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Decalibration of a Tungsten-Tungsten 25% Rhenium
Thermocouple in a Neutron Flux

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DECALIBRATION OF A TUNGSTEN-TUNGSTEN 25% RHENIUM
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S. R. Skaggs, W. A. Ranken, and A. J. Patrick

ABSTRACT

A determination has been made of the change in thermoelectric emf of a W/W-25Re thermocouple resulting from irradiation at an average temperature of 2000°K for 5328 hr in a thermal flux of 2.0×10^{13} n/cm²-sec for a total exposure of 3.8×10^{20} nvt. Comparison of the postirradiation thermoelectric output with that of an unirradiated thermocouple from the same batch showed that the thermal emf was increased by the combination of transmutation and phase separation due to irradiation at temperature. This change is noted over the entire range from room temperature to 2170°K. The difference in temperature required to generate the same thermal emf for the irradiated and unirradiated thermocouple varied from 60°K at 1200°K to 33°K at 2170°K. The lack of agreement of this measurement with investigations at General Electric Nuclear Materials and Propulsion Operation using simulated W-Re-Os alloys based on calculated compositions may be due to the separation observed in our experiment, of the W-Re leg into two phases, one of which contained a much higher relative proportion of osmium than the other.

INTRODUCTION

Measurement of high temperatures for long periods of time in a reactor core environment is a relatively new endeavor in which little knowledge and experience have yet been accumulated. Because of the severity and limited accessibility of the environment, the high temperature thermocouple is the only practical detector available. High temperature thermocouples developed to date involve the use of tungsten and rhenium, both of which have high thermal neutron capture cross sections, and hence are subject to appreciable transmutation in a reactor core environment.

Several investigators¹⁻³ have considered the effect of nuclear transmutation on the thermoelectric emf generated by W/W-Re alloy thermocouples. The group at General Electric Nuclear Materials and Propulsion Operation in Cincinnati^{1,4} (GE-NMPO) has

simulated the effect of such transmutation on W/W-25Re thermocouples by synthesizing W-Re and W-Re-Os alloys having the transmuted compositions expected from various neutron exposures, and by obtaining the relative thermoelectric emf of these alloys as a function of temperature. Investigators at Battelle⁵ have measured W/W-25Re thermocouples irradiated at coolant temperature in the Engineering Test Reactor to exposures of 5.3×10^{20} nvt thermal and 2.7×10^{20} nvt fast (>1 Mev).

This report describes the change in calibration of a single W/W-25Re thermocouple irradiated for 5328 hr in the Omega West Reactor of Los Alamos Scientific Laboratory at an average temperature of 2000°K to an integrated thermal neutron exposure of 3.8×10^{20} nvt. Because it is an isolated test, the results are primarily useful because they indicate that not transmutation alone, but the combina-

tion of transmutation and time-at-temperature, determines the change in calibration resulting from high-temperature irradiation.

Thermocouple Construction and Irradiation Procedure

The construction⁶ of the thermocouple which survived the irradiation and 65 temperature cycles is shown in Fig. 1a. It consisted of 5-mil Hoskins lot W tungsten and 5-mil Hoskins lot 33 tungsten-25% rhenium wires threaded into beryllium oxide beads inserted into a molybdenum tube. A small plug of tungsten was inserted in one open end of the tube with the wires between the plug and the inside diameter of the tube as shown in Fig. 1a. This assembly was swaged to an outside diameter of 0.053 in. The end was TIG welded to make the assembly vacuum-tight.

The thermocouple was mounted in an 0.080-in.-diam well to a depth of 1.30 in. in a sample of Mo-UO₂ cermet as shown in Fig. 1b. The entire 18-in. length of the thermocouple was located inside a hermetically sealed container. The thermoelement wires were attached separately to shorted junction, stainless steel-sheathed, chromel-alumel thermocouples by a specially constructed mica connector and were brought through the vacuum bulkhead (Fig. 1c) by ceramic feed-through connections. The chromel-alumel thermocouples monitored the cold-junction temperature of the W/W-25Re thermocouple inside the sealed container.

The test assembly containing the thermocouple measured in this report was installed in sample hole 4B of the Omega West Reactor. With only minor adjustments in vertical position, the assembly ran at a reactor power level of 5 MWth for 222 operating days.

