocouple probe was in wire diameters. Testing was again performed in a direct-current electrical heat-resistant furnace (Figure 9.1). The thermoelectric signals were measured against a standard calibration for the W versus W — 25Re wire. Temperatures were verified against optical pyrometer temperature readings on a black-body hole. The family of four curves shown in Figure 9.4 represent the deviations found, and appear to be well within the sensitivity of measuring techniques. The curves overlap each other up to 2200°C. In the higher temperature ranges the spread is insignificant.

These tests strongly indicate that thermoelement wire sizes do not need to be matched in thermocouple systems.

9.2 ELECTRICAL INSULATION FOR HIGH-TEMPERATURE THERMOCOUPLES

A vital part of the thermocouple system is the electrical insulator. Measuring temperatures up to 1700°C is usually fairly easy, because there is a wide choice of materials. Alumina is generally preferred for its economy, excellent electrical insulator properties, and fabricability in all sizes.

For temperature measurements above 1700°C the choice of materials narrows. In an attempt to expand present choices and discover better insulator materials, work was undertaken on compound oxide systems. Previous research studies^{3,4} showed that the CaZrO_3 system had a potential for high-temperature insulation. Although its melting point was not high enough ($\sim 2375^\circ\text{C}$), similar compounds such as SrHfO_3 , SrZrO_3 , and CaHfO_3 have higher melting points: 2680° , 2550° , and 2500°C , respectively. These materials have been considered possible insulators of thermocouples for center-core fuel element temperature measurements above 2500°C . Initial studies were made below

³"AEC Fuels and Materials Development Program Progress Report No. 69," GE-NMPO, GEMP-69, September 29, 1967, pp. 67–69.

⁴"Sixth Annual Report — High-Temperature Materials Program, Part A," GE-NMPO, GEMP-475A, March 31, 1967, pp. 270–271.

Fig. 9.4 — Comparative curves showing measured thermoelectric signals generated between matched and unmatched wire sizes as a function of temperature

this temperature so that the insulators could be compared with BeO (MP-2450°C), the highest resistivity insulator currently available as a thermocouple insulator.

In three separate tests, each of the above insulators was evaluated by comparing the thermoelectric output of W versus W - 25Re thermocouples insulated with BeO and one of the above three materials. The thermocouples to be compared were placed in Mo - 30Re sheaths which were closed only at the hot end. The sheathed thermocouples were placed together in an apparatus similar to that shown in Figure 9.1. Temperatures measured were referenced against black-body hole temperatures determined by a NBS calibrated optical pyrometer. The calibrations of the three different BeO-insulated thermocouples in all three tests were identical within ± 0.5 percent of the same temperature for the same millivoltage output. The thermoelectric outputs of the SrZrO_3 -, SrHfO_3 -, and CaHfO_3 -insulated thermocouples were within ± 0.5 percent of the BeO-insulated thermocouples up to 2000°C. Above this temperature, deviations occurred which are shown in Figure 9.5. The curve for SrHfO_3 shows the least deviation from the BeO-insulated thermocouple of the three materials and is therefore a potential high-temperature thermocouple insulator.

INTRINSIC VARIABLES AFFECTING THERMOCOUPLE VOLTAGE

During the course of thermocouple testing, several synergistic effects were noted which resulted in abnormalities of the thermocouple signal, especially above 2000°C. In laboratory tests exploring these effects, experiments were performed on a non-insulated loop of W wire and on a HfO_2 -insulated loop of W wire inserted into a high-temperature furnace; the thermoelectric output between the two ends of the W wires was measured. Appreciable electric outputs were obtained in both cases, although theoretically no output should be obtained.

