RADIATION MEASUREMENTS AND INSTRUMENTATION

OPTIONS EXTENDING THE APPLICABILITY OF HIGH-TEMPERATURE IRRADIATION-RESISTANT THERMOCOUPLES

KEYWORDS: *in-pile instrumentation, high-temperature thermocouples*

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Several options have been identified that could further enhance the reliability and extend the applicability of high-temperature irradiation-resistant thermocouples (HTIR-TCs) developed by the Idaho National Laboratory (INL) for in-pile testing, allowing their use in temperature applications as high as 1800°C. The INL and the University of Idaho (UI) investigated these options with the ultimate objective of providing recommendations for alternate thermocouple designs that are optimized for various applications. This paper reports results from 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, not considered in initial HTIR-TC development. In addition, this paper reports insights gained by comparing the performance of HTIR-TCs fabricated with various heat treatments and alternate geometries.

I. 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 drift because of either degradation at high temperatures (above 1100°C) or transmutation of thermocouple components. Thermocouples are needed that can withstand both high-temperature and high-radiation environments.

To address this need, the Idaho National Laboratory (INL) 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 (>4000-h) tests at high temperatures (up to 1400°C) and thermal cycling tests demonstrate the stability and reliability of the INL-developed design (typically, <2% drift was observed). Tests in INL's Advanced Test Reactor (ATR) are underway that 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 investigating these options with the ultimate objective of providing recommendations for an enhanced thermocouple design. This

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paper presents 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 not considered in initial HTIR-TC development. In addition, this paper reports insights gained by comparing the performance of HTIR-TCs fabricated with alternate heat treatments and diameters.

II. 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.

Initial materials interaction tests were completed by heating representative samples in gettered argon at 1300 and 1600°C for 30 min. As shown in Fig. 1a, the 1300°C tests indicated that significant materials interactions occurred with samples containing Zr-4 thermoelements, Al_2O_3 insulators, and Zr-4 sheaths. However, the 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 Fig. 1b).

Mandrel-wrap tests on wires exposed to temperatures up to 1600°C for 30 min provided initial insights about thermoelement embrittlement. Wire samples from each of the thermoelement materials listed in Table I were wrapped on mandrels of 2, 5, 10, and 20 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 Fig. 2a, this wire was brittle after heating at 1300°C. However, the KW-Mo (molybdenum doped with tungsten, silicon, and potassium) and ODS-Mo (oxide dispersion strengthened molybdenum containing lanthanum oxide) wires remained ductile even after heating at 1600°C (see Fig. 2b).

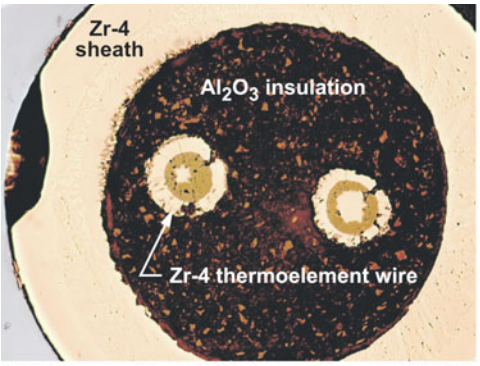
TABLE I

Candidate Swaged Thermocouple Component Materials

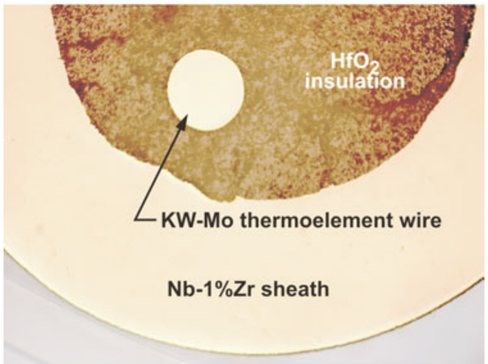
Component	Candidate Materials
Thermoelements	Molybdenum,[a] Zircaloy-4, titanium-45% niobium, niobium-1% zirconium
Insulators	Aluminum oxide, hafnium oxide, magnesium oxide
Sheaths[b]	Titanium, Zircaloy-4, niobium-1% zirconium

[a] Evaluations considered doped KW-Mo and ODS-Mo (molybdenum doped with tungsten, silicon and potassium and oxide dispersion strengthened molybdenum containing lanthanum oxide, respectively).

