INL/CON-06-11879
Rev. 1
PREPRINT

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ICAPP 2007

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May 2007

LONG DURATION PERFORMANCE OF HIGH TEMPERATURE IRRADIATION RESISTANT THERMOCOUPLES

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Abstract –*Many advanced nuclear reactor designs require new fuel, cladding, and structural materials. Data are needed to characterize the performance of these new materials in high temperature, radiation conditions. However, traditional methods for measuring temperature in-pile degrade at temperatures above 1100 ºC. To address this instrumentation need, the Idaho National Laboratory (INL) developed and evaluated the performance of a high temperature irradiation-resistant thermocouple that contains alloys of molybdenum and niobium. To verify the performance of INL's recommended thermocouple design, a series of high temperature (from 1200 to 1800 ºC) long duration (up to six months) tests has been initiated. This paper summarizes results from the tests that have been completed. Data are presented from 4000 hour tests conducted at 1200 and 1400 ºC that demonstrate the stability of this thermocouple (less than 2% drift). In addition, post test metallographic examinations are discussed which confirm the compatibility of thermocouple materials throughout these long duration, high temperature tests.*

I. INTRODUCTION

To resolve principal technical and scientific obstacles to the future long-term use of nuclear energy, new reactor designs must offer enhanced safety and overcome issues involving resistance to proliferation, economics, and nuclear waste disposition. To meet these goals, new materials are being considered for fuel, cladding, and structures in advanced and existing nuclear reactors. Data are needed to characterize the performance of these new materials in high temperature, radiation conditions. To obtain this data, robust instrumentation is needed that can survive proposed test conditions. Base-metal thermocouples for measuring temperature in-pile degrade at temperatures above 1100 ºC. Higher temperature thermocouples made from W-Re or Pt-Rh alloys degrade due to transmutation. Hence, INL initiated a project to develop specialized thermocouples for high temperature in-pile applications. Initial efforts to select materials for these specialized thermocouples and evaluate their performance are reported in Rempe *et al.*[1] This paper reports results for long duration, high temperature performance tests of these specialized thermocouples.

II. LONG DURATION TESTING APPROACH

To demonstrate the long duration performance of these thermocouples, INL initiated tests in which the proposed doped Mo versus Nb1%Zr thermocouples are held at elevated temperatures (ranging from 1200 to 1800 °C) for up to 6 months. Figure 1 shows the setup used for these tests. Thermocouples are inserted into a gettered argon flow stream inside a tube furnace. Test data are continuously recorded and stored on a computer.

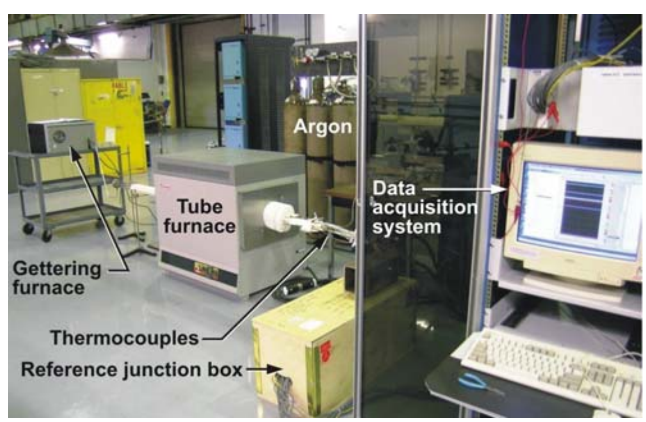


Figure 1. Long duration thermocouple test setup.

II.A. 1200°C Test

The 1200°C test, which was started in September 2005, included nineteen commercially-available Type N thermocouples, three commercially-available Type K thermocouples, and nine INL-developed doped Mo/Nb1% Zr thermocouples. One objective of this test was to evaluate the integrity of the sheath material in contact with graphite. Hence, the tip of each thermocouple was inserted in a graphite sleeve to simulate conditions similar to the planned application of these instruments.

The measured emf voltage from representative thermocouples in the 1200°C test is compared in Figure 2. Several transients were included in this test, as indicated by downward spikes in the figure, to assess the effect that transients have on the thermocouples' behavior.

