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OPTIONS TO EXTEND THE APPLICABILITY OF HIGH TEMPERATURE IRRADIATION RESISTANT THERMOCOUPLES

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ABSTRACT

Several options have been identified that could further enhance the reliability and extend the applicability of recently-developed Idaho National Laboratory (INL) High Temperature Irradiation Resistant ThermoCouples (HTIR-TCs) for in-pile testing, allowing their use in higher temperature applications (up to at least 1800 °C). The INL and the University of Idaho (UI) are investigating these options with the ultimate objective of providing recommendations for alternate thermocouple designs that are optimized for various applications. This paper reports the status of INL/UI investigations. Results are reported from tests completed to evaluate the ductility, resolution, transient response, and stability of thermocouples made from specially formulated alloys of molybdenum and niobium. In addition, this paper reports preliminary insights gained by comparing the performance of thermocouples fabricated with various heat treatments and alternate geometries.

KEYWORDS
High-Temperature Thermocouples, In-Pile Instrumentation

1. INTRODUCTION

New fuel, cladding, and structural materials offer the potential for safer and more economic energy from existing reactor and advanced nuclear reactor designs. However, insufficient data are available to characterize these materials in high temperature, radiation conditions. To evaluate candidate material performance, robust instrumentation is needed that can survive these conditions. However, traditional thermocouples either drift due to degradation at high temperatures (above 1100 °C) or due to transmutation of thermocouple components. Thermocouples are needed which can withstand both high temperature and high radiation environments.

To address this need, the Idaho National Laboratory (INL) recently developed and evaluated the performance of a High Temperature Irradiation-Resistant ThermoCouple (HTIR-TC) design that contains commercially-available alloys of molybdenum and niobium.[1] Candidate thermocouple component materials were first identified based on their ability to withstand high temperature and radiation. Then, components were selected based on data obtained from materials interaction tests, ductility investigations, and resolution evaluations. Results from long duration (over 4000 hours) tests at high temperatures (up to 1400 °C) and thermal cycling tests demonstrate the stability and reliability of the INL-developed design (typically, less than 2% drift was observed). Tests in INL's Advanced Test Reactor (ATR) are underway to demonstrate the in-pile performance of these thermocouples.

Several options have been identified that could further enhance the lifetime and reliability of INL-developed HTIR-TCs for in-pile testing, allowing their use in higher temperature applications (up to at least 1800°C). A joint INL and University of Idaho (UI) effort is underway to investigate these options and, ultimately, provide recommendations for an enhanced thermocouple design. This paper presents recently-obtained results from this INL/UI effort. Results are reported from tests completed to evaluate the ductility, temperature resolution, transient response, and stability of thermocouples made from specially-formulated alloys of molybdenum and niobium. In addition, this paper reports insights gained by comparing the performance of thermocouples fabricated with alternate heat treatments and diameters.

2. BACKGROUND

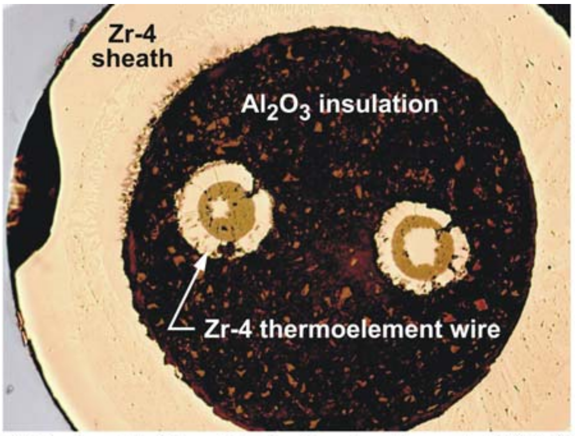
Table I lists commercially-available materials initially considered by INL for HTIR-TC components. These materials were selected for their high temperature thermal properties, nuclear properties, and cost.