[b] Only sheath materials amenable to swaging were initially considered.



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



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

Fig. 1. Initial INL materials interaction test results (wire-insulator-sheath).

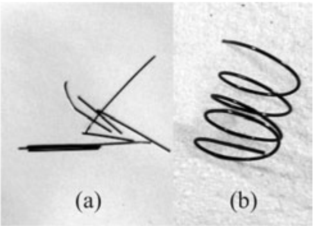


Fig. 2. Initial INL ductility test results: (a) undoped Mo wire after heating for 30 min at 1300°C and (b) doped Mo-KW wire after heating at 1600°C.

Calibration tests were also completed for candidate thermocouple combinations. Results (see Fig. 3) indicate that the thermoelectric response is single valued and repeatable for the more promising candidate thermoelements considered (pure molybdenum was eliminated because of its poor ductility and ODS-Mo was not economical to obtain). In addition, results indicate that the high-temperature resolution is acceptable for all

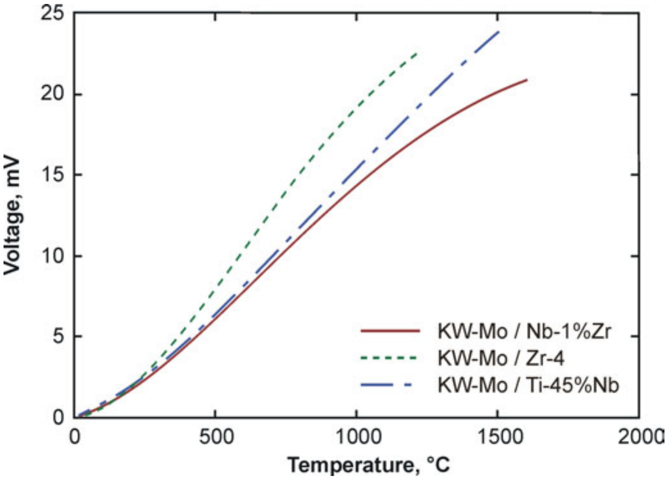


Fig. 3. Initial INL calibration curves for candidate thermocouples.

thermocouple element combinations considered (although some combinations are limited because of materials interactions at temperatures below 1600°C).

Results indicate that 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 Nb-1%Zr sheath was selected.

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 4 shows the setup used for these tests. Thermocouples are inserted into a tube furnace configured with alumina tubes with a continuous flow of gettered argon. A National Institute of Standards and Technology–traceable Type S thermocouple is used for reference temperature measurements. Test data are automatically recorded at frequent intervals and stored on a computer.

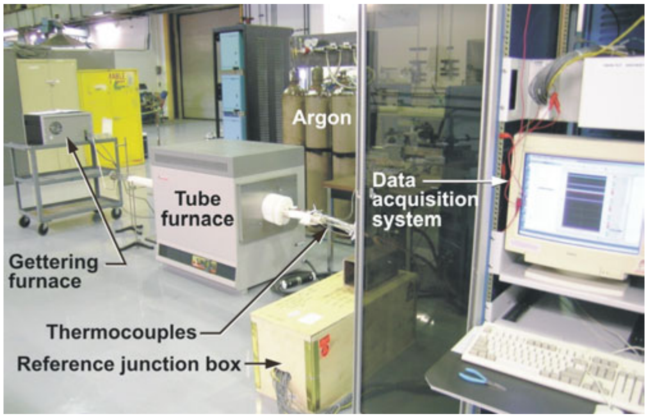


Fig. 4. Long-duration thermocouple test setup.

The 1200°C test included 19 commercially available Type N thermocouples, 3 commercially available Type K thermocouples, and 9 INL-developed "swaged" HTIR-TCs. As indicated in Fig. 5, some of the Type K and Type N thermocouples drifted by >100°C or 8%. Much smaller drifts (typically <20°C or 2%) were observed in the INL-developed HTIR-TCs with HfO_2 insulation. Similar drift was observed in swaged HTIR-TCs in a long-duration (4000-h) test completed at 1400°C.