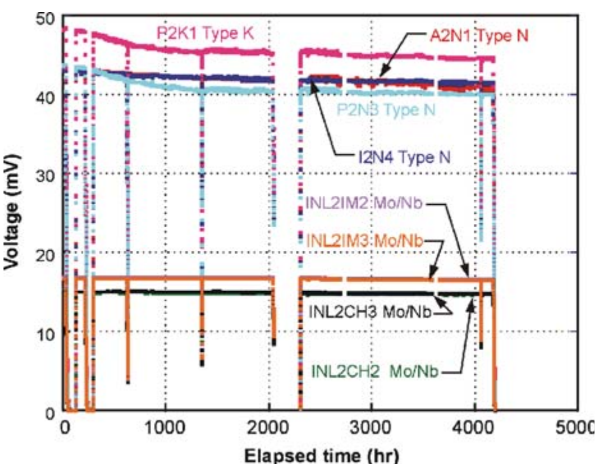


Figure 2. Measured emf voltage for representative thermocouples in 1200 °C tests.

As indicated in Figure 2, the measured emf of some thermocouples (e.g., the Type K thermocouple designated P2K1) started to drift downward from the outset. Note that this downward drift wasn't influenced by the transients; nor did the transients result in open-circuit failures. The measured emfs for INL-developed thermocouples appear to be stable (See the curves labeled, "INL CH2 Mo/Nb" and "INL CH2 Mo/Nb". These correspond to two of the doped Mo-Nb1%Zr thermocouples with Nb-1%Zr sheaths and HfO_2 insulation. The curves labeled, "INL2-IM2 Mo/Nb" and "INL2-IM3 Mo/Nb" correspond to two of the Mo-Nb1%Zr thermocouples with Inconel 600 sheaths and MgO insulation.[1])

Note that the emf corresponding to 1200 °C for the INL MgO-insulated and HfO_2-insulated thermocouples differed. This is primarily attributed to the lower heat treatment temperature selected for the MgO-insulated thermocouples (because of temperature limitations associated with materials compatibility in these thermocouples).

Figure 3 plots the temperatures for each of the TCs shown in Figure 2 (with the transients omitted). During this 4000 hour test, some of the Type K and N thermocouples (e.g., see the curves labeled, "P2K1 Type K" and "P2N2 Type N") drifted by over 100 °C. Much smaller drifts (typically less than 20 °C) are observed in the INL-developed thermocouples with HfO_2 and MgO insulation (e.g., see the curves labeled, ""INL CH2 Mo/Nb", "INL CH2 Mo/Nb", "INL2-IM2 Mo/Nb", and "INL2-IM3 Mo/Nb").

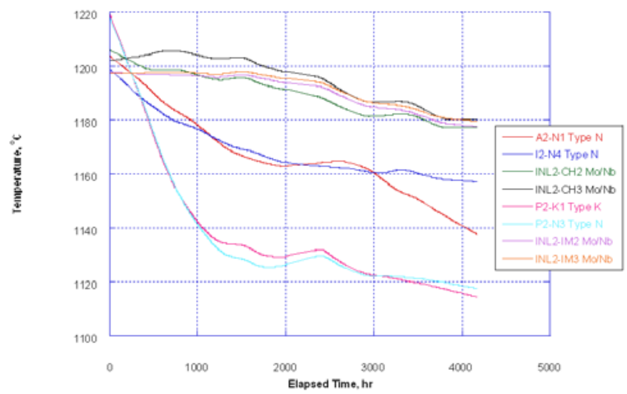


Figure 3. Temperatures for representative thermocouples in 1200 °C tests.

II.B. 1400°C Test

The 1400°C test, which was started in April 2006, was conducted using the same setup used for the 1200 °C test (see Figure 1). This test included six INL-developed thermocouples: two using commercially available thermoelement wires, KW-Mo and Nb1%Zr, in the currently-pursued INL design and four containing noncommercial Mo-low Nb alloys specially developed for INL. All of these thermocouples have hafnia insulation and Nb1%Zr sheaths. Figure 4 compares the measured emf for three representative thermocouples: KWMo-2 (containing KW-Mo and Nb1%Zr thermoelement wires), Mo1.6Nb-3 (containing Mo1.6%Nb and Nb1%Zr thermoelement wires), and Mo3Nb-6 (containing Mo3%Nb and Nb1%Zr thermoelement wires). As shown in Figure 4, the emf drift of these thermocouples after over 4000 hours at 1400 °C is minimal.