In the test furnace (Figure 9.1) an electrically insulated W T-bar made of 3-mm-diameter material was suspended inside a W muffle. Two 0.05-mm-diameter W wires, one with and one without an electrical insulator, were connected to the W T-bar as shown. This assembly was suspended in a resistively heated W tube furnace. Thermoelectric potential measurements were made between the W T-bar and both the bare and insulated 0.05-mm-dia-

Fig. 9.5 — Thermoelectric output of W-versus W — 25Re-stranded wire (ten 0.075-cm thick wires) thermocouples using BeO, SrZrO₃, SrHfO₃, and CaHfO₃ for electrical insulation in hydrogen or helium

ter wires as a function of temperature. Temperatures were measured using an optical pyrometer by focusing on the bottom surface of the W muffle. The relatively large-diameter (3 mm) W T-bar was used to provide a thermoelectrically stable reference material which could then be used to measure thermoelectric anomalies in the small-diameter W wires by forming an electric circuit with the 0.05-mm-diameter wires. A thermoelectric study was made on bare 0.05-mm wires and on 0.05-mm wires surrounded by BeO or HfO₂. Small-diameter (0.05 mm) wires were used because it was believed they would give an exaggerated effect to any causes of abnormalities.

The curves shown in Figures 9.6 through 9.8 are plots of measured voltage changes as a function of temperature between the W T-bar and either the 0.05-mm-diameter W wire or the BeO-insulated 0.05-mm-diameter W wire in hydrogen, helium, or argon. Each test was run with a new piece of 0.05-mm-diameter W wire. In these three curves, the thermoelectric output developed between the reference W T-bar and the BeO-insulated 0.05-mm-diameter W wire was more consistent than between the W T-bar and the bare 0.05-mm-diameter W wire, as the environmental gas was changed from hydrogen to helium to argon. The reference W T-bar versus 0.05-mm W bare wire output in hydrogen increased rapidly to approximately 0.6 millivolts and then remained fairly steady to 2000°C. In argon the output increased to approximately 1800°C, then began to decrease. In helium, the output increased rapidly to approximately 1.7 millivolts at approximately 1872°C, three times the values in hydrogen or argon.

This wide variation in thermoelectric signals generated between the tungsten T-bar versus bare tungsten wire in the three gases, compared to the relatively stable signals found in the insulated wire in the same gases, suggests that insulation prevents pickup of extraneous electrical signals within the muffle.

The electrical measurements made in the specialized setup (Figure 9.1) indicate that the calibration of bare wire thermocouples must be done with care since there are a number of possible sources leading to errors in calibration measurements:

Fig. 9.6 — Measured thermoelectric voltage in a hydrogen atmosphere test apparatus (Figure 9.1) designed to detect causes of anomalies noted during thermocouple calibration experiments

Fig. 9.7 — Measured thermoelectric voltage in an argon atmosphere test apparatus (Figure 9.1) designed to detect causes of anomalies noted during thermocouple calibration experiments

Fig. 9.8 – Measured thermoelectric voltage in a helium atmosphere test apparatus (Figure 9.1) designed to detect causes of anomalies noted during thermocouple calibration experiments

1. Electrical leakage through the insulation.
2. Electrical leakage through ionized gases.
3. Induced emf if container is charged.
4. Thermionics.
5. Thermoelectric effect between "insulator" and thermocouple wire.

9.3 THERMOELECTRIC CHANGES IN W – 25Re DUE TO TRANSMUTATION

The thermoelectric changes of an alloy representing the composition of W – 25Re after 1 year in 10^{14} neutron/cm²-sec thermal flux was previously evaluated and described in detail.⁵ Theoretical calculations on transmuted effects indicate that the W – 25Re alloy composition will change to W – 21.5Re – 5.4 Os (at. %) after 1 year. An alloy rod of this composition was fabricated for thermoelectric tests after heat treating at 2770°C for 3 hours; it was a single-phase alloy. When this rod was placed in a calibrating furnace which imposed a temperature gradient from room temperature to 2300°C along its length, two other phases precipitated in the rod between 2000° to 2300°C causing inhomogeneities along the rod length. This temperature-induced inhomogeneity caused differences (as much as 0.9 mv) in the emf-versus-temperature relationship, depending upon whether calibration was made while increasing or decreasing the temperature. The combination of neutron-induced thermoelectric changes (transmutation) and temperature-induced thermoelectric changes (phase precipitation) would make questionable the use of W–25Re as a thermoelement for temperature measurements when 1-year exposure in a 10^{14} neutron/cm³-sec thermal flux is required.

