INL/EXT-19-55295
Revision 0

Out-of-pile performance of High Temperature Irradiation Resistant and Cladding Thermocouples

Richard Skifton, Lance Hone, Joe Palmer[1]
Ember Sikorski, Scott Riley, Brian Jaques, Lan Li[2]

[1]Idaho National Laboratory
[2]Boise State University

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Idaho National Laboratory
C670 Measurement Sciences
Idaho Falls, Idaho 83415

http://www.inl.gov

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C670 Measurements Sciences

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Approved by:

Name Title [optional]	Date
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ABSTRACT

The High Temperature Irradiation Resistant thermocouple (HTIR-TCs) has proven to be the nuclear temperature sensor. It outlast and outperforms all other commercially available thermocouples above 1100 °C inside reactor pressure vessels; also, recent calibration methods have pushed the HTIR-TC to accurately read temperatures through thermal transients during reactor shutdowns and restarts. The new temperature range of HTIR-TCs is from 0 °C to 1650 °C. The main objective of this study is to address manufacturing a more robust TC for handling and inserting into reactor experiments; to also apply the TC to a wider application. The TC has shown to be mainly susceptible to oxygen levels inside the heat treatment and calibration process and it is recommended that O_2 levels be brought to as low as possible. However, through modeling efforts the O_2 has been found to intercalate only within the first few layers of niobium on the outer sheath. Lastly, multiple materials were used for the sheath and insulators; all with similar outcomes when testing occurred over a long period of time.

CONTENTS

ACRONYMS

AGR	Advanced Gas Reactor
ATR	Advanced Test Reactor
BSU	Boise State University
EBSD	Electron Backscatter Diffraction
HTTL	High Temperature Test Laboratory
HTIR-TC	High Temperature Irradiation Resistant thermocouple
INL	Idaho National Laboratory
TC	Thermocouple

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1. Introduction

The High Temperature Irradiation Resistant thermocouple (HTIR-TCs) is the pinnacle of temperature sensing inside reactor vessels. They are sheathed thermocouples based on molybdenum and niobium alloys as sensing elements. The scope of this subtask is to improve the reliability of HTIR-TCs across a wider range of target operational parameters. The following are the main parameters to consider in the design optimization process: sensing elements alloy composition, sheath material composition, insulation material, and heat treatment process. Following common practice for commercial TCs, the objective is to define the most reliable instrument configuration and (if applicable) alternative options for sheath and insulation materials for different temperature ranges, starting from 1100 °C - the operational limit of commercial TCs in radiation environments – up to 1600 °C.

2. Background

The high temperature and radiation environment deep inside the core quickly de-calibrates all other thermocouple builds. How other commercially available thermocouples compare to the HTIR-TC can be seen in Table 1.

Table 1. Quality comparison of commercially available thermocouples and how they pair up to the HTIR-TC inside a high temperature radiation environment.

Thermocouple	Type K	Type B	Type N	HTIR-TC
Materials	Chromel vs Alumel	PtRh30% vs PtRh6%	Nicrosil vs. Nisil	Molybdenum vs. Niobium
Temperature Range	-270°C to 1260°C	250°C to 1700°C	-270°C to 1260°C	0°C to 1700°C
Cost	~$30/ft	~$250/ft	~$50/ft	~$250/ft
Radiation Tolerance as Compared to HTIR-TC	1/10th	~1/100th	1/4th	

The HITR-TC has been monitored over the last 1.5 years inside the Advanced Gas Reactor (AGR) 5/6/7 tests currently being performed at the Advanced Test Reactor (ATR) located at the remote site of Idaho National Laboratory (INL). The overwhelming success of the HTIR-TC in this experiment is staggering. The HTIR-TC has successfully measured 1500 °C for ~9 months; with intermittent shut down and restarts of the reactor putting the thermocouples through drastic thermal gradients. During such times the HTIR-TC has not only successfully measured the extreme high temperatures, but the low coolant (e.g. water) temperatures as well. Figure 1a shows the positioning of the various thermocouples inside Capsule 3 of the AGR 5/6/7 test; with about half as HTIR-TCs, while the other half are of a Type N construction. Specifically looking at TC-3-5, a HTIR-TC at the geometric center of the experiment, it can be seen in Figure 1b measuring ~1500 °C during reactor operation. This is the hottest, sustained temperature ever recorded inside a reactor. Further, the ATR has on average 10x more fluence than any commercial reactor; justifying the incredible nature of this new temperature sensor.