Swaged HTIR-TCs were installed in a multicapsule experiment that is currently being irradiated at INL's ATR. This multicapsule experiment is designed to irradiate samples at temperatures up to 1200°C. The irradiation started in February 2007, and it is planned to continue for >2 yr. Figure 6 shows the signal from two INL-developed HTIR-TCs and one Type N thermocouple located at cooler regions within one of the test capsules. Temperature variations in thermocouple data are due to ATR outages and power fluctuations. As shown in Fig. 6, the HTIR-TC located near the Type N thermocouple (TC-4-1) initially gives a signal consistent with the signal from the Type N thermocouple (TC-4-3). However, after October 2008, this Type N thermocouple failed. As shown in Fig. 6, the HTIR-TC located at a higher-temperature region within the capsule (TC-4-2) is yielding a consistent, but higher-temperature, signal.

III. ENHANCEMENT INVESTIGATIONS

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

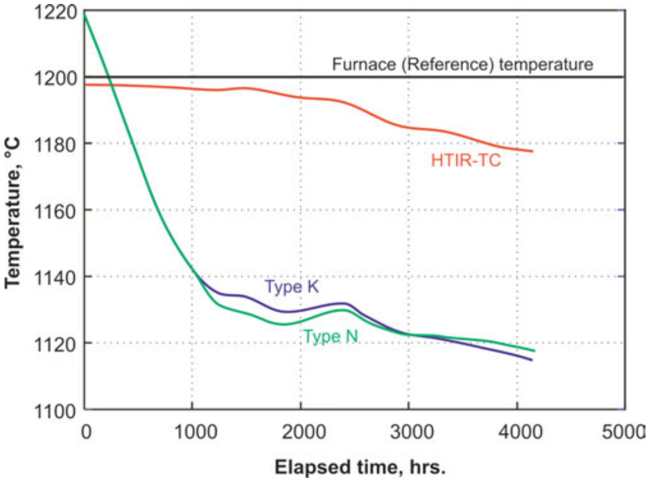


Fig. 5. Representative thermocouples in long-duration 1200°C test.

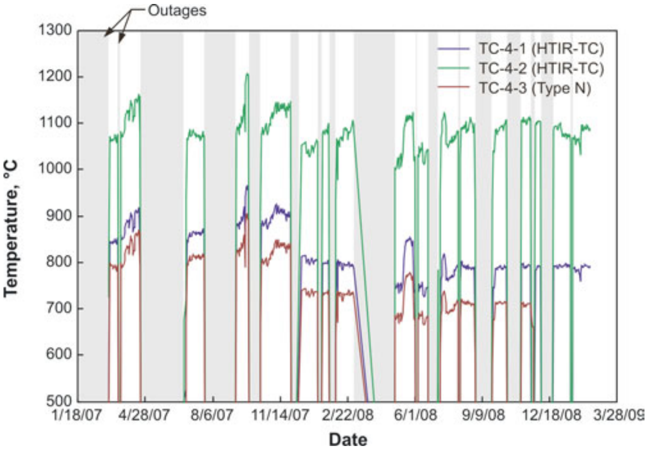


Fig. 6. Representative HTIR-TC and Type N data from during ATR irradiation.

TABLE II

Molybdenum and Niobium Alloys Evaluated

Designator	Description
+ wire	
KW-Mo	Molybdenum doped with W, K, and Si
ODS-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

III.A. 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 (<1%) of zirconium to niobium raises its recrystallization temperature by 25°C. The addition of molybdenum (up to 4%) may delay recrystallization by 75°C for temperatures up to 1200°C. Investigations by Schley and Metauer[7] show that the addition of small amounts of molybdenum (<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 (<5% to molybdenum) will improve its thermoelectric properties.

Table II lists developmental alloys of the molybdenum and niobium evaluated. Ductility and resolution evaluations were completed by INL and UI in this project (since developmental alloys primarily contained molybdenum and niobium, no additional materials interaction evaluations were completed). In addition to the two types of doped molybdenum and niobium alloy with a small amount of zirconium initially evaluated by INL, two alloys of molybdenum with small amounts of niobium and three alloys of niobium with small amounts of molybdenum were investigated. Note that none of the developmental alloys contained doped molybdenum, which may improve their performance.

