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HIGH TEMPERATURE IRRADIATION-RESISTANT THERMOCOUPLE PERFORMANCE IMPROVEMENTS

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ABSTRACT

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 (HTIR-TC) that contains doped molybdenum and a niobium alloy. Data from high temperature (up to 1500 ºC) long duration (up to 4000 hours) tests and on-going irradiations at INL's Advanced Test Reactor demonstrate the superiority of these sensors to commercially-available thermocouples. However, several options have been identified that could further enhance their reliability, reduce their production costs, and allow their use in a wider range of operating conditions. This paper presents results from on-going Idaho National Laboratory (INL)/University of Idaho (UI) efforts to investigate options to improve HTIR-TC ductility, reliability, and resolution by investigating specially-formulated alloys of molybdenum and niobium and alternate diameter thermoelements (wires). In addition, on-going efforts to evaluate alternate fabrication approaches, such as drawn and loose assembly techniques will be discussed. Efforts to reduce HTIR-TC fabrication costs, such as the use of less expensive extension cable will also be presented. Finally, customized HTIR-TC designs developed for specific customer needs will be summarized to emphasize the varied conditions under which these sensors may be used.

Key Words: Thermocouples, Radiation, High Temperature, In Pile Measurements

1 INTRODUCTION

New fuel, cladding, and structural materials offer the potential for safer and more economic energy from existing 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, standard thermocouples (TCs) either drift due to degradation at high temperatures (above 1100 °C) or due to transmutation of thermoelement wires. Thermocouples are needed which can withstand both high temperature and high radiation environments.

To address this need, the Idaho National Laboratory (INL) developed a design and evaluated the performance of a high temperature irradiation-resistant thermocouple (HTIR-TC) that contains commercially-available doped molybdenum and a niobium alloy thermoelements [1]. Candidate thermocouple component materials were first identified based on their ability to withstand high temperatures 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 (less than 2% drift was observed). Tests underway in INL's Advanced Test Reactor (ATR) demonstrate the in-pile performance of these thermocouples.

2 BACKGROUND

When INL initiated the current thermocouple development effort, various types of instrumentation that might be employed for in-pile, high temperature applications were reviewed [2, 3]. For temperatures above 1100 °C, specialized thermocouples were deemed to be the simplest and most economic approach for in-pile high temperature measurements.

3 RECENT EFFORTS

A joint University of Idaho/INL initiative tested options to improve the performance and reduce costs of the HTIR-TC. These options include new thermoelement materials, alternate thermocouple fabrication methods, improved heat treatments, and evaluation of suitable extension wire.

3.1 Thermoelement Material Evaluations

Historically, thermocouple designs have been improved by the use of alloys, rather than pure metals [4]. Previous efforts to develop a Mo/Nb thermocouple suggest that similar improvements may be made using Mo and Nb alloy thermoelements [5-7].

D. A. Prokoshkin and E. V. Vasil'eva [8] indicate that the addition of small amounts (less than 1%) of zirconium to niobium has been found to raise its recrystallization temperature by 25 ºC. The addition of molybdenum (up to 4%) may delay recrystallization by 75 ºC (up to 1200 ºC). Methodical investigations by Schley and Metauer [9] show that the addition of small amounts of molybdenum (less than 10%) to niobium will improve its temperature resolution.

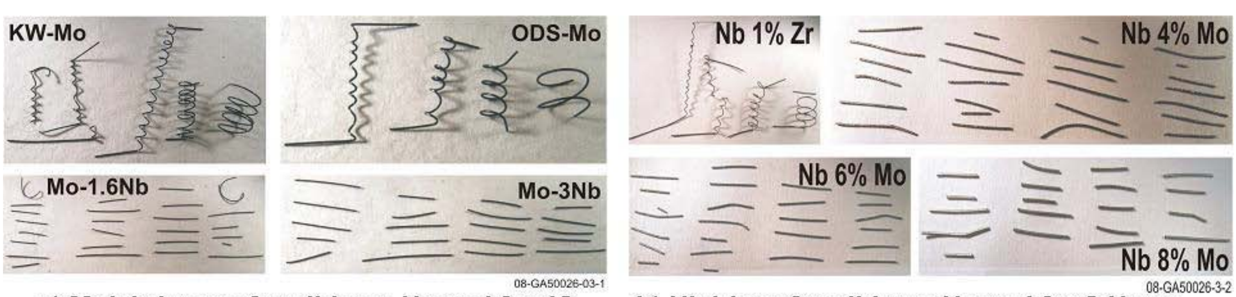
Efforts have also been completed to improve the ductility and resolution of molybdenum. D.A. Prokoshkin and E.V. Vasil'eva [8] indicate that the recrystallization temperature of molybdenum is increased if it is alloyed with small amounts of niobium. To control molybdenum crystal structure during recrystallization, 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 [9] suggest that the addition of small amounts of niobium (less than 5% to molybdenum) will improve its thermoelectric properties.