Table I. Candidate Thermocouple Component Materials

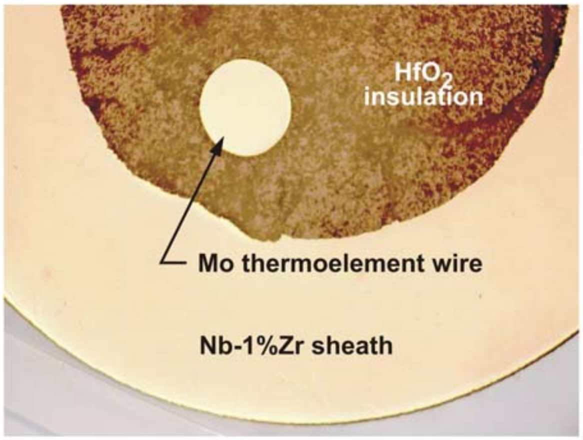
Component	Candidate Materials
Thermoelements	Molybdenum,* Zircaloy-4, Titanium-45% Niobium, Niobium-1%Zirconium
Insulators	Aluminum Oxide, Hafnium Oxide, Magnesium Oxide
Sheaths	Titanium, Zircaloy-4, Niobium-1%Zirconium

*Evaluations considered several types of Molybednum: undoped Mo, Mo-1.6% Nb, KW-Mo (doped with Tungsten, Silicon and Potassium), and ODS-Mo (containing Lanthanum Oxide).

Initial materials interaction tests were completed by heating representative samples in gettered argon at 1300 and 1600 °C for 30 minutes. As shown in Figure 1(a), 1300 °C tests indicated significant materials interactions occurred with samples containing Zr-4 thermoelements, Al_2O_3 insulators, and Zr-4 sheaths. However, 1600 °C results for Nb-1%Zr and Mo thermoelement wires and Nb-1%Zr sheaths indicate that no discernible materials interactions occurred between these materials and HfO_2 insulators (see Figure 1(b)).



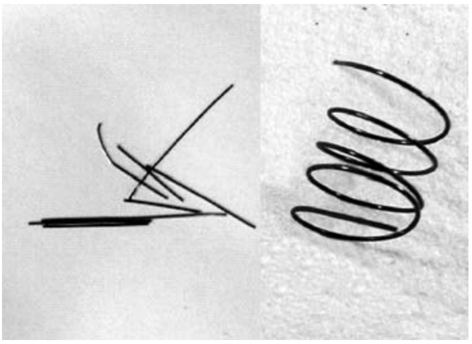
(a) Zr-4 – Al_2O_3 – Zr-4 after heating at 1300 °C



(b) Mo – HfO_2 – Nb-1%Zr after heating at 1600 °C

Figure 1 Materials interaction test results (wire-insulator-sheath).

Mandrel-wrap tests on wires exposed to temperatures up to 1600°C for 30 minutes provided initial insights about thermoelement embrittlement. Wire samples from each of the thermoelement materials listed in Table I were wrapped on mandrels of two, five, ten, and twenty times the wire diameter. Those metals that wrap without damage on a small-diameter mandrel after high-temperature exposure are better candidates from the standpoint of embrittlement. Most Table I thermocouple wire materials exhibited suitable ductility. The one exception, undoped Mo wire, recrystallizes at 1200 °C. As illustrated in Figure 2(a), this wire was brittle after heating at 1300 °C. However, other tested Mo wires (e.g., KW-Mo, ODS-Mo, and Mo-1.6%Nb) remained ductile even after heating at 1600 ºC (see Figure 2(b)).



(a) (b)

Figure 2 Ductility test results [(a) Undoped Mo wire after heating at 1300 °C; (b) Doped Mo-KW wire after heating at 1600 °C].

Calibration tests were also completed for candidate thermocouple combinations using the setup shown in Figure 3. As shown in the figure, thermoelement combinations were inserted into a tube furnace configured with a continuous flow of gettered argon. Data were obtained from room temperature (approximately 20 ºC) up to 1600 ºC. An ice point cell was used to obtain a 0º C reference temperature. The emf response of the candidate thermoelement combination was obtained at selected temperatures. In addition, a Type C thermocouple (W-5%Re versus W-26%Re) was used for reference temperature measurements. Several runs were completed to demonstrate repeatability of the thermoelectric response.