To determine which materials better retained ductility, it was planned to complete testing at 1400, 1600, and 1800°C for 2-, 5-, and 12-h durations. 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 Fig. 7, the Mo-1.6%Nb and the Mo-3%Nb samples became brittle after 12 h 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. As shown in Fig. 8, only the Nb-1%Zr wires remained ductile after heating at 1600°C for 2 h. Hence, no tests were conducted for longer durations or higher temperatures.

Figure 9 compares calibration evaluation data obtained from thermocouples containing candidate thermoelement materials. The thermocouples with Nb-1%Zr

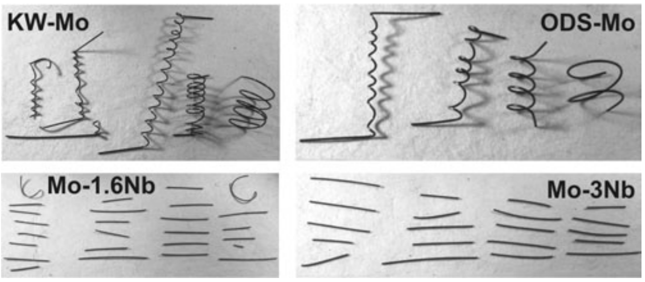


Fig. 7. Candidate molybdenum doped and alloy samples heated for 12 h at 1800°C.

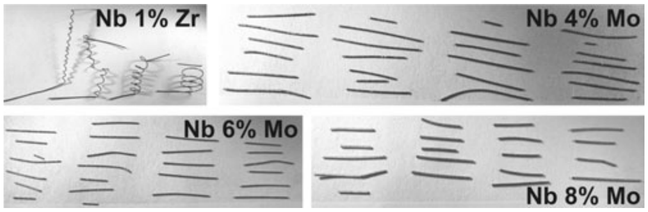


Fig. 8. Candidate niobium alloy samples heated for 2 h at 1600°C.

negative thermoelements all show higher sensitivity than any thermocouples constructed with other candidate negative thermoelements, with the ODS-Mo/Nb-1%Zr thermocouple showing the best sensitivity by a significant margin. All thermocouples constructed with Nb-8%Mo negative thermoelements show lower sensitivity than any others and show a flattening of the output signal over the high-temperature range. The signals from thermocouples constructed with Nb-4%Mo and Nb-6%Mo negative thermoelements all lie between the Nb-8%Mo and Nb-1%Zr thermocouple signals, with no definitive trends setting them apart from each other.

In summary, evaluations indicate that doped molybdenum alloys, either ODS-Mo 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. Although the resolution of the thermocouple containing ODS-Mo and Nb-1%Zr is superior, the lower cost of the commercially available KW-Mo makes a thermocouple containing KW-Mo and Nb-1%Zr the best option at this time.

III.B. Alternate Geometries

Initial INL efforts focused on swaged thermocouples fabricated from 0.254-mm-diam thermoelement wires. Evaluations by Ludtka 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 thermoelement wires of three different diameters: 0.127-mm wire, 0.254-mm wire, and 0.508-mm wire. Note that commercially available materials (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 results from a long-duration (1000-h) test at 1500°C with thermocouples from each diameter. This test was performed using a setup similar to that shown in Fig. 4. As shown in Fig. 10, the thermoelectric response of thermocouples made from larger-diameter wire is more stable.