Table I lists molybdenum and niobium alloys evaluated. Two types of doped molybdenum, two alloys of molybdenum with small amounts of niobium, and four alloys of niobium with small amounts of zirconium or molybdenum were evaluated. It should be noted that the molybdenum-low niobium and niobium-low molybdenum alloys were specially made for this project. Efforts were limited to Mo-3%Nb and Nb-8%Mo because efforts to fabricate small diameter wires with larger amounts of niobium in molybdenum or molybdenum in niobium were unsuccessful.

Table I: 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

Applying the approach initially used by INL for commercial materials, 0.010” (0.254 mm) diameter wires for Table I candidate materials were tested for ductility after being exposed to high temperatures (1400 °C, 1600 °C, and 1800 °C) for various durations (2, 5, and 12 hours). Wire ductility was then tested by wrapping the samples tightly around mandrels of 2, 5, 10, and 20 times the wire diameter. As shown in Figure 1a, the ODS-Mo and KW-Mo samples exhibited suitable ductility after heating for 12 hours at 1800 °C. However, the Mo-1.6%Nb samples became brittle after heating for 5 hours at 1400 °C and the Mo-3%Nb samples became brittle after heating for 12 hours at 1600 °C. It was observed that the niobium alloys are the limiting factor for thermoelement ductility. Figure 1b shows niobium candidate materials after heating for 2 hours at 1400 °C. Only Nb-1%Zr has retained ductility.



a) Molybdenum Candidates Heated for 12 Hours at 1800 °C.

b) Niobium Candidates Heated for 2 Hours at 1400 °C.

Figure 1. Alternate material ductility evaluation results.

A comparison (Figure 2) of thermoelectric potential of thermocouples constructed with Nb-1%Zr thermoelements paired with all Mo candidates shows that all combinations exhibit suitable resolution, although the ODS-Mo/Nb-1%Zr TC is slightly superior.

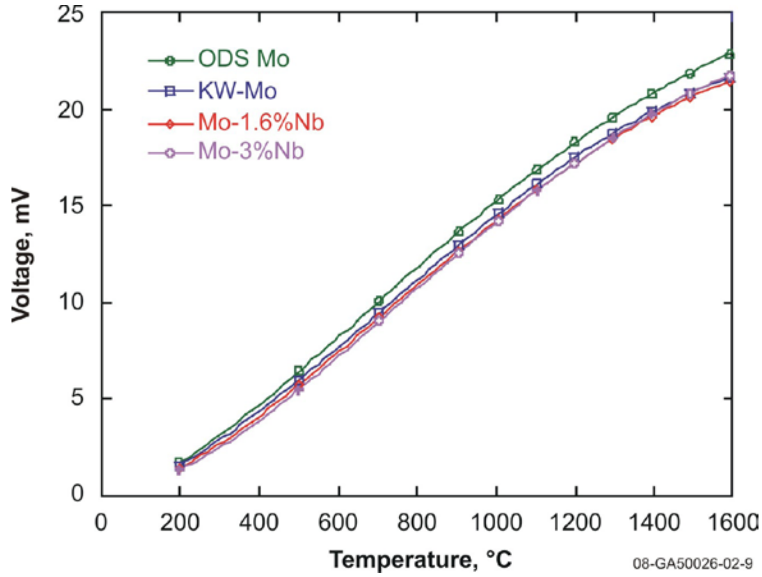


Figure 2. Thermoelectric potential comparison.