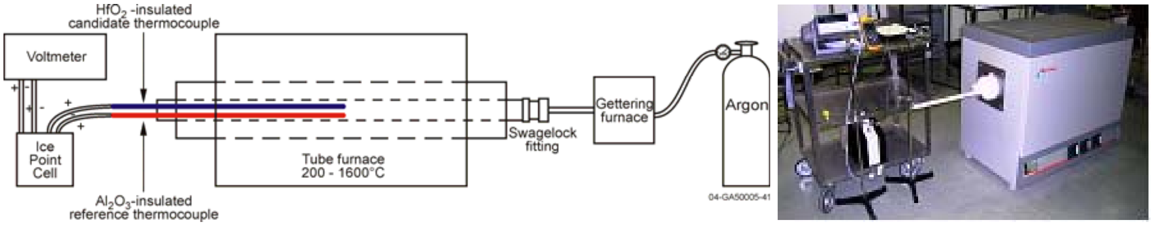


Figure 3 Calibration test setup.

Results (see Figure 4) indicate that the thermoelectric response is single-valued and repeatable for the candidate thermoelements considered. In addition, results indicate that the high temperature resolution is acceptable for all thermocouple element combinations considered (although some combinations are limited due to materials interactions at temperatures below 1600 ºC).

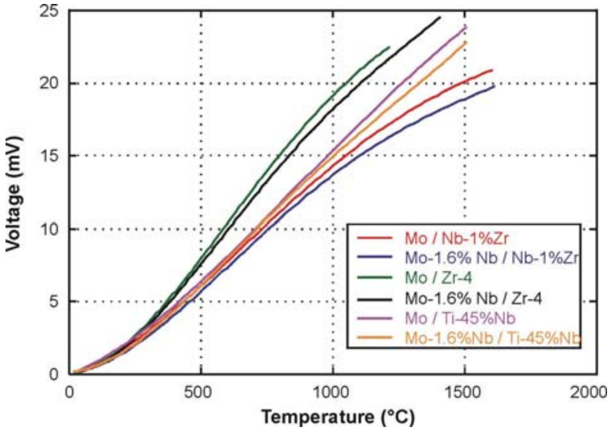


Figure 4 Calibration curves for candidate thermocouples.

Results indicate several candidate low neutron cross-section thermocouple component materials experience minimal interactions and remain ductile at high temperatures. The selection of thermocouple materials will depend on the desired peak temperature and accuracy requirements. However, for the high temperature in-pile applications envisioned for HTIR-TCs, a design containing doped Mo / Nb-1%Zr thermoelement wires with hafnia insulation and a Nb1%Zr sheath is being pursued by INL.

To demonstrate the long duration performance of HTIR-TCs, INL is conducting tests in which thermocouples are held at elevated temperatures (from 1200 to 1800 °C) for up to 6 months. Figure 5 shows the setup used for these tests. Thermocouples are inserted into a tube furnace configured with a continuous flow of gettered argon. A National Institute of Standards and Technology (NIST)-traceable Type S thermocouple is used for reference temperature measurements. Test data are automatically recorded at frequent intervals and stored on a computer.

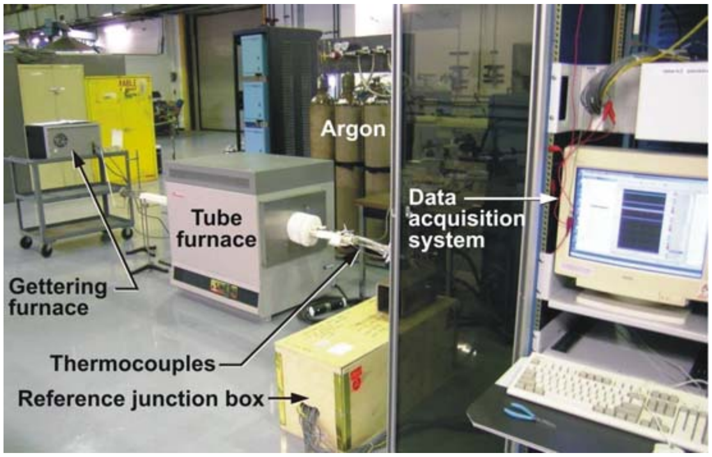


Figure 5 Long duration thermocouple test setup.