(a)

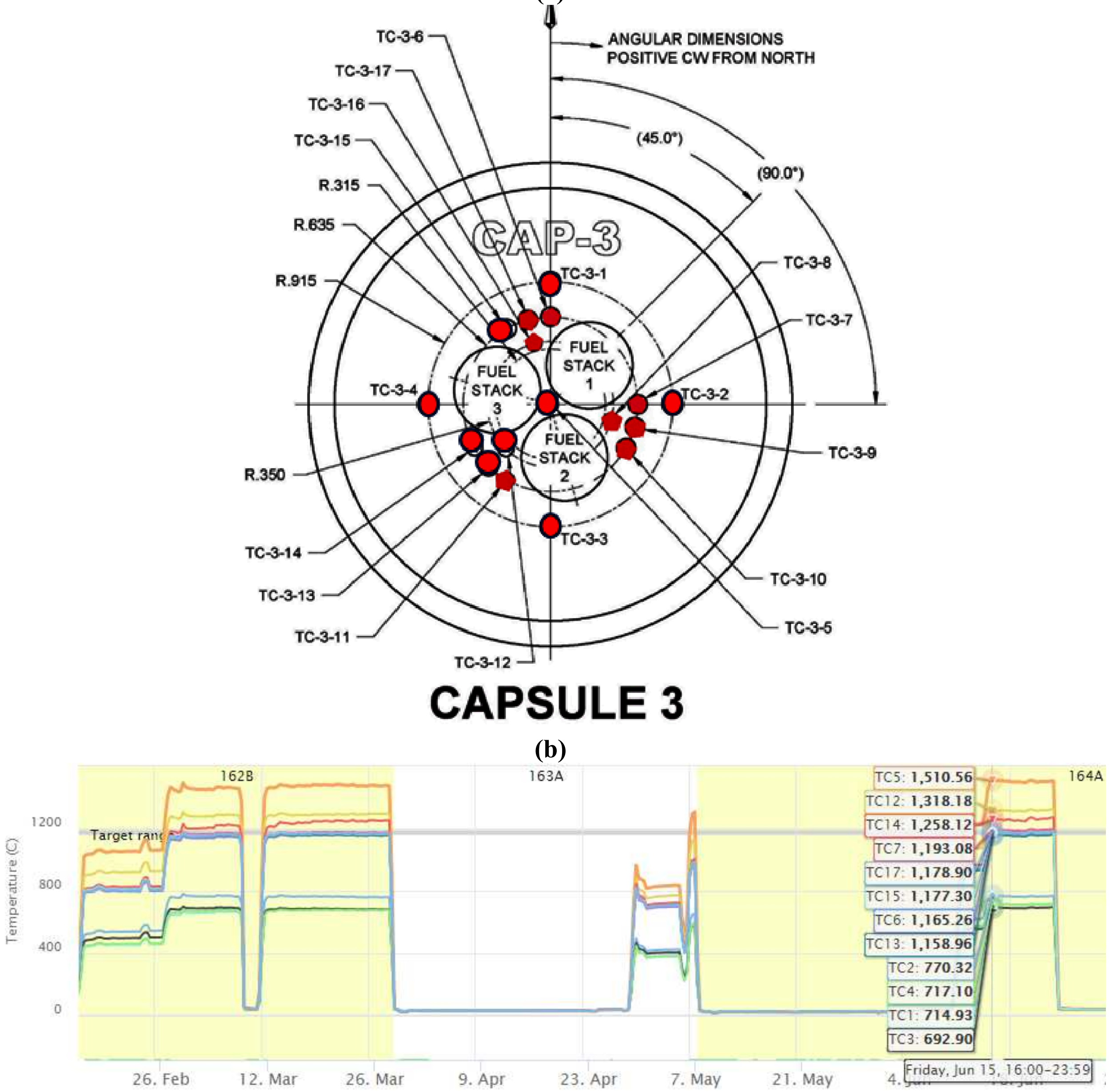


Figure 1. (a) Map of thermocouple positions inside capsule 3 of the AGR 5/6/7 experiment. (b) Measured temperatures over a period of time of the AGR 5/6/7 experiment with HTIR-TC matching the Type N thermocouple readings in the periphery of the experiment, and outperforming all others at the geometric center.

3. Experimental Work Performed at Boise State University

The heat treatment of the HTIR-TC thermoelements (e.g. niobium and molybdenum) is necessary to move all the as-manufactured wire (state A) to the heat treated condition (state B). This dampens out any potential drifting during operation. In order to maintain ductility of the HTIR-TC after the extensive heat treatment and calibration process, Boise State University (BSU) has performed heat treatments at various temperatures with the HTIR-TC under two different sheathing materials. The experiment design can be seen in Table 2 with temperature ranging from no heat cycle up to 1600 °C for 24 hours. Afterwards the HTIR-TC samples were placed in a 3-point bending apparatus and the effective stress vs. effective strain was measured.

Table 2. Experiment design for down-selecting ductile sheathing material after heat treatment and calibration.

HTIR-TC Sheathing Material	No Heat Treatment	1450 C for 6 hours	1600 C for 6 Hours	1600 C for 24 Hours
Pure Nb Sheath	x	x	x	x
Nb 1% Zr	x	x	x	x