These evaluations indicate that a doped Mo candidate paired with a Nb-1%Zr thermoelement will yield a Mo/Nb thermocouple with acceptable resolution and durability. Due to the cost associated with ODS-Mo, a thermocouple constructed from KW-Mo and Nb-1%Zr thermoelements is currently the best choice.

3.2 Improved Heat Treatments

Metallic grain growth in thermoelements during operation causes signal drift and degradation. HTIR-TCs are heat treated prior to use to stabilize grain growth and mitigate signal degradation. The temperature and duration of the heat treatment is selected based on the anticipated peak temperature and temperature gradient to which the thermocouple will be exposed. Data are limited for optimizing heat treatment temperature and duration. Evaluations of heat treatments listed in Table II were completed to improve heat treatments.

Signal drift for HTIR-TCs heat treated at 1300 °C for various durations is shown in Figure 3. The untreated thermocouple (12-1300-0) shows a short period of drift near the start of the test. All other thermocouples are stable from the beginning. This indicates that increasing heat treat duration does not significantly improve the effectiveness of heat treatments.

Table II: Investigated heat treatments

Operating temp., °C	Heat treat. temp., °C	Heat treat. duration, hrs.	TC designator	Evaluations completed
1200	1300	0	12-1300-0	Response to 1200 °C, 100 hour drift test at 1200 °C
		5	12-1300-5	
		10	12-1300-10	
		20	12-1300-20	
	1400	20	12-1400-20	Response to 1200 °C
	1500	20	12-1500-20	Response to 1200 °C
1500	1600	0	15-1600-0	Response to 1500 °C, 100 hour drift test at 1500 °C
		4	15-1600-4	
		8	15-1600-8	
		16	15-1600-16	
	1700	4	15-1700-4	Response to 1500 °C

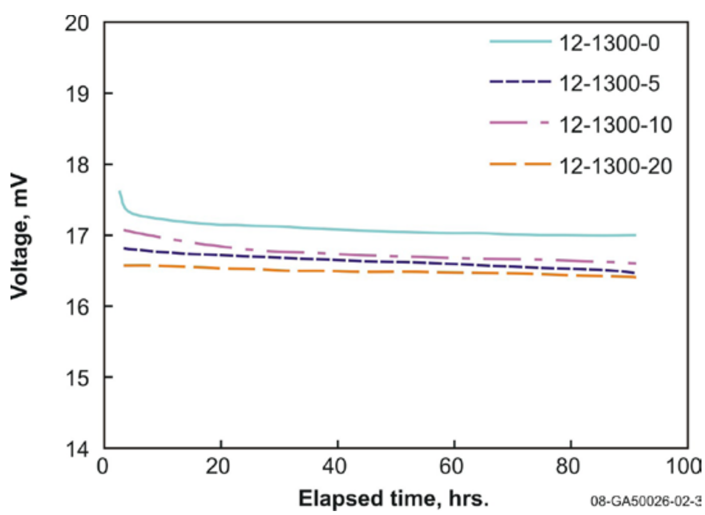


Figure 3. Signal drift comparison for HTIR-TCs tested at 1200 °C.

Figure 4 shows the thermoelectric response of thermocouples heat treated at 1600 °C and 1700 °C for various durations. These results also indicate that duration does not have a significant impact on heat treat effectiveness. Also, increasing heat treat temperature from 1600 °C to 1700 °C has negligible effect. Subsequent tests suggest that heat treat temperature has more effect than duration. A heat treatment of 4 hours at 100 °C over the TC service temperature was determined to be sufficient.