The 1200 °C test included nineteen commercially-available Type N thermocouples, three commercially-available Type K thermocouples, and nine INL-developed thermocouples. As indicated in Figure 6, some of the Type K and N thermocouples drifted by over 100 °C or 8%. Much smaller drifts (typically less than 20 °C or 2%) were observed in the INL-developed HTIR-TCs with HfO_2 insulation. As documented in Ref. 1, similar drift was observed in the INL-developed thermocouples in a long duration (4000 hour) test completed at 1400 °C.

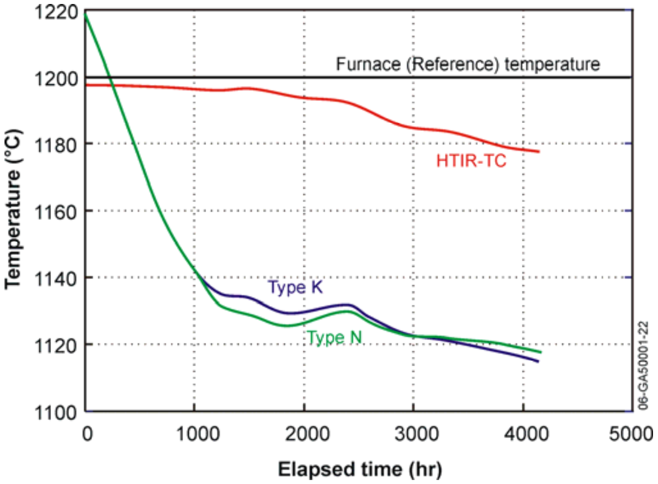


Figure 6 Representative thermocouples in 1200 °C tests.

HTIR-TCs were installed in a test capsule that is currently being irradiated at INL's Advanced Test Reactor (ATR). This test capsule is designed to irradiate samples at temperatures up to 1200 ºC. The irradiation started in February 2007, and it is planned to continue for at least a year. Figure 7 shows the signal from two INL-developed HTIR-TCs and one Type N thermocouple located at cooler regions within the test capsule. Temperature decreases in thermocouple data are due to ATR outages. As shown in this figure, the HTIR-TC located near the Type N TC is giving a signal consistent with the signal from the Type N thermocouple. In addition, the HTIR-TC located at a higher temperature region within the capsule is yielding a consistent, but higher temperature, signal.

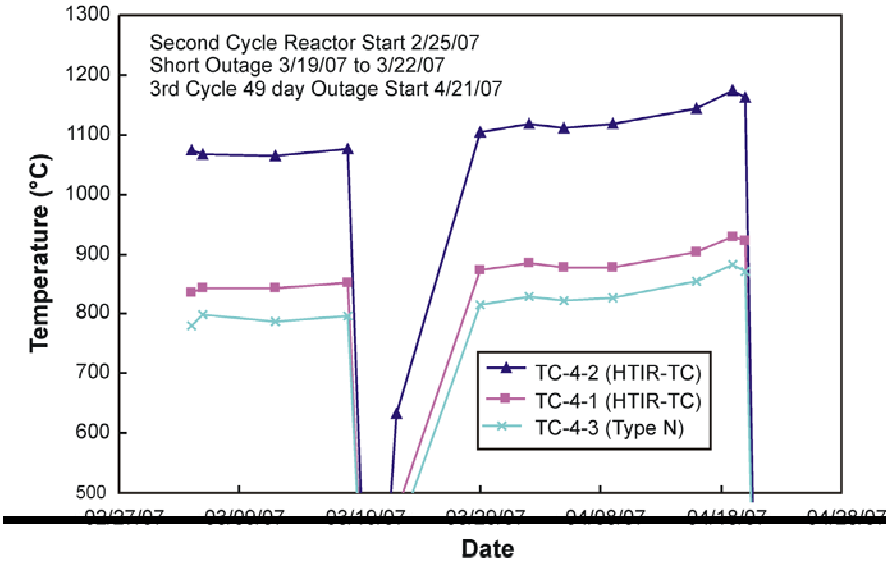


Figure 7 Representative HTIR-TC and Type N data from during ATR irradiation.