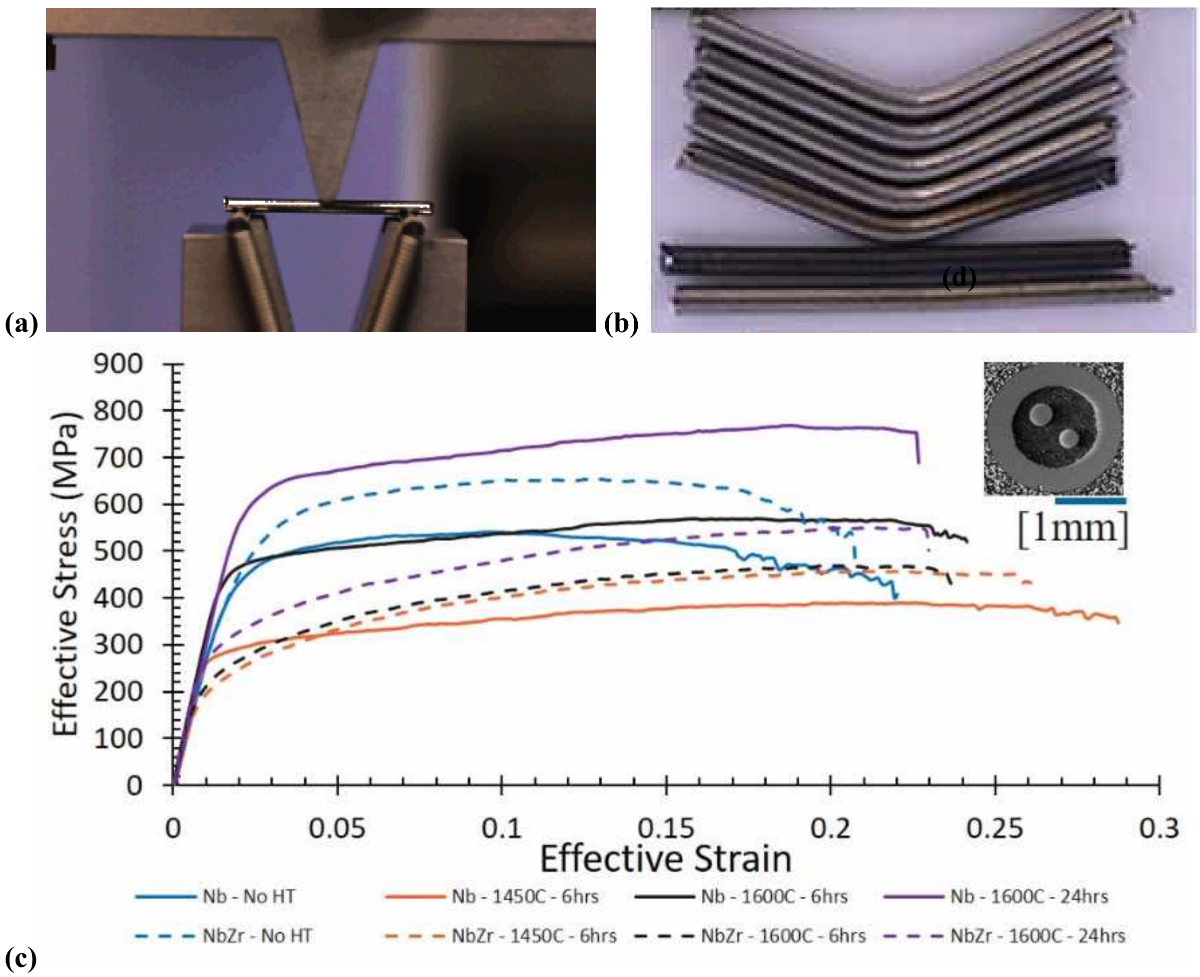


Figure 2. (a) pre-test set up of 3-point bending being performed on HTIR-TC samples. (b) Bend test samples after the 3-point bend test. (c) Effect stress vs. Effective Strain outcome of each sample tested in the 3-point bend test. (d) Typical cross section of the HTIR-TC.

In regard to the ductility of the TC, the effective percent total elongation, %, of each test sample was then plotted vs. the respective heat treatment temperatures as seen in Figure 3. This shows that heat treating the HTIR-TC for 6 hours at 1600 °C is a sufficient heat soak.