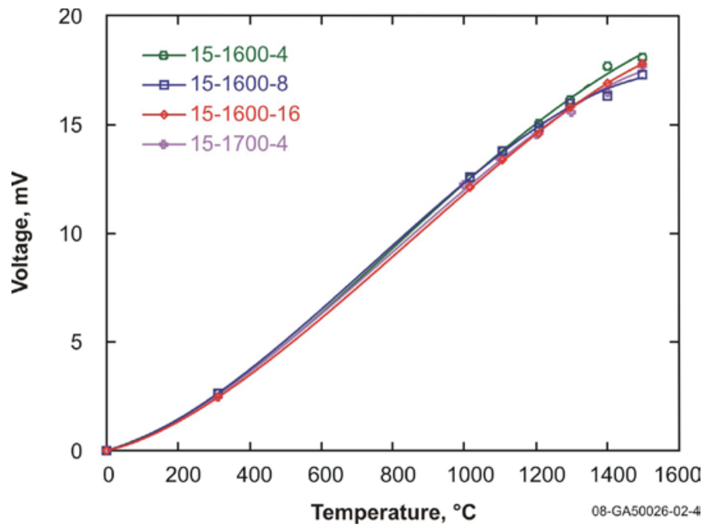


Figure 4. Thermoelectric response of TCs heat treated for 1500 °C service.

3.3 Alternate Fabrication Methods

Comparisons of alternate thermocouple designs also include studies of the effects of thermoelement diameter on performance as well as comparisons of swaged, drawn, and loose assembly thermocouples. The standard INL HTIR-TC is constructed with 0.010" (0.254 mm) diameter wires. Ludtka et al. [10] have determined that increasing wire diameter improves reliability of Type-K and Type-N thermocouples. INL tested HTIR-TCs constructed from 0.005" (0.125 mm), 0.010" (0.254 mm), and 0.020" (0.508 mm) thermoelements. The results of a 1000 hour drift test at 1500 °C are shown in Figure 5.

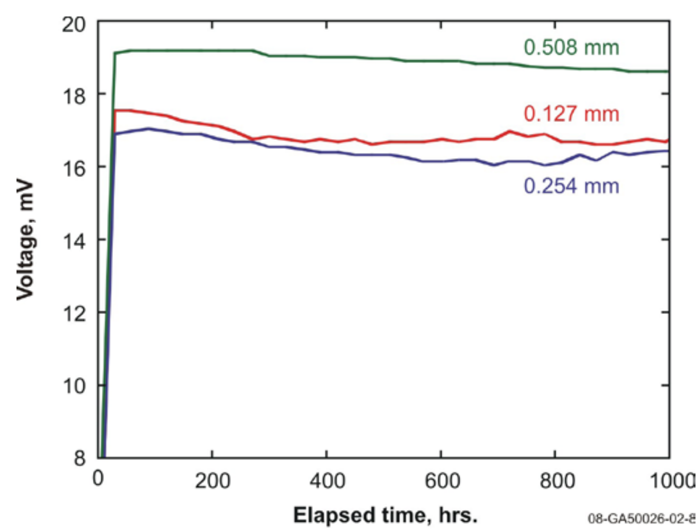


Figure 5. Results from 1500 °C drift test for HTIR-TCs with alternate diameters.

These results indicate that reliability of the HTIR-TC design may be improved through the use of larger diameter wires.

In addition to the swaged design, thermocouples may also be constructed using drawn or loose assembly methods. A swaged thermocouple is made by threading crushable insulator beads onto the thermoelements. This insulator stack is loaded into a metallic sheath and swaged (compacted using a rotating die). This method can cause the wires to twist and deform non-uniformly. A drawn thermocouple is made similarly, except it is pulled through a non-rotating die. INL evaluations show that drawing results in less wire damage and more uniform insulator compaction than swaging. Loose assembly thermocouples are constructed using hard fired (non-crushable) insulators. The insulator/wire assembly is loaded into a metallic sheath. The thermocouple is then vacuum purged, backfilled with an inert gas, and sealed. The loose assembly thermocouple may improve reliability by reducing contact and thermal stresses between the components. Figure 6 shows simple diagrams of a swaged/drawn thermocouple and a loose assembly thermocouple.