3. ENHANCEMENT INVESTIGATIONS

INL and UI are investigating several options to enhance the performance of the INL-developed HTIR-TCs. Initial results from this effort are reported in this section.

3.1. Specially-formulated Alloys

Historically, industry has relied on alloys (e.g, W/Re alloys and Pt/Rh alloys), rather than pure metals, in thermocouples to improve their high temperature performance with respect to ductility, stability, and reliability.[2] Prior experience with Mo/Nb thermocouples[3-5] suggests that similar efforts are warranted.

Prokoshkin and Vasil 'eva[6] indicate that the addition of small amounts (less than 1%) of zirconium to niobium raises its recrystallization temperature by 25 ºC. The addition of molybdenum (up to 4%) may delay recrystallization by 75ºC for temperatures up to 1200 ºC. Investigations by Schley and Metauer[7] show that the addition of small amounts of molybdenum (less than 10%) to niobium will improve its temperature resolution.

Efforts have also been completed to improve the ductility and resolution of molybdenum. Prokoshkin and Vasil 'eva[6] indicate that the recrystallization temperature of molybdenum is increased if it is alloyed with small amounts of niobium. To control molybdenum crystal structure during recrystallization, suitable “dopants” are added to molybdenum. In the case of molybdenum, the dopant is typically tungsten and potassium silicate. In more recent years, lanthanum oxide has been used as a dopant for molybdenum. Furthermore, investigations by Schley and Metauer[7] suggest that the addition of small amounts of niobium (less than 5% to molybdenum) will improve its thermoelectric properties.

Table II lists alloys of molybdenum and niobium being evaluated in this project. Two types of doped molybdenum, two alloys of molybdenum with small amounts of niobium, three alloys of niobium with small amounts of molybdenum, and one alloy with a small amount of zirconium are being investigated. Three types of high temperature testing will be completed: (1) Ductility evaluations, (2) Resolution evaluations, and (3) Long duration testing with transients.

TABLE II. Molybdenum and Niobium Alloys Evaluated

Designator		Description
+ wire	KW-Mo	Molybdenum doped with W, K, and Si
	Doped Mo	Molybdenum doped with LaO
	Mo-1.6% Nb	Molybdenum-1.6% Niobium alloy
	Mo-3% Nb	Molybdenum-3% Niobium alloy
- wire	Nb-1%Zr	Niobium-1% Zirconium alloy
	Nb-4%Mo	Niobium-4% Molybdenum alloy
	Nb-6%Mo	Niobium-6% Molybdenum alloy
	Nb-8%Mo	Niobium-8% Molybdenum alloy

Ductility testing was completed at 1400, 1600, and 1800 °C. Results indicate that the ODS-Mo and KW-Mo samples retain suitable ductility (e.g., the wire samples could be wrapped around the mandrel several times without breaking) for all tested temperatures and heating durations. As shown in Figure 8, the Mo-1.6%Nb and the Mo-3%Nb samples became brittle after 12 hours at 1800 °C, but the doped molybdenum samples remained ductile. Mandrel wrap tests indicate that the niobium wires were generally less ductile than the doped molybdenum samples tested.

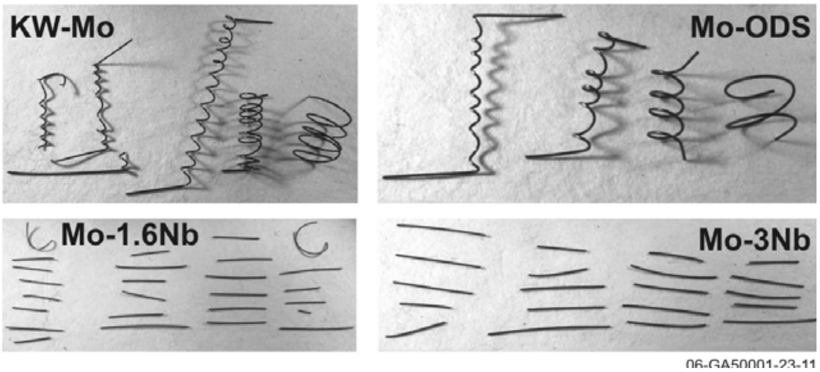


Figure 8 Candidate molybdenum doped and alloy samples heated for 12 hours at 1800°C.