[1] Although Inconel 600 sheaths and MgO insulator materials were not investigated for higher temperature applications, the test sponsor requested that they be included because of interest in using these thermocouples at 1200 ºC.

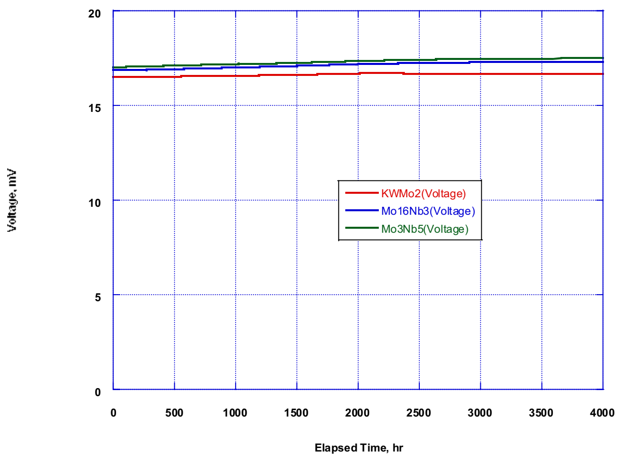


Figure 4. Temperatures for representative thermocouples in 1400 °C tests.

II.C. 1500°C Test

Table I lists the thermocouples that will be included in a long duration test at 1500 °C. In addition to the original INL design (with 0.0254 cm wires), this test will include Mo/Nb alloy thermocouples of other diameters (made with 0.0127 and 0.0508 cm diameter wire), Mo/Nb alloy thermocouples made with non-commercial Mo-low Nb alloys developed for INL, and several commercial Type C (W-Re) thermocouples.

TABLE I: 1500 °C Long Duration Test Thermocouples

TC Type	Wire Size, cm	Insulation	Sheath
KW-Mo/Nb1%Zr	0.0127	HfO_2	Nb1%Zr
KW-Mo/Nb1%Zr	0.0254	HfO_2	Nb1%Zr
KW-Mo/Nb1%Zr	0.0508	HfO_2	Nb1%Zr
Mo1.6%Nb/Nb1%Zr	0.0254	HfO_2	Nb1%Zr
Mo3Nb/Nb1%Zr	0.0254	HfO_2	Nb1%Zr
C(W26%Re/W5%Re)	0.0508	HfO_2	Mo

Type C thermocouples are included in this test to examine their behavior at 1500 °C. Although these thermocouples may be used at temperatures up to 2000 °C (Zysk and Robertson[2]), the phase diagram shown in Figure 5 (Massalski, et al.[3]) suggests the potential for phase separation if a W26%Re wire is heated at 1500 °C. If such phase separation occurs, it could adversely affect the calibration of Type C thermocouples. Removal of a Type C thermocouple at 1000 hour intervals is planned, so that sectioning can be performed to assess what, if any, phase changes occurred during each heating period and correlate the appearance of such phases with any drift in the Type C emf.

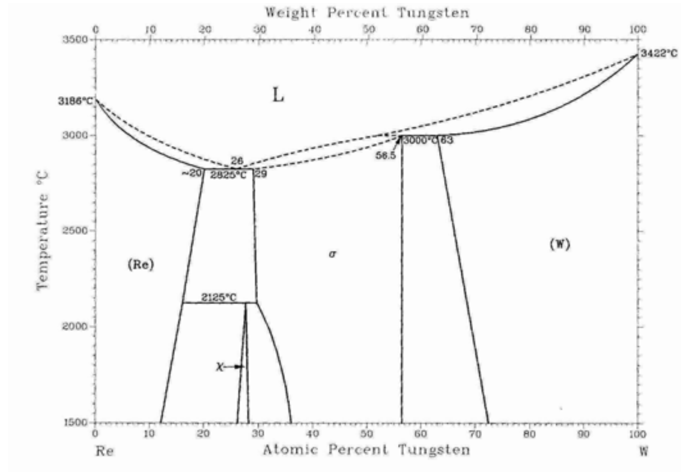


Figure 5. Tungsten-Rhenium phase diagram.

III. POST TEST EXAMINATIONS

Post-test evaluations are underway to evaluate materials compatibility in the INL-developed thermocouples. Preliminary insights from these examinations are summarized in this section.