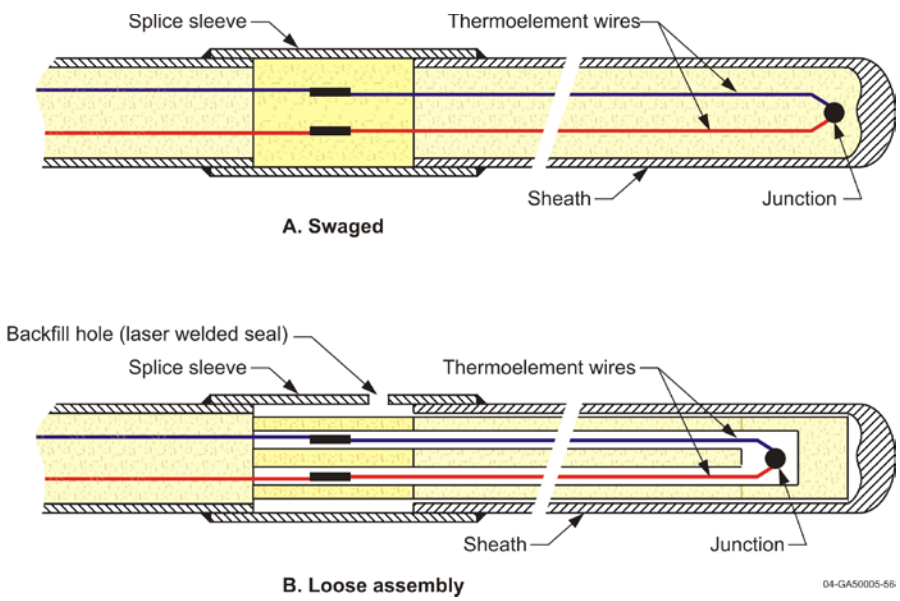


Figure 6. Swaged/drawn and loose assembly thermocouple designs.

Testing is currently underway to compare the performance of the swaged, drawn, and loose assembly thermocouples. The test is scheduled to last at least 1000 hours at a steady temperature of 1500 °C. After the first 1000 hours, the surviving thermocouples will be tested at 1800 ^{o}C for an as yet undetermined duration. This test is being performed in a high temperature vacuum furnace, pictured in Figure 7.

Multiple swaged, drawn, and loose assembly thermocouples were included in this test. The test thermocouples were heat treated for four hours at 1600 ^{o}C prior to the start of the test. Previous testing indicates that the loose assembly thermocouples may benefit from an insulator "bake out" before assembly. This is due to the possible off-gassing of oxygen from the ceramic at test temperatures. To evaluate the effectiveness of baking out the insulators, some of the loose assembly thermocouples were constructed using insulators that had been heated in vacuum at 1650 ^{o}C and stored in argon prior to assembly. Specifications for tested thermocouples are summarized in Table III.

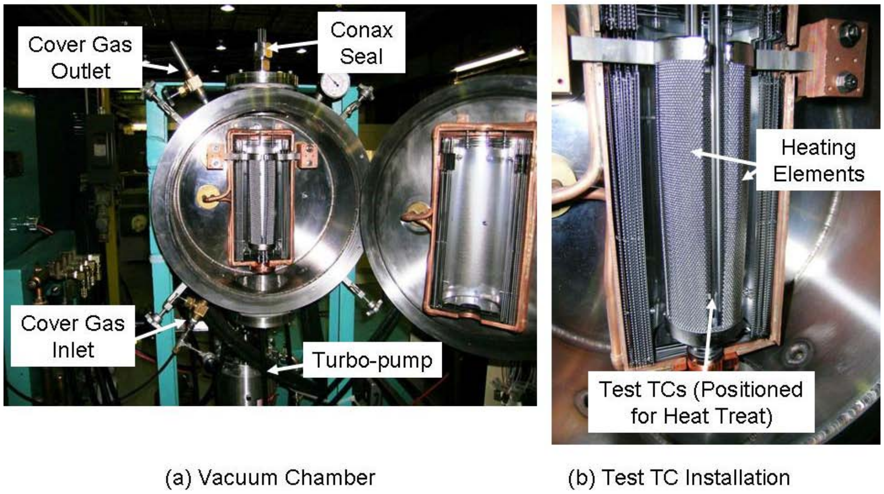


Figure 7. Vacuum furnace test setup.

Table III. Thermocouple specifications.