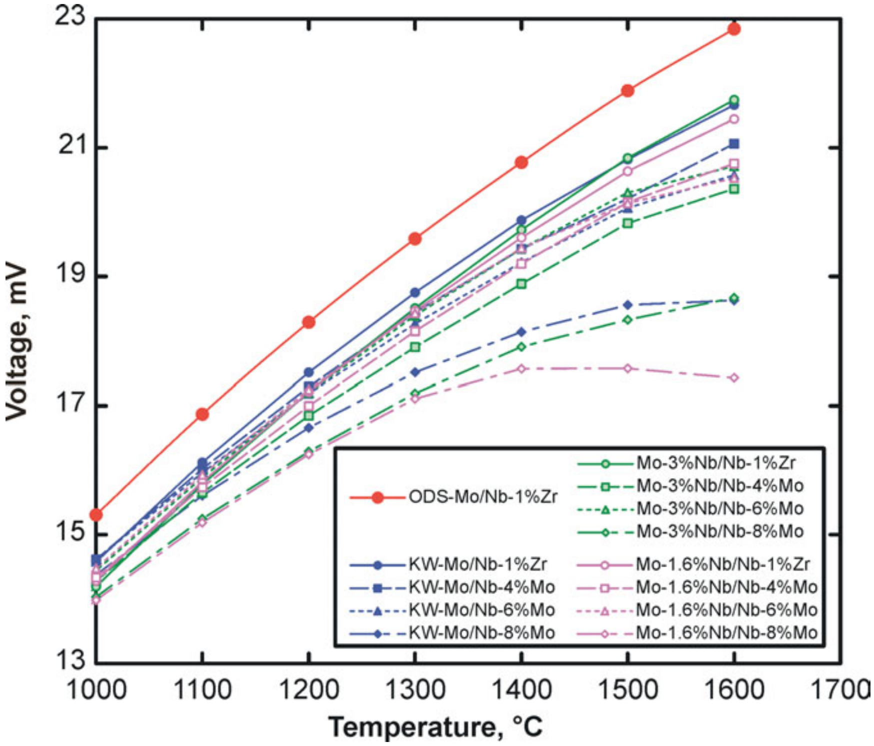


Fig. 9. Comparison of calibration curves obtained for thermocouples containing candidate thermoelement wires.

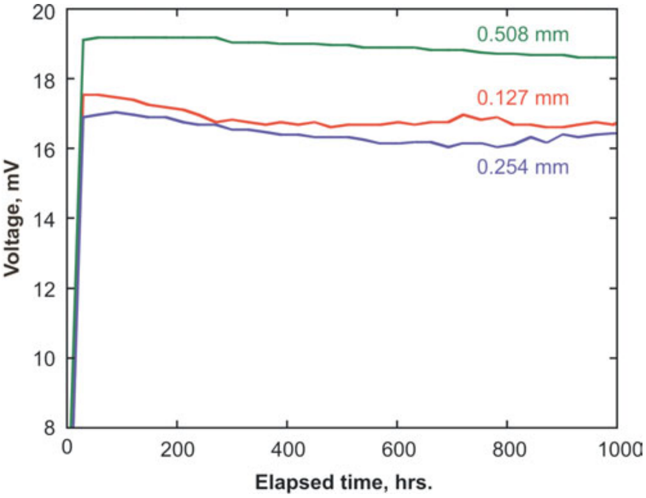


Fig. 10. Impact of diameter on HTIR-TC stability during long-duration 1500°C test.

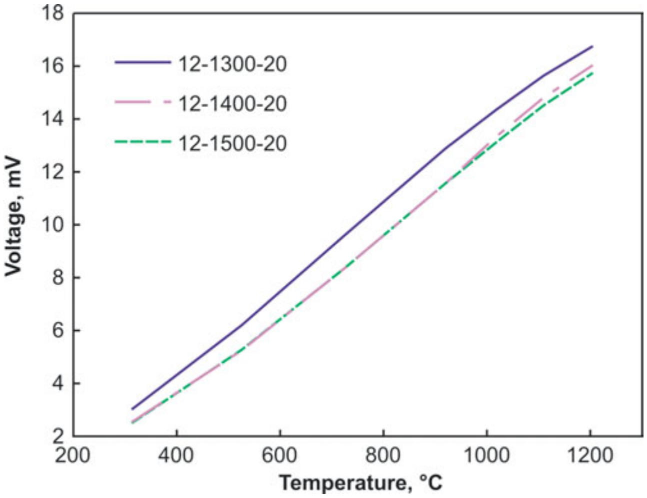


Fig. 11. Calibration data obtained from thermocouples heat treated for 20 h at 1300°C (12-1300-20), 1400°C (12-1400-20), and 1500°C (12-1500-20).