III.A. 1200°C Test

For the 1200°C test, several types of Scanning Electron Microscope (SEM) exams are being completed. For example, quantitative linescans and semi-quantitative composition point profiles are used to determine changes in elemental concentration across interfaces. This section presents results for a representative INL thermocouple containing hafnia insulation and a Nb1%Zr sheath.

Images of the full thermocouple cross section are shown in Figure 6. The left image was taken using the secondary electron (SE) detector, which emphasizes surface topography, while the right image was taken using the backscatter electron detector, which emphasizes compositional differences, with darker areas representing lighter elements. As shown in Figure 6, the insulator in this sample is cracked (this cracking may have been occurred during sample preparation for SEM analysis). In addition, the images reveal an outer reaction layer along the perimeter of the TC sheath. Within the sheath there appear to be two reaction phases, one slightly darker in contrast than the other.

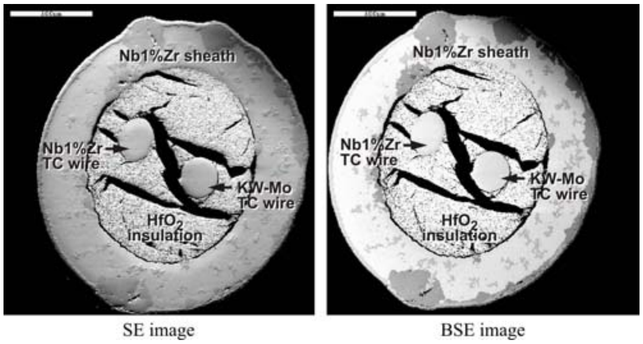


Figure 6. SE (left) and BSE (right) images of INL2 CH3 thermocouple after heating at 1200 ºC for over 4000 hours.

X-ray maps of individual elements in the sheath are shown in Figure 7. In these maps, the element being investigated appears lighter. Hence, the Nb map reveals that the darker reaction phase in the sheath has a lower Nb concentration than the surrounding sheath material. The cavities in the sheath material appear to be the result of material fallout during sample polishing.

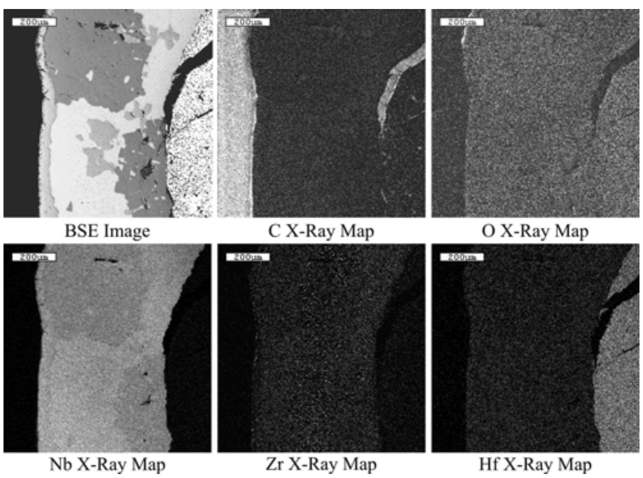


Figure 7. X-ray maps of individual elements in the sheath.

Because of masking by the palladium coating used to eliminate sample charging, differences in oxygen content are not very pronounced. However, the slightly lighter reaction phase in the map suggests that this region is enriched in oxygen. Palladium also masks the carbon, yet faint contrast in the carbon map suggests that the light outer ring and the lighter reaction phases in the sheath may be enriched in carbon. As noted in Section II.A, the thermocouple tips were placed inside graphite sleeves for the 1200 ºC test. The maps indicate that there is little or no hafnium diffusion into the sheath from the insulator. Although not evident at the scale shown in Figure 7, a region of fine porosity appears to have formed around the inner perimeter of the sheath adjacent to the insulator.

A higher magnification image and carbon x-ray map (Figure 8) reveal the enrichment of carbon in the perimeter of the sheath. Similarly, a higher magnification x-ray map of the three phase regions present in the sheath (lightest region being the surrounding sheath material) shows more clearly the constituents of the reaction phases (Figure 9). Compared to the surrounding sheath material, carbon is enriched in the light grey phase, oxygen is enriched in the dark phase; Nb is slightly depleted in the light grey phase and more so in the darker phase; and Zr appears to form small precipitates throughout all three phases.