TC	+ Wire	- Wire	Insulator	Sheath	Leak Tightness (cc/min)	Vacuum Purge (torr)
Swaged	0.020" KW-Mo	0.020" Nb-1%Zr	Crushable Hafnia	Nb-1%Zr	$<10^{-8}$	N/A
Drawn	0.020" KW-Mo	0.020" Nb-1%Zr	Crushable Hafnia	Nb-1%Zr	$<10^{-8}$	N/A
Loose Assembly	0.020" KW-Mo	0.020" Nb-1%Zr	Hard-Fired Hafnia	Molybdenum	$<10^{-8}$	$7.2*10^{-4}$

Representative results from the test (in progress) are shown in Figure 8.

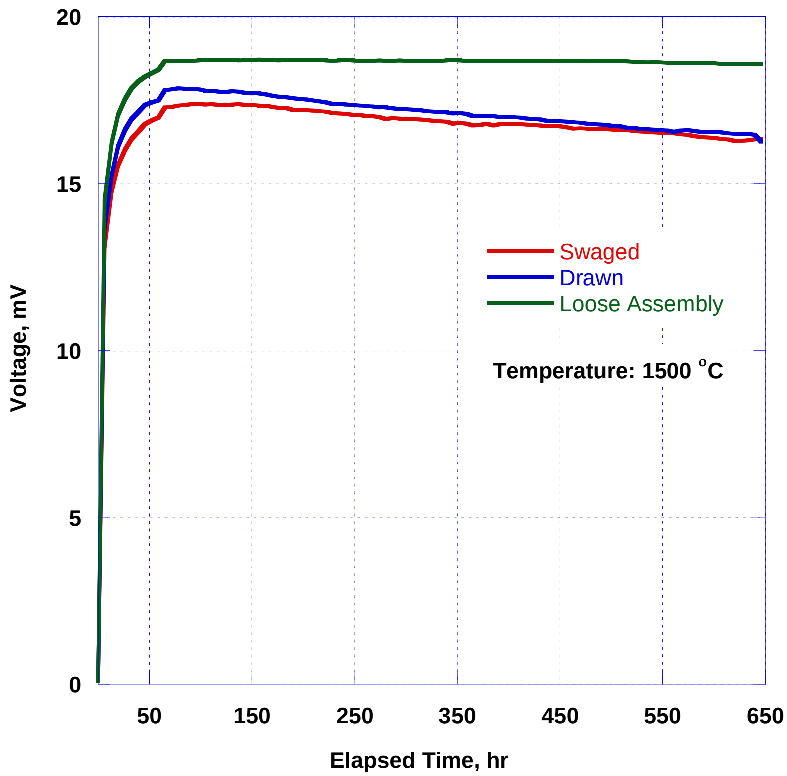


Figure 8. Thermocouple performance after 650 hours at 1500 °C

There are several observations that can be made from this plot. The signals from the swaged and drawn thermocouples are observed to steadily decrease over the test duration. This may indicate that the identified heat treatment is insufficient for swaged and drawn thermocouples with 0.020" (0.508 mm) wires (the heat treatment trials were performed using thermocouples with 0.010" (0.254 mm) wires). The swaged and drawn thermocouples do show very consistent performance. This may mean that neither fabrication method yields a measurable performance advantage. The loose assembly thermocouple displays greater stability and resolution than the swaged or drawn thermocouples. This indicates that while the heat treatment appears insufficient for the tested swaged and drawn thermocouples, it may be sufficient for loose assembly thermocouples.

3.4 Customized Fabrication for Specific Application

INL HTIR-TCs are often customized so they can operate in harsh environments. For example, HTIR-TCs with alternate sheath materials, such as molybdenum or Inconel, have been fabricated for customers to prevent unwanted interactions between the HTIR-TC standard Nb-1%Zr sheath material and test environments. Once recent example involved the use of HTIR-TCs installed in zirconium diboride (ZrB_2) samples, which must be sintered at temperatures above 1300 °C and then exposed to oxygen at temperatures up to 800 °C. The HTIR-TC standard sheath material (Nb-1%Zr) was observed to oxidize rapidly during ZrB_2 oxidation. To solve this problem, an Inconel 600 sheath was tested. The Inconel sheath failed, however, due to a eutectic reaction between nickel and zirconium at a temperature below the required sintering temperature.