III.C. 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. Reference 1 reported results from limited tests to gain insights about heat treating durations required to stabilize thermocouples for use at 1200 and 1400°C. In this INL/UI project, a systematic evaluation was completed by exploring heat treatment temperatures and durations for thermocouples to be operated at two temperatures: 1200 and 1500°C. Table III lists the evaluations completed on thermocouples to assess their performance.

Figure 11 compares results from calibration runs obtained for thermocouples heat treated at various temperatures (1300 to 1500°C) for 20 h. Results indicate that the electromotive force (emf) is reduced as the heat treatment temperature increases but that the decrease in emf is reduced at temperatures >1400°C. Figure 12 compares results from calibration runs obtained for thermocouples heat treated at 1300°C for 5, 10, and 20 h. Differences between the measured emf were not significantly impacted by differences in heat treatment duration. Figure 13 compares the drift measured in thermocouples heat treated at 1300°C for various durations. Results indicate that the

TABLE III

Heat Treatments Investigated

Operating Temperature (°C)	Heat Treatment Temperature (°C)	Heat Treatment Duration (h)	Designator	Evaluations Completed
1200	1300	0	12-1300-0	Calibration to 1200°C, 100 h at 1200°C
		5	12-1300-5	
		10	12-1300-10	
		20	12-1300-20	
	1400	20	12-1400-20	Calibration to 1200°C
	1500	20	12-1500-20	Calibration to 1200°C
1500	1600	0	15-1600-0	Calibration to 1500°C, 100 h at 1500°C
		4	15-1600-4	
		8	15-1600-8	
		16	15-1600-16	
	1700	4	15-1700-4	Calibration to 1500°C

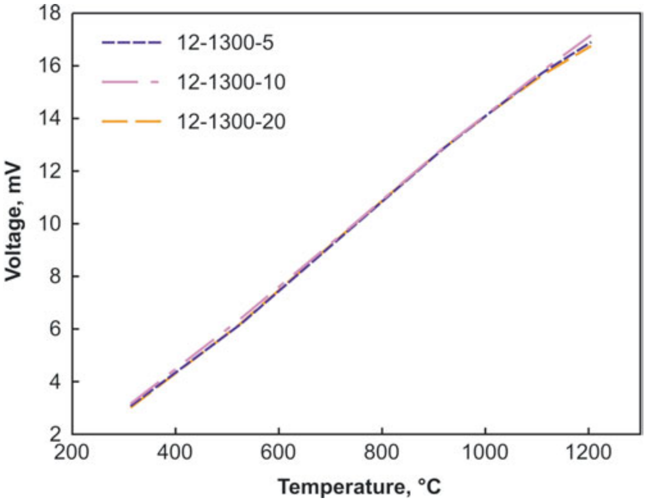


Fig. 12. Comparison of calibration data obtained from thermocouples heat treated at 1300°C for 5 h (12-1300-5), 10 h (12-1300-10), and 20 h (12-1300-20).

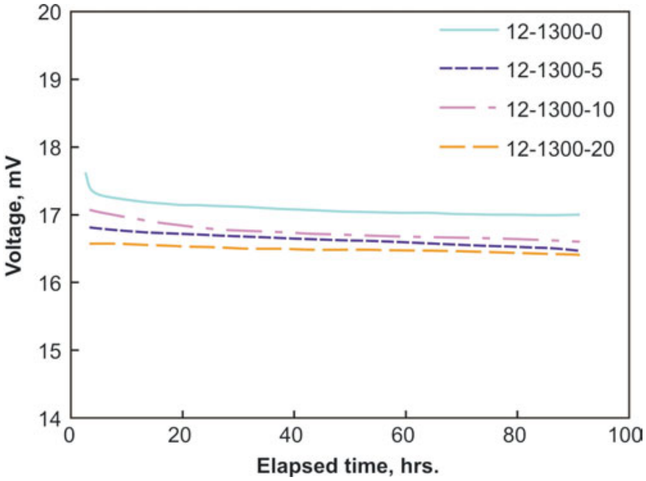


Fig. 13. Measured drift of thermocouples heat treated at 1300°C at 0 h (12-1300-0), 5 h (12-1300-5), 10 h (12-1300-10), and 20 h (12-1300-20) in 1200°C constant temperature test.

thermocouple without any heat treatment (12-1300-0) drifted more than the other thermocouples. However, the observed drift was minimal in all of the heat-treated thermocouples. Hence, investigations suggest that heat treatment times of at least 5 h for temperatures of at least 1300°C are needed to stabilize thermocouples for operating temperatures of 1200°C.