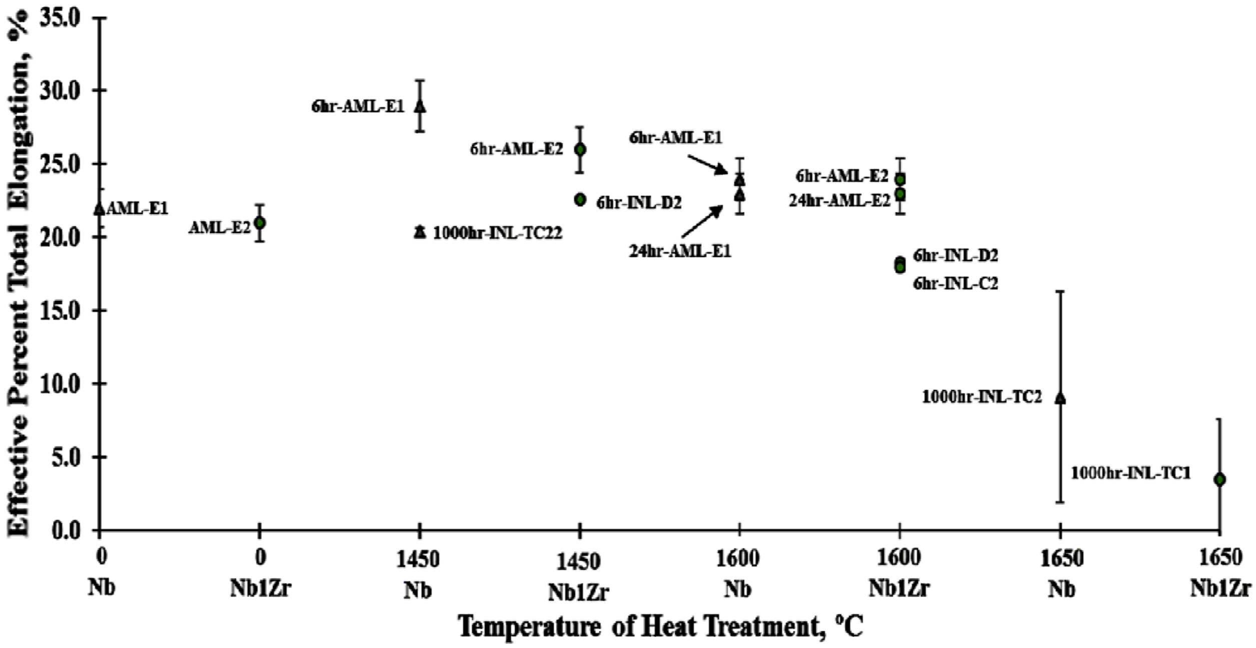


Figure 3. Effective percent total elongation for AML and INL heat treated HTIR-TCs showing 1600 °C for 6 hours is sufficient for heat treating time and temperature.

4. Modeling Work Performed at Boise State University

To better understand possible causes of drift in HTIR-TC performance, computational modeling is being performed. The goal is to first validate the modeling method with experiment and then extend the method to predict the effects of various heat treatments, dopants, oxygen and hydrogen uptake, and fission products.

A 3-step method is under development correlate structural changes with resultant voltage. The process begins with atomistic-scale modeling using Density Functional Theory on the HTIR-Mo and HTIR-Nb materials. Each consists of a 128-atom supercell including one La and one O atom for HTIR Mo and one P and one O atom for HTIR Nb. Once the geometry of each cell has been optimized, the electronic structure is calculated. The electronic structure, in turn, is used to calculate the absolute voltage the respective leg of the TC will produce. In summary, the method consists of:

Step 1. Optimize atomic structure

Step 2. Use atomic structure to calculate electronic structure

Step 3. Use electronic structure to calculate the Seebeck coefficient and integrate for voltage

The first iteration, referred to in Figures 4 and 5 as method 1, only considered temperature during Step 3 when the Seebeck coefficient was integrated. Method 1 worked well for HTIR Mo as shown in Figure 4, but poorly for HTIR Nb. This suggests that HTIR Mo maintains the same structure with increasing temperature, while HTIR Nb undergoes structural change with increasing temperature. A second process, method 2, was developed in which Step 1 considers the effects of temperature, using *Ab initio* molecular dynamics. In method 2, the atomic structure is calculated at each temperature and the voltage will be evaluated for only that temperature. While method 2 is still in progress, the improvement of using the 300 °K HTIR Nb structure integrated over the full temperature range is shown in Figure 5. It is expected that as the higher temperature atomic structures are incorporated, the modeled voltage will better match the experimental voltage.