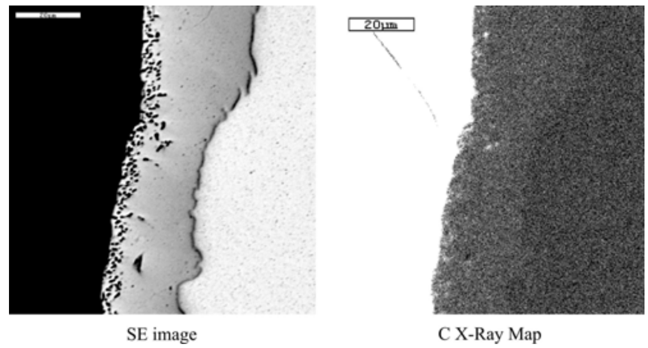


Figure 8. SE image and carbon x-ray map of reaction layer on outer perimeter of sheath.

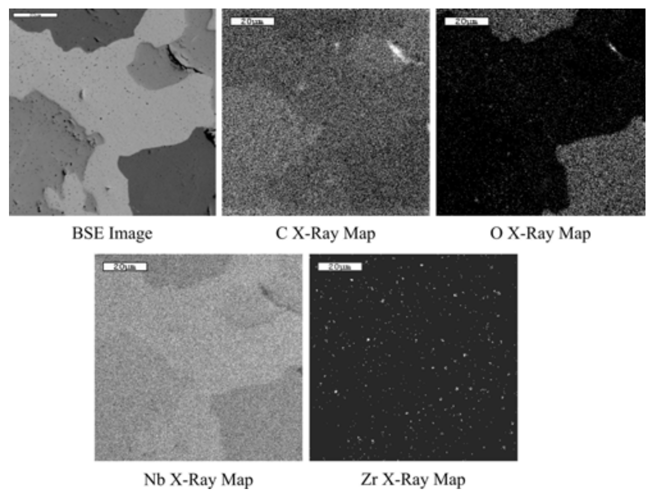


Figure 9. Elemental x-ray maps of 3 phases major present in sheath matrix.

Figure 10 shows a high magnification image of the Nb1%Zr wire, along with elemental profiles across the insulator/wire interface. The x-axis represents distance along the line (160µm total), and the y-axis represents x-ray counts. Higher y-axis values correspond to higher concentrations of the element (Zr, O, Nb, and Hf) being measured. As with the sheath, there does not appear to be significant inter-diffusion of the hafnium into the wires or Nb into the insulator. There also is a region of fine porosity around the perimeter of the Nb1%Zr wire.