As shown in Figure 9, only the Nb-1%Zr wires remained ductile after heating at 1600 °C for 2 hours. In summary, evaluations indicate that doped molybdenum alloys, either ODS molybdenum or KW-Mo, and the Nb-1%Zr retain ductility better than the developmental molybdenum –low niobium alloys and the niobium–low molybdenum alloys evaluated.

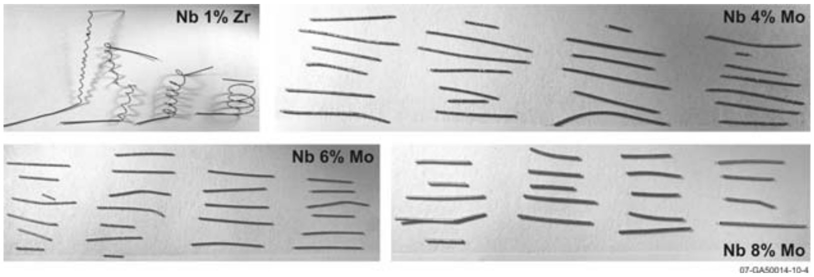


Figure 9 Candidate niobium alloy samples heated for 2 hours at 1600 °C.

3.2. Alternate Geometries

Initial INL efforts focused on swaged thermocouples fabricated from 0.254 mm diameter thermoelement wires. Evaluations by Ludka, et al.[8] indicate that the reliability of Type K and Type N thermocouples increases with wire diameter, especially at higher temperatures.

Prototype thermocouples were fabricated with thermo-element wires of three different diameters: 0.127 mm wire, 0.254 mm wire, and 0.508 mm wire. Note that commercially available materials (doped KW-Mo and Nb-1%Zr) were used because these materials are less expensive to obtain. For each size of thermocouple, sheath tubing and insulator materials were obtained and an appropriate process was developed for swaging reductions.

Figure 10 compares initial results from a long duration (4000 hour) test at 1500 °C with thermocouples from each diameter. This test is being performed using a setup similar to that shown in Figure 5. As shown in Figure 10, the thermoelectric response of thermocouples made from larger diameter wire is more stable.

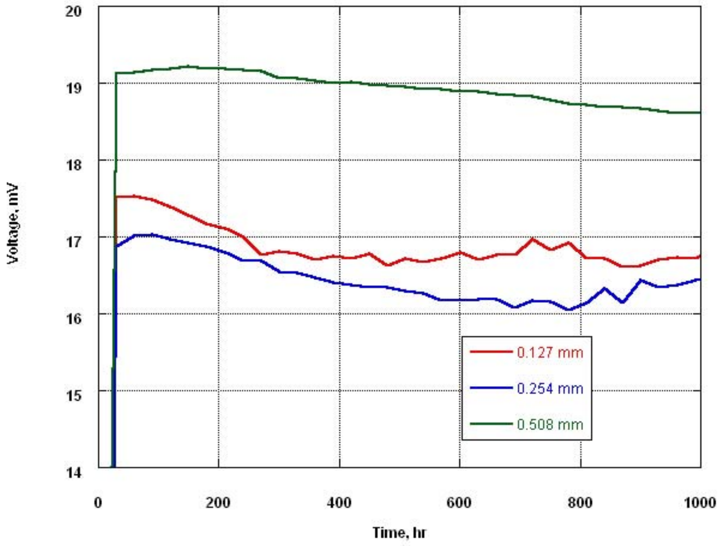


Figure 10 Initial results from long duration 1500 °C test.

3.3 Alternate Heat Treatment Techniques

Grain growth in HTIR-TC thermoelement wires is stabilized by heat treating. However, limited data are available to select appropriate temperatures and durations for this heat treatment. Table III lists the heat treatment temperatures and durations initially explored for thermocouples to be operated at 1200 °C. Table III also lists the initial evaluations completed on these thermocouples to assess their performance.