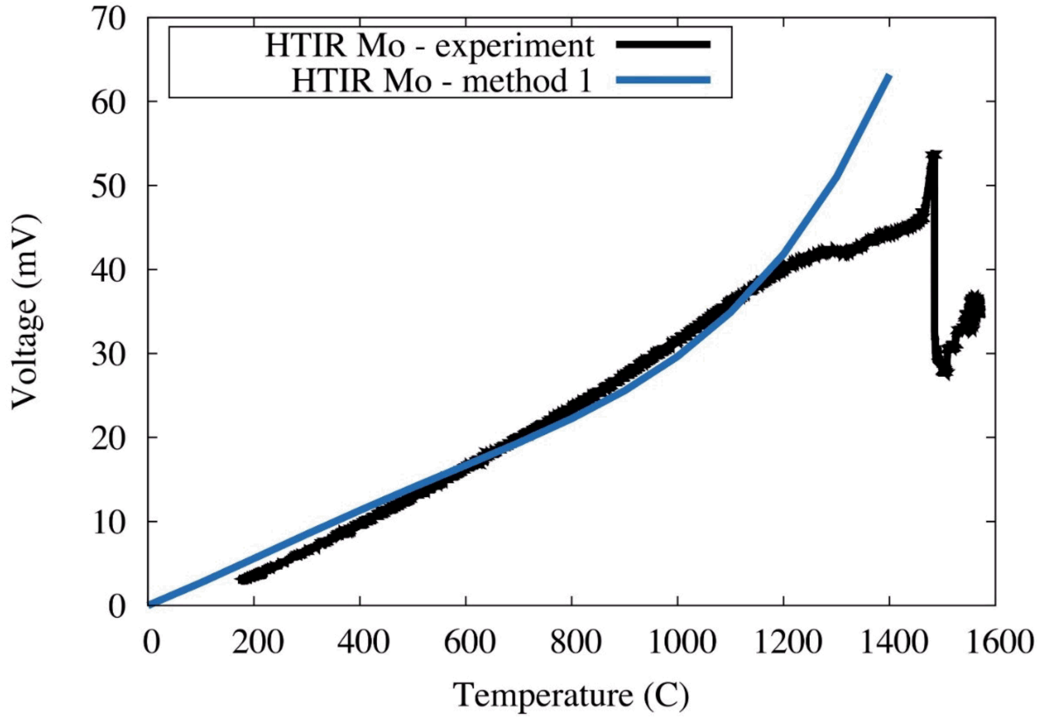


Figure 4. Comparison of HTIR-Mo voltage from modeling results following method 1, where temperature effects are not considered during atomic structure calculation, to experimental data. The experimental voltage was taken by pairing a HTIR Mo leg with the industry standard Pt leg and subtracting out the Pt contribution.

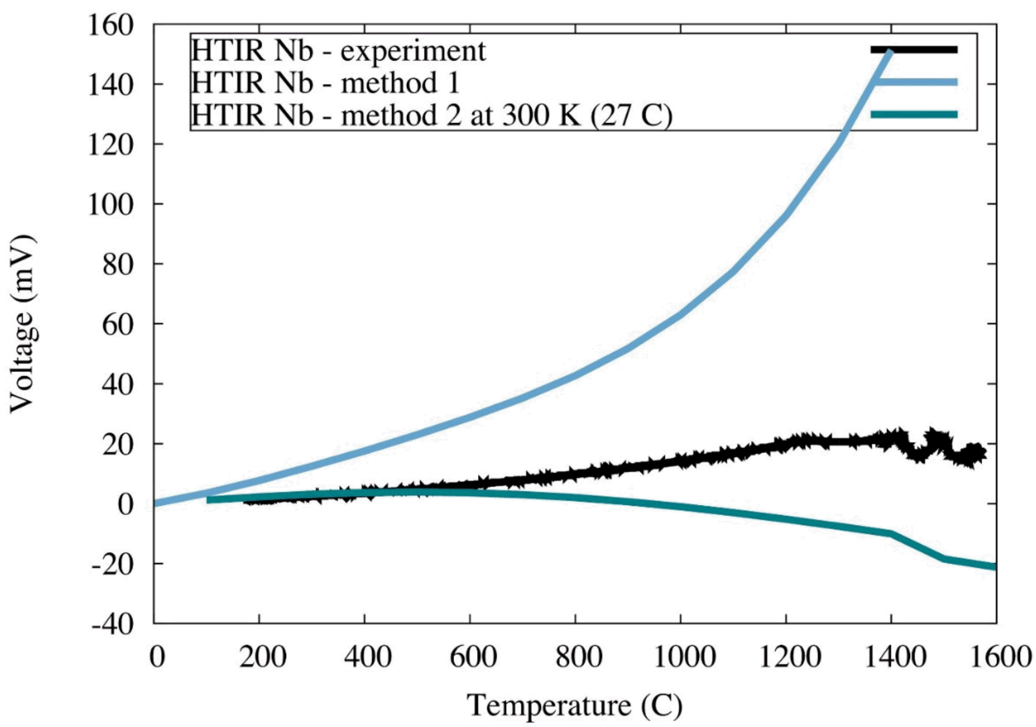


Figure 5. Comparison of HTIR-Nb voltage from modeling and experiment. Method 1 does not consider temperature effects during atomic structure calculation. Method 2 does consider temperature effects during atomic structure calculation. The experimental voltage was taken by pairing a HTIR-Nb leg with the industry standard Pt leg and subtracting out the Pt contribution.

One potential cause if drift is the incorporation of oxygen. Electron Backscatter Diffraction (EBSD) data suggests that after heating, oxygen may enter the HTIR Nb thermoelement. Preliminary *Ab initio* Molecular Dynamics runs were performed towards a better understanding of how likely oxygen diffusion into the HTIR Nb is (Figure 6). However, these runs incorrectly predict that oxygen does not diffuse into the Nb surface. This is likely the result of the boundary conditions applied to the simulation, in which the unit cell is repeated infinitely in each direction. Thus, the calculations show that if there is one oxygen atom to every four surface Nb atoms and if every oxygen atom must behave the same way, the oxygen will not penetrate the surface. Further calculations will be conducted with unit cells with greater surface area and more oxygen atoms to get a more accurate look at the diffusion mechanism.