Operation

The Mo-UO₂ cermet fuel slug, A in Fig. 1b, in which the thermocouple was located was initially at 2100°K and when the test terminated was at 1900°K as measured by this thermocouple. The integrated thermal neutron flux during the 5328 hr test was 3.8×10^{20} nvt (average flux = 2.0×10^{13} n/cm²-sec) as determined by radiochemical ¹⁴⁴Ce determination of fission density in the fuel sample. Self-shielding was not an important effect because of the low enrichment of the uranium in the fuel. The fuel specimen and thermocouple were tested in an

initial atmosphere of 20 torr of spectroscopic grade argon in which 5 torr of fission-product xenon and krypton accumulated during the course of the test.

Before irradiation the thermocouple total resistance was 16.1 ohms. Measurements made while the reactor power was down for weekends showed that this value did not vary over the thermocouple's operating lifetime.

The irradiated thermocouple was removed intact from the test assembly and put in storage for 234 days before recalibration. During this time, 90% of the ¹⁸⁵W atoms and all of the ¹⁸⁷W atoms present at the end of irradiation decayed to rhenium, changing the content of rhenium in the pure tungsten leg of the thermocouple by a negligible amount. The total calculated amount of rhenium in the tungsten leg at time of measurement in the hot cell was approximately 0.47%.

Investigators at General Electric¹ have shown that the emf of the pure tungsten leg of a W/W-25Re thermocouple is strongly influenced by small amounts of rhenium. The GE-NMPO data also contain information on the influence of small amounts of osmium on the W-25Re leg based on a homogeneous composition. The calculated amount of osmium in the W-25Re leg of the thermocouple measured at LASL was 1.32%.

Postirradiation Thermocouple Calibration

Postirradiation thermocouple calibration was carried out in a small induction-heated vacuum furnace in a hot cell. The irradiated thermocouple and a precalibrated unirradiated W/W-25Re thermocouple from the same batch were placed in two thermocouple wells, each 1.30 in. deep and 0.080 in. in diameter. The wells were 180° apart and 13/64 in. off center in a 1.5-in.-high, 0.75-in.-diam cylindrical tantalum susceptor.

With the unirradiated thermocouple serving as a standard, the thermoelectric emf of the irradiated thermocouple was measured as a function of temperature for three separate cycles between room temperature and 2170°K. Considerable time was taken while determining each data point above 1200°K to ascertain that temperature vs time equilibrium had been established. Despite this precaution there was considerable dispersion of data points taken during the increasing temperature portion of the cycle but very little dispersion during the descending portion.

Above 1800°K dispersion was small for ascending or descending temperature determination. Because the vacuum in which the calibration was done was relatively poor ($\sim 10^{-4}$ torr), the ascending temperature data might have been affected by oxygen picked up while the thermocouple was at low temperature. The ascending temperature data were not used in the final plot in Fig. 2.

The power supply used in this measurement would not operate below a minimum power that provided a temperature of 1200°K at the tantalum susceptor. Thus no data were taken under equilibrium conditions below this temperature; nevertheless, data points were obtained under transient conditions of startup and shutdown of the power supply. These points are plotted in Fig. 2 for comparison, but they are not included in the curve which was fit over the range from 1200°K to 2170°K.

All the steady-state data points in this range taken during descending temperature profiles were fitted with a least squares program by a fourth degree polynomial. The 54 data points between 1200°K and 2170°K have a standard deviation from this curve of $\pm 6^\circ$. Hoskins Manufacturing Company has reported⁷ that data from a particular batch of wire is repeatable within $\pm 1/2\%$ for any piece of wire from that spool. The Hoskins calibration curve for batch W tungsten wire and batch 33 tungsten-25% rhenium wire is plotted as the upper curve in Fig. 2. The lower curve is the polynomial fit of the data measured on the irradiated thermocouple. The error to be expected at any point using this set of curves varies from $\pm 9^\circ$ at 1200°K to $\pm 12^\circ$ at 2170°K.