TABLE III. Heat Treatments Investigated

Temperature, °C	Duration, hours	Designator
1300	0	PG15
	5	PG00
	10	PG09
	20	PG10
1400	0	PG16
	10	PG12
	20	PG11
1500	0	PG19
	10	PG17
	20	PG18

Figure 11 compares results from calibration runs obtained for thermocouples heat treated at various temperatures (1300 to 1500 °C) for 20 hours. Results indicate that the emf is reduced as the heat treatment temperature increases, but that the reduction in emf decreases at heat treatment temperatures greater than 1400 °C. Figure 12 compares results from calibration runs obtained for thermocouples made from 0.254 mm wire that were heat treated at 1300 °C for 5, 10, and 20 hours. Differences between the measured emf were not significantly impacted by the differences in heat treatment time. Figure 13 compares the drift measured in thermocouples heat treated at 1300 °C for various durations. Results indicate that the thermocouple without any heat treatment (PG15) drifted more than the other thermocouples (especially during the first 20 hours at temperature). However, the observed drift was minimal in thermocouples heat treated for at least 10 hours. Hence, preliminary investigations suggest that heat treatment times of at least 10 hours at 1300 °C are needed to stabilize thermocouples for operating temperatures of 1200 °C.

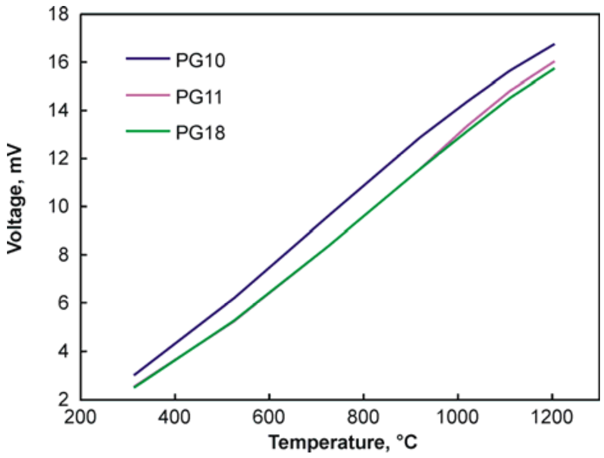


Figure 11 Calibration data obtained from thermocouples heat treated for 20 hours at 1300 °C (PG10), 1400 °C (PG11), and 1500 °C (PG18).

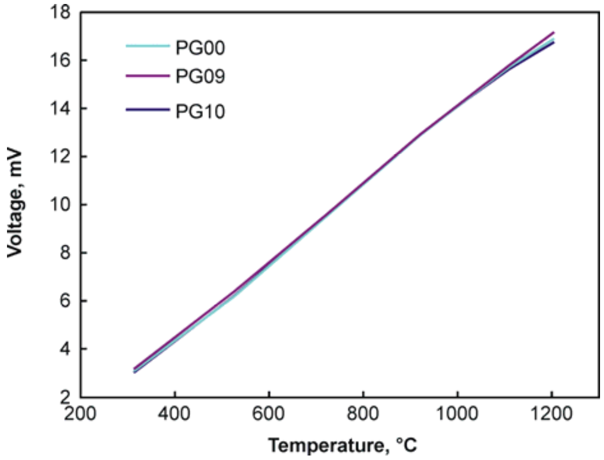


Figure 12 Comparison of calibration data obtained from thermocouples heat treated at 1300 ºC for 5 (PG00), 10 (PG09), and 20 (PG10) hours.

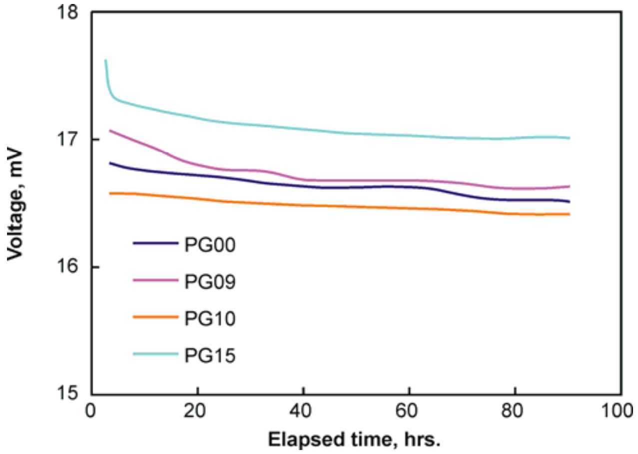


Figure 13 Measured drift of thermocouples heat treated at 1300 °C at 0 (PG15), 5 (PG00), 10 (PG9), and 20 (PG10) hours in 1200 °C constant temperature test.