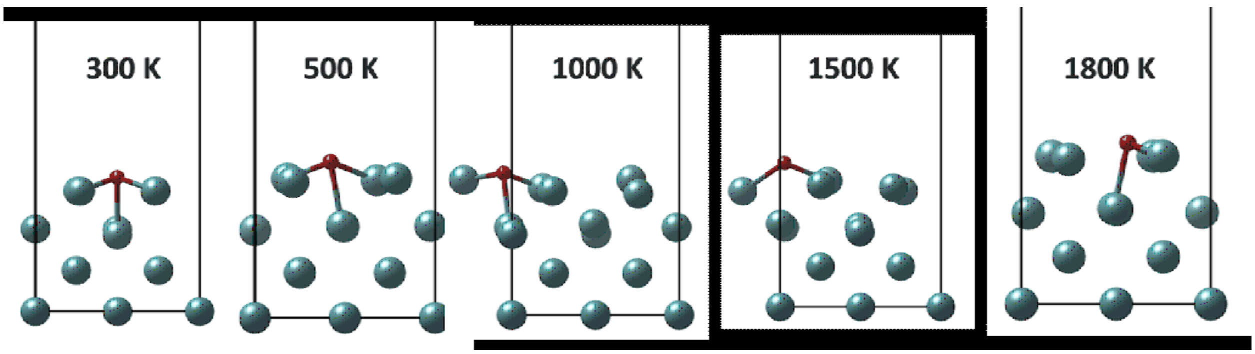


Figure 6. Preliminary studies of O at the Nb (100) surface. While these figures suggest O does not intercalate into the Nb surface, this is likely the result of inappropriate boundary conditions. Further work is underway to improve the models.

5. Idaho National Laboratory Furnace Testing

As part of broadening the HTIR-TC applicability as a low cost alternative to replace other commercially available TCs at their absolute maximum temperature (i.e. Type K and N both at 1260 °C and Type B at ~$250/ft, to date), the HTIR-TC was built with alumina, magnesia, and hafnia insulators inside a niobium with 1% zirconium sheath. Where other thermoelements begin to quickly drift away from their calibrated values, the HTIR-TC is performing exceptionally well at 1260 °C. As can be seen in Figure 7, even after ~1500 hours the three different HTIR-TC builds are still within 0.4% of the furnace set point. Note: These values have been normalized as it was found a calibration using both room and boiling water temperature as a data point was needed. It appears that Magnesia (i.e. MgO), although had minimal drift for several months began to drift quite considerably after about 3-4 months. MgO insulation was the worst performer. This means that the HTIR TC is compatible with most common utilized oxides as insulators, therefore the sheathing material can be changed out for a non-oxidizing material. This potentially makes the HTIR-TC capable of most high temperature applications – not just nuclear. However, it is recommended for nuclear applications to use either pure niobium or niobium 1% zirconium sheathing with an alumina insulating layer. This is due to the performance of MgO in the out-of-pile testing and hafnia becoming highly activated after previously performed in-pile tests.

Table 3. Summary of HTIR-TC out-of-pile performance at 1250°C furnace set point.

TC ID	Construction Details	Performance Summary	Ultimate Fate
HTIR-TC-62	Al_2O_3 insulation, Nb/1%Zr sheath. La-Mo/P-Nb thermoelements. 1600 °C heat treat for 6 hrs. Mo protective sleeve.	Read about 54 °C high (1294 °C) upon initial startup with hot block at 1250 °C. Drifted up about 4 °C over next 6 weeks. Insulation resistance was initially about 7000 ohms and increased to about 25000 ohms.	As of 8/27/2018 reading 1298 °C. So the drift has been minimal since startup. 9/17/18=1300 °C. 9/24/2018=1301.5 °C 11/20/18=1317 °C 12/19/18=1321.7 °C 1/30/19=1326.3 °C 7/22/19=1284 °C.
HTIR-TC-64	Same as TC-62 except MgO insulation	Read about 38°C low (1212 °C) upon initial startup with Hot block at 1250 °C. Drifted up about 2 °C over the next 6 weeks. Insulation resistance was initially about 40 ohms and gradually increased to about 140 ohms. 40 ohms is sure low, but it doesn't seem to be affecting the reading much and it did increase as the test progressed.	As of 8/27/2018 reading 1214 °C. So the drift has been virtually nil since startup. 9/17/18= 1210.5 °C. 9/24/2018=1211.5 °C 11/20/18=1196 °C 12/19/18=1182 °C 1/30/19=1173 °C No chart readings after 1/30/2019 although resistances still look good. It had drifted a lot by the time of the last reading.
HTIR-TC-66	Same as TC-62 except HfO_2 insulation	Read about 54 °C low (1196 °C) upon initial startup with Hot block at 1250 °C. Stayed essentially dead flat over the next 6 weeks. Insulation resistance was initially about 230 ohms and gradually increased to about 270 ohms.	As of 8/27/2018 reading 1197 °C. No drift since startup. It's easier to solve calibration errors than drift problems so this is promising. 9/17/18=1197.5 °C. 9/24/2018=1195.5 °C 11/20/18=1201 °C 12/19/18=1207 °C 1/30/19=1208 °C 3/26/19=1198 °C 5/7/19=1184 °C. Failed 5/9/2019. It did very well.