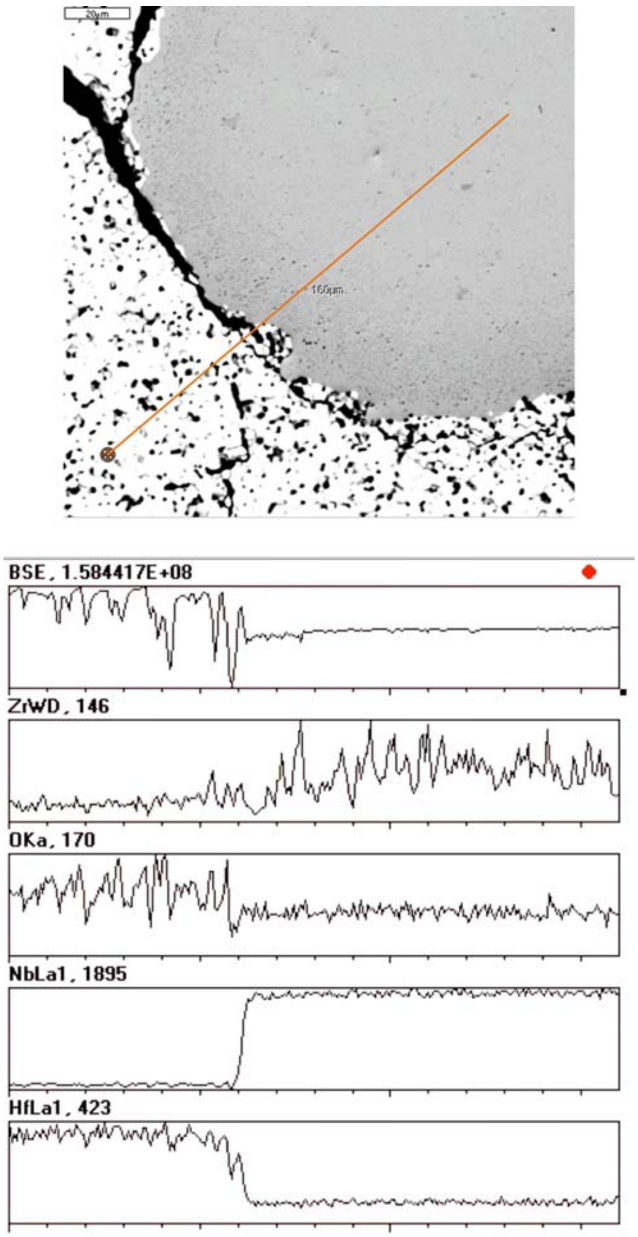
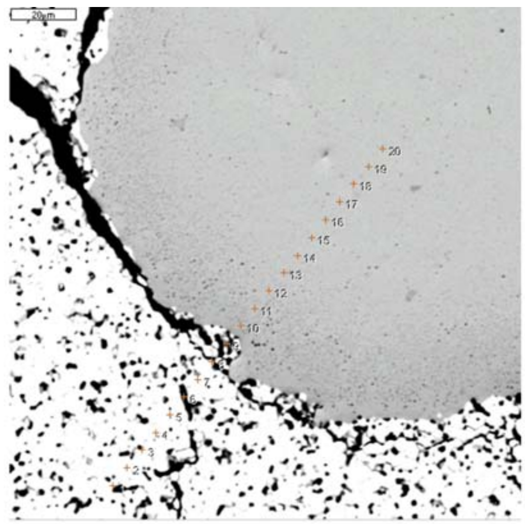


Figure 10. Elemental profiles across Nb1%Zr wire in sample INL2 CH3.

In addition to the line scan, which gives relative changes in elemental concentration, a point composition profile scan was performed (Figure 11) which provides semiquantitative elemental concentrations at the points indicated by a + sign on the image and listed in the table of this figure. Negative values for concentration mean the element is not present.

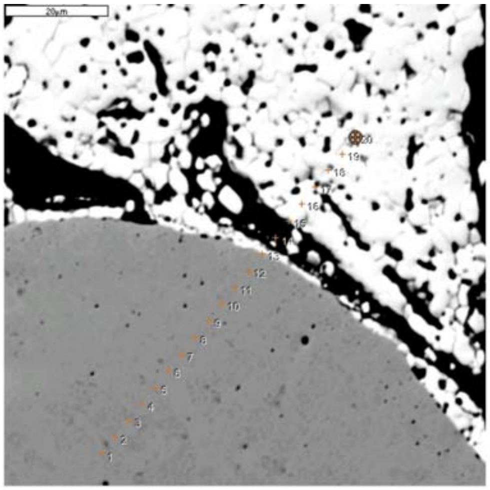
Negative values, which originate from the way the software calculates concentration, tend to skew concentrations of the other elements present to higher values. Also, within the statistical variation of the measurements, there does not appear to be any clear depletion of Zr going from the center of the wire to the edge. The concentration of oxygen, while less than the insulator, is still quite high, indicating oxygen is diffusing into the wire.

A point composition profile across the Mo wire is provided in the image and table shown in Figure 12. In this case, there do not seem to be any points where both the Hf and Mo concentrations are nonzero, indicating negligible inter-diffusion of these elements. Oxygen is once again relatively high in the wire.



#	Elem%	O K	Elem%	Zr L	Elem%	Nb L	Elem%	Hf M
1		13.35		0.61		0.14		85.9
2		12.87		1.24		0.47		85.42
3		10.31		0.48		-0.25		89.46
4		11.16		0.57		-0.24		88.51
5		11.13		1.05		0.01		87.81
6		12.89		0.29		-0.65		87.47
7		13.06		0.13		-0.27		87.07
8		14.04		0.94		0.8		84.22
9		7.46		1.6		24.16		66.77
10		9.02		4.47		88.45		-1.94
11		8.1		6.14		89.62		-3.86
12		8.14		4.18		88.79		-1.11
13		6.45		3.7		90.54		-0.7
14		9.65		4.62		86.55		-0.83
15		6.98		5.17		88.54		-0.69
16		8.87		5.23		85.74		0.16
17		7.77		4.37		88.4		-0.54
18		7.77		4.2		88.62		-0.59
19		8.21		4.59		87.5		-0.3
20		8.03		4.15		88.49		-0.66

Figure 11. Point composition profiles across Nb1%Zr wire in sample INL2 CH3.