Figure 14 compares calibration results of swaged thermocouples that were prepared for operating at 1500°C. Similar to the results shown in Fig. 12, the results in Fig. 14 indicate that similar emf's were measured for thermocouples that were heat treated at 1600°C for 4, 8, and 16 h. In addition, the Fig. 14 curves indicate that the measured emf for the thermocouple heat treated at 1700°C is similar to values obtained for thermocouples heat treated at 1600°C.

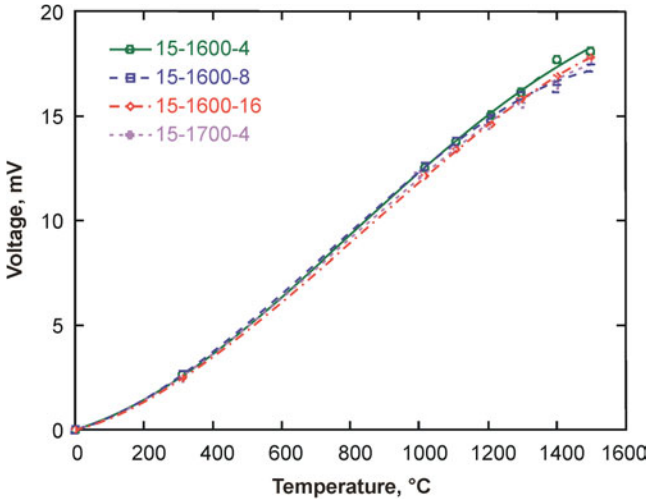


Fig. 14. Calibration data obtained from thermocouples heat treated at 1600°C for 4 h (15-1600-4), 8 h (15-1600-8), and 16 h (15-1600-16) and 1700°C for 4 h (15-1700-4).

III.D. Alternate Fabrication Techniques

As documented in Ref. 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 Fig. 15a). Swaged designs were initially pursued by INL because such thermocouple designs are easier to fabricate and are typically more rugged, even allowing some bending during installation. However, efforts have been initiated to investigate "loose assembly" HTIR-TC fabrication approaches, which are used for several types of commercial thermocouples and which have been selected by Commissariat à l'Energie Atomique and Thermocoax in recent efforts to develop an in-pile thermocouple containing pure molybdenum and niobium thermoelements.[9] In a loose assembly thermocouple configuration (see Fig. 15b), 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 $\sim 10^{-5}$ torr). The instrument assembly is then backfilled at room temperature with high-purity inert gas (either argon or helium) and seal-welded. Higher operating temperatures may be possible using a loose assembly design because thermoelement thinning and irregular