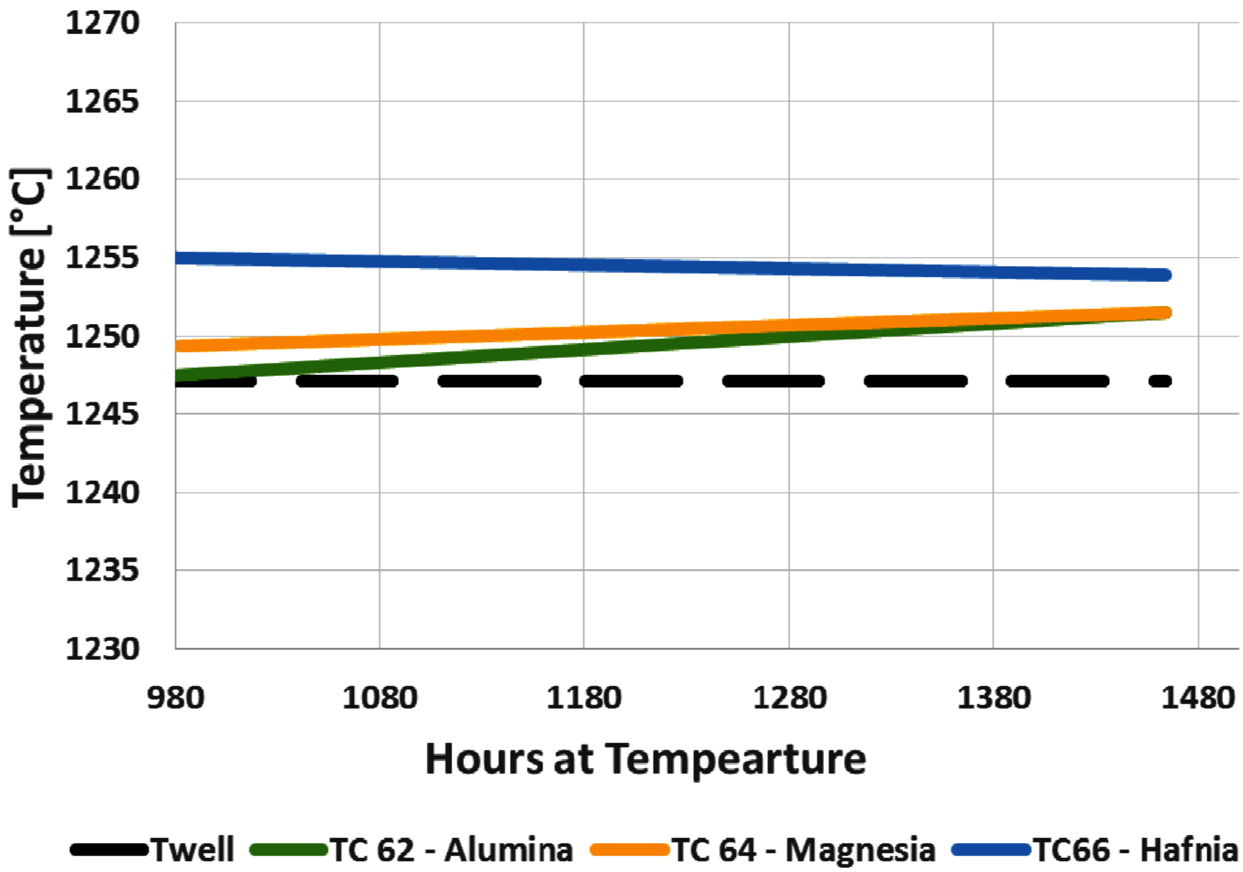


Figure 7. Longevity tests of various HTIR-TC builds at 1250 °C. Notice the HTIR-TCs are within 0.4% of set point temperature after ~1500 hours of testing. These temperatures have been normalized to the furnace thermal well temperature.

6. Cladding Thermocouples

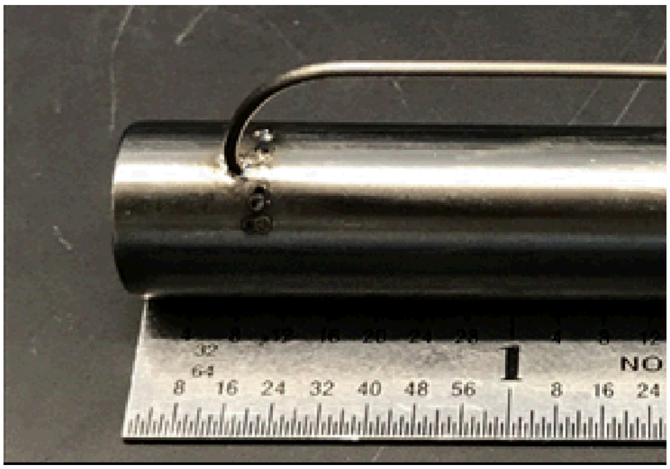
Attaching TCs to nuclear fuel cladding proves most effective when a strong material bond can be formed between the heat source and at or near the thermocouple junction using welding techniques. The main benefits of this attachment type are for temperature measurements requiring high accuracy and time response in targeted areas. Other strategies for measuring temperature with thermocouples include using tie wire to wrap TCs against an area of interest, using spring clips to press a TC against a sample, attaching with epoxies or cements, suspending a TC in a steady state environment, etc. However, these methods are inferior in performance when a need for fast and accurate data is desired while measuring nuclear fuel cladding.

Welding the TCs to nuclear fuel cladding required considerations for material types, cladding and sheath thickness, TC orientation, and other minor components. Concerning material selection, the welding of common alloys used for nuclear fuel cladding can result in increased brittleness and variations in hardness (at the joint) as a result of the formation of hydrides, intermetallic phases, and the $\alpha \rightarrow \beta$ phase transition. This is especially noticeable when welding dissimilar materials (i.e. sheath-to-cladding or wire-to-cladding). Therefore, TC sheath material choices were made based on commonalities between metals while still providing their essential function.