Point #	Elem% O K	Elem% Mo L	Elem% Hf M
1	5.51	94.98	-0.49
2	12.12	88.4	-0.52
3	10.06	90.43	-0.49
4	7.1	93.69	-0.79
5	8.95	92.58	-1.53
6	8.67	94.08	-2.75
7	11.05	89.49	-0.54
8	7.44	93.17	-0.61
9	10.17	90.4	-0.57
10	11.43	88.96	-0.39
11	10.45	88.91	0.64
12	9.91	90.76	-0.67
13	15.88	-0.28	84.4
14	18.07	4.9	77.03
15	10.02	-0.01	89.99
16	12.68	-0.39	87.71
17	16.87	0.01	83.12
18	12.34	-0.28	87.94
19	10.14	0.13	89.72
20	9.38	-0.3	90.91

Figure 12. Point composition profiles across Mo wire in sample INL2 CH3.

III.A. 1400°C Test

This section presents initial SEM examination results from a representative thermocouple heated at 1400 °C. Images (SE and BSE) images of the full thermocouple cross section for KWMo-2 (containing KW-Mo and Nb1%Zr wires with HfO_2 insulation and a Nb1%Zr sheath) are shown in Figure 13. Although the insulator in this sample is cracked, it is suspected that this cracking occurred during sample preparation for SEM analysis because insulation in most thermocouples from this test wasn't cracked. As in Figure 6, the images reveal an outer reaction layer along the perimeter of the TC sheath and there appear to be two reaction phases, one slightly darker in contrast than the other. X-ray maps of individual elements in the sheath and thermoelement wires for this thermocouple have not yet been completed. However, results from Figure 7 suggest that the darker reaction phase in the sheath has a lower Nb concentration than the surrounding sheath material. In addition, both of the thermocouple wires shown in Figure 13 suggest that little, if any, reactions occurred between the hafnia insulation and the wires.

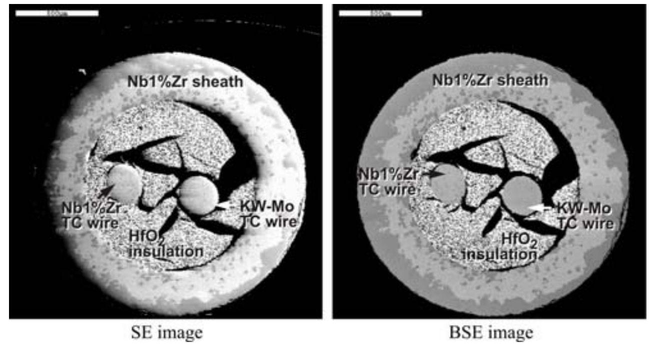


Figure 13. SE (left) and BSE (right) images of INL2 CH3 thermocouple after heating at 1400 ºC for over 4000 hours.

IV. CONCLUSIONS

To demonstrate the long duration performance of INL-developed doped Mo/ Nb1%Zr thermocouples, INL initiated tests in which thermocouples are held at temperatures ranging from 1200 to 1800 °C for periods up to 6 months. Data from 4000 hour tests conducted at 1200 and 1400 ºC demonstrate that the proposed thermocouples remain thermoelectrically stable at these temperatures. Typically, less than 2% drift has been measured.

Post-test evaluations are underway to evaluate the compatibility of thermocouple materials interactions in these tests. Preliminary results from examinations of thermocouples tested at 1200 and 1400 ºC indicate minimal materials interactions.

In summary, results to date indicate that the proposed INL doped Mo/Nb1%Zr thermocouples are well suited for long duration, in-pile tests at temperatures above 1100 ºC. Upcoming tests will focus on determining an upper temperature limit for these thermocouples.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science, and Technology, under DOE-NE Idaho Operations Office Contract DE AC07 05ID14517.

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