Final Report

Project Details
Title: 880305700 - High Temperature Thermocouple Degradation Study
WBS: C.3.03.03.02.38.01

Contacts:
Arthur D. Watkins
Idaho National Engineering and Environmental Laboratory
P.O. Box 1625
Idaho Falls, ID 83415-2210

Alfred Thorne
Schott Glass Technologies, Inc.
400 New York Ave
Duryea, PA 18642

Introduction:
Glass manufacturers use precious metal thermocouples as the primary temperature sensors throughout the manufacturing process. It is well known that thermocouples degrade (drift) over time at high temperatures, but very little has been published that quantifies and characterizes this loss of accuracy at real operating temperatures over long periods of time. The primary indication of thermocouple degradation is EMF (voltage) drift as a function of time when the thermocouple is immersed at a constant temperature. Most tests described in the literature consisted of holding thermocouples at different high temperatures (e.g approximately 1300 to 1700 °C) for an extended period of time and then testing the thermocouples for EMF output at a single, lower reference temperature (e.g. 860 °C.) The EMF change from the original thermocouple output is drift and is normally associated with compositional changes in the "legs" or junction of the thermocouple. These resistance and EMF changes generally result from contamination (impurities) contained in the furnace atmosphere or ceramic protection tubes, from exchange of alloying elements at the welded junction, or from preferential volatilization of one metal (or oxide) from the alloy leg. Sometimes volatilization or embrittlement (in association with stresses on the thermocouple) will lead to breakage of the thermocouple wire.

Contamination from impurities is the most frequently cited cause of drift in thermocouples after exposure to high temperatures. In most of the testing cited in the literature, thermocouples were given positive protection from test furnace environments; thus, impurities in the ceramic components of the thermocouple assemblies were found to be the principle source of contamination. Ceramic components can include single or double bore electrical insulators (bores are for the wires), ceramic powder insulation, and ceramic protection tubes for isolation of the thermocouple from the furnace atmosphere. The ceramic composition generally used is high purity alumina (Al_2O_3), but high purity magnesia (MgO), and (to a lesser extent) zirconia (ZrO_2) and thoria (ThO_2) are sometimes used. Time, temperature, atmosphere, wire size, and geometry affected the magnitude of the EMF drift.

Approach:
The Idaho National Engineering and Environmental Laboratory performed a literature search, integrated a self-verifying temperature sensor into their furnace control system, calibrated and exposed five commercially available precious metal thermocouples, supplied by Engelhard-CLAL, to approximate temperatures of 1400 °C and 1610 °C for a period of 2 months. Trending, drift, and metallurgical analyses were performed on all and/or selected thermocouples and the

results published in a final report. The report included recommendations for follow-on experiments.

Literature Search Results:

A very limited literature search was performed regarding long term degradation of thermocouples during high temperature operation. The primary emphasis was on thermocouples constructed using various combinations of platinum and rhodium. The primary indication of thermocouple degradation is EMF (voltage) drift as a function of time when the thermocouple is immersed at a constant temperature. Contamination from impurities was the most frequency cited cause of drift in thermocouple after exposure to high temperatures, and a common impurity that seemed to cause the most drift was iron. Silicon was also associated with drift, but did not have as large of effect as iron. The drift was worse in reducing (or inert gas) atmospheres where the iron transport was enhanced. High temperature refractory metal protection tubes (e.g. tantalum) exacerbated contamination effects by enhancing the reducing atmosphere (by reacting with available oxygen). The drift could be lessened (but not eliminated) by using high temperature ceramics for the various components.

The iron impurity problem was documented in the 1962-1965 time period in two articles by Walker, Ewing, and Miller[1,2] of the U. S. Naval Research Laboratory. They exposed platinum/rhodium type thermocouples at about 1380 °C for up to 240 hours and then tested at 860 °C using various suppliers' grades of alumina (Fe ranged from about 0.04 wt% to 0.18 wt%) thermocouple protection tubes. After immersion in air at 1380 °C, the measured instabilities (at 860 °C) ranged from +6.7°C to 0.0 °C to -3.5 °C. After immersion in argon, the measured instabilities at 860 °C ranged from <0.2 °C to -40°C. The larger instabilities were associated with alumina grades that were analyzed as having higher Fe concentrations. Much larger instabilities were predicated (calculated values up to -231 °C) at 860 °C by decreasing the immersion depth of the thermocouple in the furnace after firing. Generally, in vacuum and neutral (argon) atmospheres, both the degree and distribution of contamination were influenced by wire size, temperature, firing time and other geometry effects. Therefore, large diameter wires were advisable for maximum stability in neutral and vacuum atmosphere. The larger wires are not needed for firing in oxidizing (air) atmospheres. The instabilities increased rapidly with firing temperatures and with decreasing rhodium content in the thermoelements (legs). Thermocouples with pure rhodium in one leg can be more reliable than other Pt-Rh combinations for conditions of gross iron contamination, but will be less reliable if iron contamination is not a factor. While iridium, and Ir-Rh alloy thermoelements show excellent resistance to instability resulting from contamination by iron, those tested appeared to exhibit instabilities from internal changes in the wires. For conditions where gross iron contamination is expected in argon and vacuum, the Ir/Ir=50%Rh couple is potentially more reliable than any of the Pt-Rh couples. If thermocouples are used under conditions of uniform thermal gradients and if compositional changes in either elements are suspected, the depth of immersion should be maintained constant or increased if maximum stability is required.