Originally, these attachments were to be done using laser welding, but when considering minimal cladding thickness and sheath thickness, low energy welds were required. This was obtained using a relatively new welding system by Sunstone Engineering called Orion 200i[2] system. This welding system utilizes a 1 mm diameter tungsten electrode, which facilitates the formation of an arc to the grounded work piece. The arc produced generates the heat necessary to fuse components while the system also provides an argon cover gas to the welding location for the duration of the arc-pulse. This micro-arc welding system is capable of delivering an arc-pulse at energy levels more favorable for small diameter sheathed thermocouples.

TC orientation proves to be of significant importance. When attaching the end of a TC perpendicular, or normal, to the cladding, accuracy severely decreases when compared to a paraxial attachment where the TC is attached axially along the cladding surface.

(a)



(b)

Figure 8. (a) Perpendicular (⊥) thermocouple orientation and (b) paraxial (||) orientation

This can be seen below from data collected in an out-of-pile experiment using an electric heater cartridge placed inside a cladding tube. This experiment was performed by pulsing the heater cartridge in a manner that simulates a potential transient reactor test to evaluate the response from different thermocouple orientations.

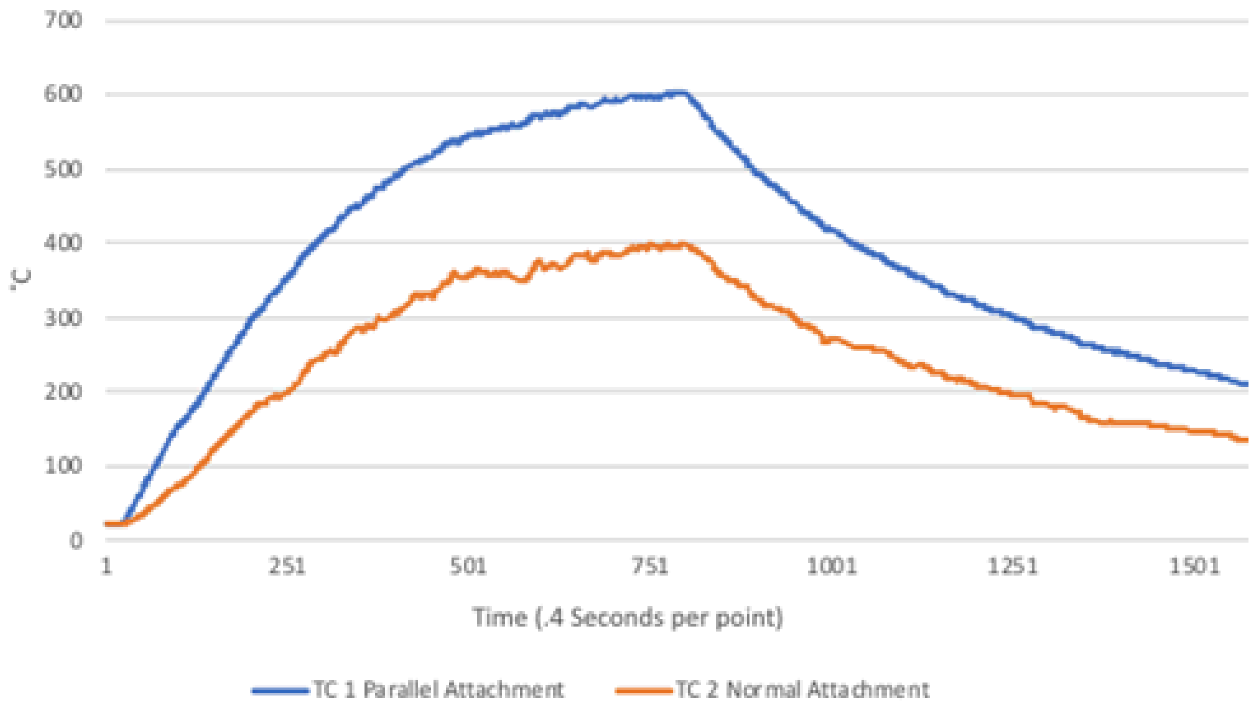


Figure 9. Recorded temperatures during an electrically heated pulse test

At the High Temperature Test Laboratory (HTTL) at the INL, TC attachment methods have been developed and studied in many different combinations such as grounded TCs, ungrounded TCs, various TC sheath materials, filler metal attachments, wire-to-cladding attachments with an intrinsic junction, and various TC types (type K, type R, type C, etc.) completed to support scenarios that can prove useful for measuring cladding temperatures with TCs.

7. Conclusion

The HTIR-TC is the world's leading nuclear thermocouple. Achieving higher temperatures with longevities no other thermocouple has been able to achieve deep inside the reactor core. From the various builds and tests performed in this study, it is recommended that for nuclear applications a pure niobium sheath with alumina insulating layer be used. For other applications, the molybdenum and niobium thermoelements have shown to withstand high temperatures with other insulators and sheaths.