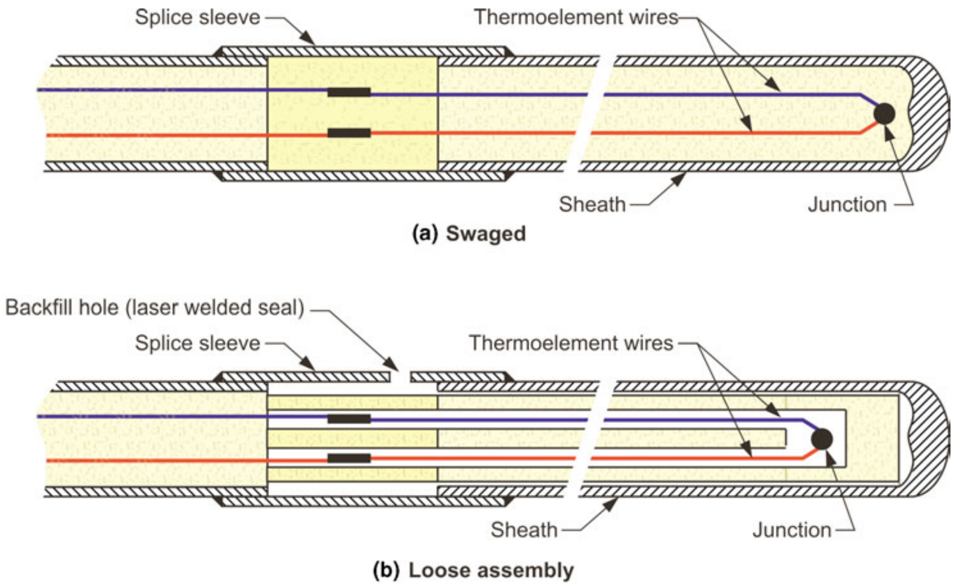


Fig. 15. Comparison of (a) swaged versus (b) loose assembly designs.

deformation associated with swaging are avoided. Furthermore, loose assembly designs may be better able to accommodate the differential thermal expansion of thermocouple components that occurs during thermal cycling without inducing thermoelement stress.

Efforts are underway in this program to develop loose assembly HTIR-TCs. Note that in the case of these designs, alternate sheath materials that cannot be swaged, such as molybdenum, may be used. A long-duration (1000-h) test was recently completed in which the performance of prototype loose assembly and swaged HTIR-TC designs was compared. Curves in Fig. 16 compare the performance of swaged and loose assembly HTIR-TCs containing 0.508-mm thermoelement wires. As shown in Fig. 16, the HTIR-TCs exhibit similar stability. Posttest examinations are underway to compare the end state of thermocouple components and identify any processes that could improve the performance of each of these HTIR-TC designs.

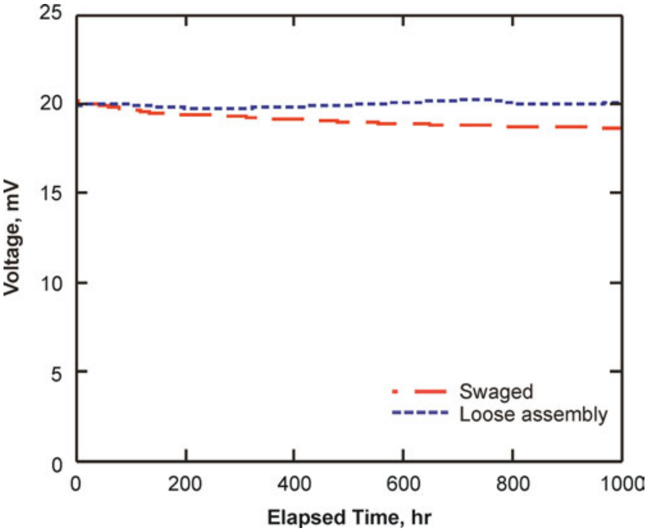


Fig. 16. Comparison of swaged versus loose assembly HTIR-TCs during 1000-h test at 1500°C.

IV. 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 (ultimately, up to at least 1800°C). A joint INL/UI project is evaluating several of these options: alternate materials that are not 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-Mo or KW-Mo, and Nb-1%Zr resist embrittlement better than the developmental, molybdenum–low niobium and niobium–low molybdenum alloys evaluated. Although the resolution of the thermocouples containing ODS-Mo and Nb-1%Zr is slightly superior, the lower cost of the commercially available KW-Mo makes a thermocouple containing KW-Mo and Nb-1%Zr the best option at this time. Evaluations suggest that molybdenum-niobium alloy thermocouples containing larger-diameter thermoelement wires are even more stable than the standard HTIR-TCs containing 0.254-mm-diam thermoelement wires. Optimization efforts in this project also included a systematic study of heat treatments for HTIR-TCs for two operating temperatures and the use of a loose assembly HTIR-TC design. Results indicate that HTIR-TCs should be heat treated at temperatures that are at least 100°C above their anticipated operating temperature. Initial evaluations of prototype loose assembly and swaged HTIR-TCs suggest that both designs exhibit similar stability during long-duration (1000-h) tests at 1500°C. However, additional evaluations are needed to understand if any additional fabrication process enhancements are needed to ensure long-duration stability of HTIR-TCs for operation at higher temperatures.

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