REACTOR STABILITY OF W VERSUS W – 25Re THERMOCOUPLE

A second reactor test of W versus W – 25Re thermocouples was performed under conditions very similar to one previously reported.⁶ This test was designed to measure the neutron-induced thermoelectric changes in the W and W – 25Re thermoelements and to

⁵GEMP-69, pp. 67–69.

⁶GEMP-475A, pp. 268–270.

minimize the uncertainty previously experienced⁷ in interpreting data relating to the W-25Re leg. The test had considerable difficulty with W wires breaking; the small amount of W data obtained were inconclusive. Figures 9.9 and 9.10 show the results of thermoelectric deviations of W and W-25Re as a function of temperature and time in the ORR with a flux of 1.2×10^{14} neutron/cm²-sec thermal and 2.1×10^{13} neutron/cm² sec fast ($E_n \geq 1$ Mev). Data of Figure 9.9 indicate that the W thermoelement at low temperature (600°C) becomes more thermoelectrically positive with dosage, and at approximately 1400°C changes very little with dosage. At approximately 1800°C no data were obtained, but the shape of the curve indicates that W becomes more thermoelectrically negative in this region. The W data appear to confirm previous findings⁶ although at 600°C the latest test shows a greater positive increase in thermoelectric potential. The data of Figure 9.10 for W-25Re indicate that the shapes of the curves are very similar to those obtained for W; this differs from conclusions of the first test⁷ whose data were difficult to interpret. The similarity of the W and W-25Re curves indicates that changes in the W thermoelement are compensated by changes in the W-25Re thermoelement. There is a degree of difference between the W and the W-25Re thermoelectric changes which results in a small net increase in thermoelectric output of a W versus W-25Re thermocouple. For the time period represented by the two curves, the maximum increase in indicated temperature would be approximately 5°C.

Fig. 9.9 — Relative stability of W thermoelements as a function of temperature and time in a 1.2×10^{14} n/cm²-sec thermal flux

REACTOR TESTING OF THERMOCOUPLE MATERIALS

Test capsules containing 0.25-mm-diameter wires of W, W-25Re, W-3Re, Mo, Fe, Chromel, Alumel, Constantan, BeO, and Al₂O₃ were shipped to the EBR-II. They were originally scheduled for insertion in December 1967, but have been delayed until March 1968. These capsules contain 15-cm lengths of the above thermocouple materials. After exposure to approximately 10^{22} to 10^{23} neutron/cm² fast neutrons, all materials will be removed from the reactor and each will be compared thermoelectrically in the laboratory with unirradiated specimens of the identical materials.

9.4 SUMMARY AND CONCLUSIONS

Studies of very high-temperature thermocouple characteristics revealed that the thermoelectric emf produced along BeO, HfO₂, or ThO₂ insulators can affect the output of the

⁷"High-Temperature Materials Program Progress Report No. 63," GE-NMPO, GEMP-63, December 30, 1966, pp. 129-133.

Fig. 9.10 — Relative stability of W — 25Re thermoelements as a function of temperature and time in a 1.2×10^{14} n/cm²-sec thermal flux

thermoelements. Bare-wire thermocouples were found to be influenced by the environment.

The nuclear radiation effect on W versus W — 25Re thermocouples in the ORR after approximately 2 months in a 1.2×10^{14} neutron/cm²-sec thermal and 2.1×10^{13} neutron/cm²-sec fast flux was studied. Results indicate that the W and the W — 25Re thermoelements shift similarly in thermal emf, resulting in a small (5°C) positive error.

SrHfO₃, SrZrO₃, and CaHfO₃ were found to be inferior to BeO and HfO₂ as thermocouple insulator materials.

9.5 PLANS AND RECOMMENDATIONS

Evaluations will continue of neutron-flux-induced thermoelectric changes with emphasis on the effects of fast neutron dosage.

Methods will be investigated to improve thermocouple performance at very high temperatures by improving techniques and optimizing material selection. This effort is aimed at improving reliability and accuracy of center-core temperature measurement of LMFBR fuel pins.

Studies will be made to improve the reliability of thermocouples for measuring the liquid metal coolant temperature of fast breeder reactors.