The change in calibration as determined by the difference between the standard curve and the post-irradiation curve is plotted as a positive error in Fig. 3. The temperature indicated by the irradiated thermocouple, as determined from the standard calibration curve, was higher than the true temperature by the amount shown in Fig. 3. Also shown in Fig. 3 is a curve obtained by the investigators at GE-NMPO which shows the differential thermoelectric emf vs temperature obtained for alloys having the amounts of rhenium and osmium calculated for a one-month irradiation in a thermal flux of 10^{14} n/cm²-sec. The total exposure for this irradiation would have been 2.68×10^{20} nvt, whereas the LASL exposure was 3.8×10^{20} nvt or an equivalent of 1.42 months in a

flux of 10^{14} n/cm²-sec. The difference in the error curves is very pronounced with the present results reflecting much less error over the range of measurement than is predicted by the GE results. Curves for exposures of 3 and 6 months in a flux of 10^{14} n/cm²-sec calculated by GE¹ show that the error due to increased irradiation tends to approach our data in Fig. 3 at lower temperatures but diverges from it at higher temperature.

Postirradiation Microstructure

The post-test examination of the irradiated thermocouple included metallographic and electron microprobe examinations of the tungsten and tungsten-rhenium legs approximately 3/8 in. from the tip which was about 9/32 in. from the junction of the 5-mil wires with the tungsten block.

The microstructure of the thermocouple legs is shown in Fig. 4. Fig. 4a shows the tungsten wire, and 4b shows the W-Re wire. Neither sample has been etched. Portions of the two wires, etched in 6:3:1 lactic-nitric-hydrofluoric acids are shown at a higher magnification in Fig. 5 with 5a showing the tungsten, and 5b the W-25Re wire. It is clear upon examining Fig. 4b that phase separation has occurred in the W-25Re leg of the thermocouple. It is also apparent that the light colored regions in Fig. 4b are, in themselves, multiphase regions as shown in Fig. 5b. The small dark spots in these regions may be sigma-phase material⁸ or an accumulation of precipitated impurities. In comparison with unirradiated W-25Re wire, some grain growth is observable. The results of Miller and Ray at Battelle⁵ show some grain growth with sigma-phase material in a thermocouple irradiated in the Materials Test Reactor and subsequently heated out of pile.

The electron microprobe demonstrated that phase separation had indeed occurred in the W-25Re wire. The microprobe-generated x-ray intensity for rhenium from the light-colored regions was 1.6 times that of the rest of the wire. One can roughly estimate, on the basis of the relative areas of the two regions and known initial Re concentration, that the main portion of the wire was 23% rhenium and the light-colored portion was approximately 37% rhenium. The osmium x-ray signal was nine times greater in the light-colored region than in the remainder of the wire, indicating that the

osmium concentration may have been as high as 5% in the light-colored region of the W-25Re wire. This is in sharp contrast to the 1.32% calculated for this wire at this exposure.

Discussion

Because of the phase separation occurring in the W-25Re leg of the W/W-25Re thermocouple during high temperature neutron irradiation, it is obvious that the expected change in calibration cannot be predicted by synthesizing suitable alloys of W, Re, and Os. It is possible that the same phase separation described here would be observed in the synthesized alloys if they were subjected to the same long term heat treatment as the irradiated thermocouple. In any case, the present results indicate that the change in calibration of a W/W-25Re thermocouple during irradiation depends not only on the amount of transmutation occurring, but also on the time-temperature conditions experienced during irradiation. The results also indicate that the use of W-5Re/W-25Re thermocouples to reduce the sensitivity of the thermocouple to changes of rhenium content in the low-rhenium-content leg may not be as satisfactory as has been predicted in the literature. Certainly the time-temperature behavior of the various alloys involved should be carefully investigated.

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Fig. 1. High temperature thermocouple construction and installation details.

Fig. 2. Comparison of unirradiated Hoskins wire calibration with same batch after irradiation.

Fig. 3. Change in calibration vs temperature of a W/W-25Re thermocouple irradiated to 3.8×10^{20} nvt at 2000°K .

Fig. 4a

~250X

Fig. 4b

~250X

Fig. 4. Unetched cross section of W wire in a and W-25Re wire in b. 5 mil wires are separated from BeO insulation by sample mounting material.

Fig. 5a

~1000X

Fig. 5b

~1000X

Fig. 5. Etched cross section of W wire in a and W-25Re wire in b. Dark spots and heavy grain boundaries in b are probably sigma-phase material. Osmium concentration is 9 times higher in the light colored grains than in surrounding metal.