A customized HTIR-TC was then devised with an Inconel 600 under-sheath and an Nb-1%Zr over-sheath. The Nb-1%Zr over-sheath isolated the Inconel 600 from the zirconium and the Inconel under-sheath protected the thermocouple as the Nb-1%Zr over-sheath eroded during oxidation. Figure 9 shows a double sheathed HTIR-TC installed in a ZrB_2 sample. The sample was sectioned for examination after sintering and oxidation.

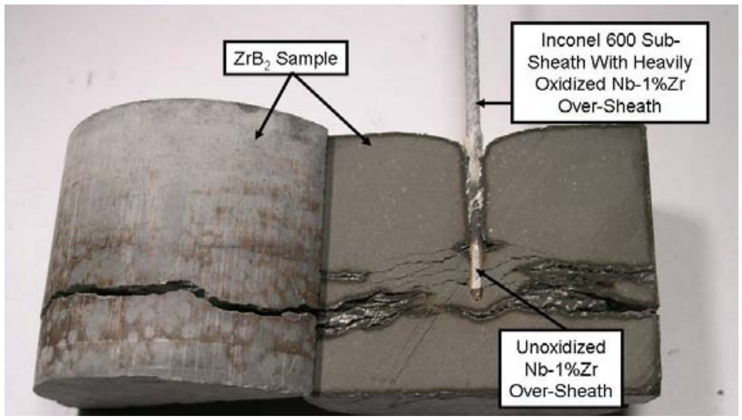


Figure 9. Double sheathed HTIR-TC installed in ZrB_2 sample.

4 COST REDUCTION

Efforts to reduce the cost of HTIR-TCs have focused on reducing fabrication costs and identifying less expensive compensating extension wires.

4.1 Automated Fabrication Development

Swaged HTIR-TCs have been fabricated in lengths of up to 30 feet. This process may require up to three people, as the thermocouple must be fed into the swager, lubricated upon entry, rotated during swaging, and caught upon exit. To reduce costs of fabrication, an automated swaging device has been developed at INL. This device, shown in Figure 10, automatically feeds, rotates, and lubricates the thermocouple. This reduces the personnel requirement from three to one (to monitor the process and catch the TC). The device also allows for an improvement in the uniformity of feed rate. This results in a more uniform sensor in terms of surface condition and wire deformation.

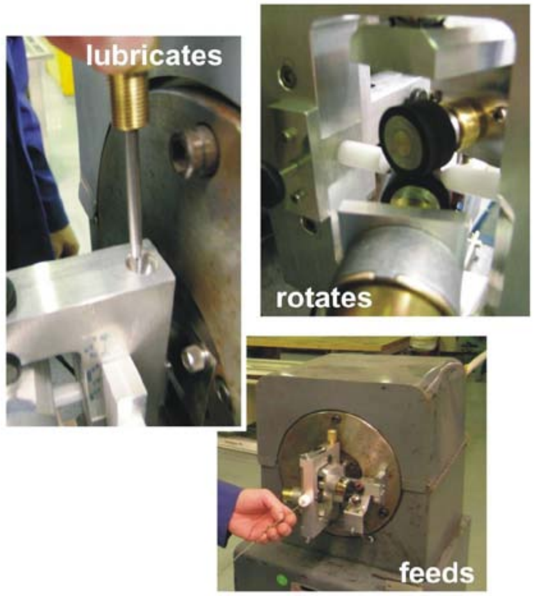


Figure 10. Automated swaging feed device.

The process used to calibrate HTIR-TCs has also been improved through the use of programmable furnace controllers and multiple furnace tubes (such that multiple TCs may be calibrated simultaneously).