3.4 Alternate Fabrication Techniques

As documented in Reference 1, initial HTIR-TC development and evaluation efforts focused on "swaged" fabrication approaches. A swaged thermocouple is formed by loading insulator beads onto thermoelement wires and placing them in sheath tubing that is compacted by a swager (see Figure 14a). However, an alternate fabrication approach has been identified that may have the potential to enhance in-pile instrumentation performance. Specifically, the use of a "loose assembly" geometry fabrication approach is being investigated. In a loose assembly thermocouple configuration (see Figure 14b), insulator beads are loaded onto the thermoelement wires and placed within the sheath. However, the sheath tubes are not swaged. Instead, the assembly is typically placed within an enclosure in which a vacuum is achieved (down to approximately 10^{-5} torr). The instrument assembly is then backfilled at room temperature with high purity helium and seal-welded.

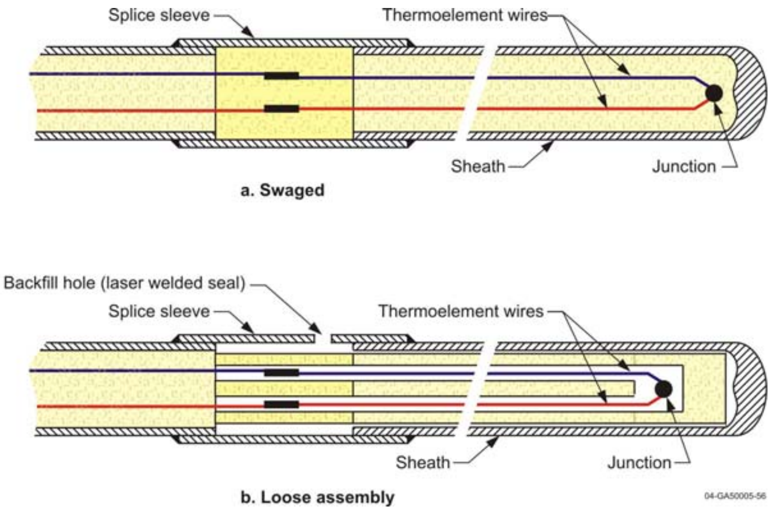


Figure 14 Comparison of "swaged" versus "loose assembly" thermocouple configurations.

Efforts are underway in this program to fabricate a “loose assembly” thermocouple with doped molybdenum and niobium 1%zirconium wire, hafnia insulation in a niobium-1%zirconium sheath. Tests will be completed in the second year of this program to compare the performance of this “loose assembly” thermocouple design with the “swaged thermocouple” design at high temperatures.

4. SUMMARY

Several options have been identified that could further enhance the reliability of INL-developed HTIR-TCs for in-pile testing, allowing their use in higher temperature applications (up to at least 1800 °C). A joint INL/UI project is underway to evaluate several of these options: alternate materials that aren’t commercially available, alternate geometries, alternate heat treatments, and alternate fabrication techniques. Initial results are presented in this paper.

Ductility evaluations indicate that doped molybdenum alloys, either ODS molybdenum or KW-Mo, and Nb-1%Zr resist embrittlement better than the developmental, molybdenum-low niobium and niobium-low molybdenum alloys evaluated. Initial evaluations suggest that molybdenum-niobium alloy thermocouples containing larger diameter thermoelement wires are even more stable than the standard HTIR-TCs containing 0.254 m diameter thermoelement wires. Efforts for the remainder of this project will focus on alternate heat treatments and an alternate fabrication approach- the use of a “loose assembly” design.

ACKNOWLEDGMENTS

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