4.2 Compensating Extension Wire Identification

The materials used in the construction of HTIR-TCs are relatively expensive. Therefore, costs may be significantly reduced through the use of compensating extension wire made from less expensive materials. Compensating extension wires mimic the thermoelectric response of the HTIR-TC thermoelements at lower temperatures (but cannot be used for high temperature applications due to low melting temperature). Previous studies indicate that some copper/nickel alloys may be suitable for use with Mo/Nb thermocouples [11-13]. However, the HTIR-TC does not use pure Mo or Nb. Therefore INL evaluated various copper/nickel alloys [14]. Copper/nickel alloys were selected from commercially available stock and ranged in nickel content from 0% (99.99% pure copper) to 30% (Cu-30%Ni). Bare wire thermocouples were constructed by pairing each Cu/Ni alloy wire with KW-Mo wire and with Nb-1%Zr wire. Each pairing was calibrated from 0 °C to 500 °C. The data produced was used to predict which Cu/Ni alloy pairs may best simulate the response of the HTIR-TC at low temperatures. Thermocouples were then constructed from the predicted pairings, for which calibration curves were developed. The response curves are shown in Figure 11, along with the low temperature response of the HTIR-TC (designated as KW Mo/Nb1Zr).

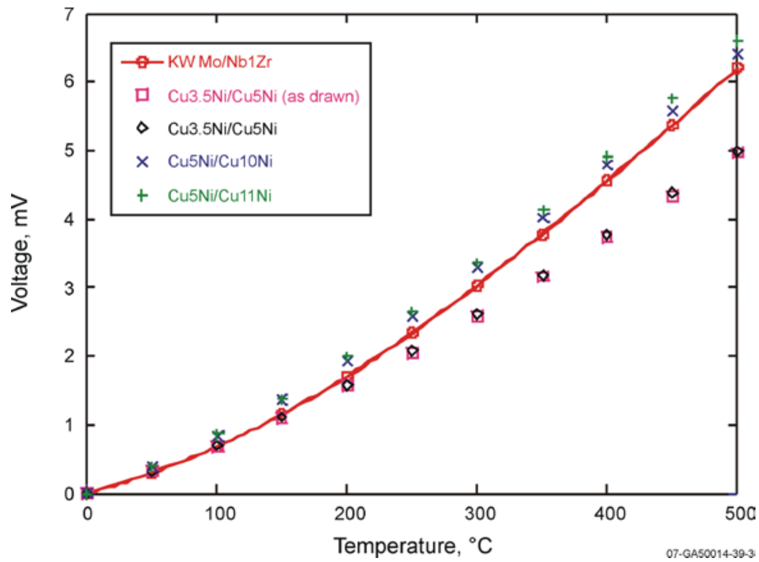


Figure 11. Compensating extension wire trials.

It was determined that a combination of Cu-3.5%Ni and Cu-5%Ni was the best match to the HTIR-TC for temperatures between 0 °C and 150 °C, while a combination of Cu-5%Ni and Cu-10%Ni is the best match for temperatures between 150 °C and 500 °C.

5 CONCLUSIONS

Several options have been identified and explored to enhance the performance and reduce the costs of recently developed INL HTIR-TCs. These options, evaluated through a joint INL/UI initiative, include the use of developmental alloys, alternate geometries, improved heat treatments, automated fabrication, and compensating extension wire.

Evaluation of developmental alloys indicates that the tested thermoelement candidate Mo/low-Nb and Nb/low-Mo alloys show no improvement in performance over the INL KW-Mo/Nb-1%Zr HTIR-TC design. The one candidate thermoelement that shows noticeable improvement is ODS-Mo, but the cost associated with this material offsets the small improvement seen.

Evaluation of various heat treatment temperatures and durations suggests that heat treat temperature has a more significant impact on thermocouple signal stability than heat treat duration. Results show that a heat treatment of 4 hours at 100 °C above expected service temperature is sufficient for the standard design HTIR-TC.

Alternate wire diameter evaluations indicate that the diameter of the thermoelements should be as large as a specified application allows, as stability and durability are improved with increasing wire diameter. Testing is underway to compare swaged, drawn, and loose assembly thermocouples. This test is scheduled to run for at least 1000 hours at 1500 °C, with survivors being subsequently tested at 1800 °C. Early results indicate that a loose assembly thermocouple constructed with yields superior resolution and stability to other tested thermocouple types.

Finally, devices and procedures have been developed to reduce the cost of producing HTIR-TCs. Automated swaging and calibration reduces the manpower required for production. Additionally, an inexpensive compensating extension wire has been identified that may reduce the costs associated with the materials used in the construction of the HTIR-TC.

6 ACKNOWLEDGMENTS

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