The theory that reducing conditions at high temperatures can be very deleterious to platinum based thermocouples was investigated by Darling and Sellman[3] in 1972. They state that if platinum thermocouples are used in air and both legs are adequately supported and protected against metallic and vapor contamination, then "satisfactory" performances can be obtained for long periods at temperatures up to 1500 °C. However, under reducing conditions (e.g. "gettered" argon or vacuum) they found reactions between platinum and alumina, zirconia, magnesia, and thoria components at temperatures below 100 °C. These reactions were often severe enough to cause complete failure (breakage) of the thermocouple legs. The mechanism was thought to be reduction of the metal oxide refractory, followed by vapor transport of volatile

species (e.g. Al vapor over alumina) to the thermocouple wire. Even though the vapor pressure of magnesium is much higher than that of aluminum, under reducing conditions magnesia didn't appear to cause much instability. After 100 hours at 1675 °C, a Pt/Pt-13% Rh thermocouple in contact with magnesia changed less that 1 °C when retested at the gold melting point. When run for 450 hours at 1650 °C under purified argon, recalibration at the palladium melting point only indicated a decrease in output equivalent to 4 °C. This result may point to impurity content as being the controlling factor. Certainly impurities like Fe in alumina or phosphorus (75 ppm) in throia can promote the deleterious reactions. At temperatures over 1600 °C, platinum evaporates in vacuum at a significant rate (10^{-7} g/cm^2 s) and intermetallic phases such as Pt_3Al can be formed.

Therefore, it is advisable to provide an oxidizing environment at the interior or the ceramic protection tube when using platinum based thermocouples at high temperatures. Extremely pure magnesia may be more stable than alumina for the insulator and protection tube.

Sometimes refractory metals are utilized for the protection tube or "sheath" that covers the platinum based thermocouples (if they are to be used in a reducing atmosphere). However, this generally is a bad idea at even the moderate temperatures range of 1100 °C to 1200 °C. Kollie, et.al. [4] showed that tantalum-sheathed, Al_2O_3-insultated Pt90Rh10/Pt (type S) and Pt70-Rh30/Pt94-Rh6 (type B) thermocouple assemblies were unstable when heated above 100 °C. Decalibrations of -152 °C were measured when one lot of type S assemblies were heated to 1330 °C. The type B assemblies were more stable and decalibrated only -11 °C during heating to 1330 °C. Metallographic and ion microprobe analyses showed that reactions had occurred at the Al_2O_3 interface, resulting in solutions of up to 27 atomic percent (at. %) Al in the thermocouple wires. Aluminum was not found in the tantalum sheath, but an oxygen concentration gradient did exist in the sheath with a higher oxygen concentration at the Ta-Al_2O_3 interface. The exact mechanism is not known, but thermodynamics show that the reaction (1) will proceed (ΔG = (at least) -48.9 kcal/mol) at 1200 °C,

(1) $3Pt + \frac{1}{2} Al_2O_3 + 6/10\ Ta \rightarrow AlPt_3 + 3/10\ Ta_2O_5$

This indicates that (a) oxidation of the Ta sheath reduced the partial pressure of O_2 inside the sheath and, (b) in the low O_2 environment, Pt reduced the Al_2O_3 to form intermetallic Pt-Al compounds.

Later Christie et.al.[5] presented similar results for inconel-600 sheathed MgO-insulated Pt90-Rh10Pt compacted thermocouples that had decalibrated so badly that they were no longer useful. Recalibration of one thermocouple assembly at 400 °C and 700 °C showed a decalibration of 5% to 47%, depending on the depth of insertion into the calibration furnace. Metallographic and ion microprobe analyses showed that reactions had occurred at the Pt-MgO and Pt90-Rh10/MgO interface, resulting in a solution of up to 12 at. % Mg in the thermocouple wires. It was concluded that oxidation of the Inconel-600 sheath reduced the partial pressure of O_2 inside the sheath to produce the low O_2 environment needed for the reduction of MgO by Pt.

Glaw and Szaniszlo [6] reported some interesting long term drift data for both Pt/Rh and W/Re (refractory metal) thermocouples at 1327 °C (1600 K) for up to 10,000 hours. The thermocouples pairs tested were Pt87-Rh13/Pt, Pt70-Rh30/Pt94-Rh6, and W95-Re5/W74-Re26 with "high" purity alumina insulators. They concluded that in argon, the 0.5 mm diameter noble metal thermocouples drifted very little in the first few thousand hours, but the drift rate increased. After 10,000 hours, the average total drift was -22 °C for the Pt87-Rh13/Pt and -13 °C for the Pt70-Rh30/Pt94-Rh6 pair. By comparison, in argon the refractory metal

thermocouple (W95-Re5/W74-Re26) drift was more rapid initially, resembling a decaying exponential. After 10,000 hours, the average drift was 122 °C. Fe and Si impurities were the main impurities commonly picked up by both the noble and refractory wires in quantities ranging from 200 to 2000 ppm, with Fe having the highest concentration increase at the junction and the largest concentration gradient near the junction.

The references follow:

1. B. E. Walker, C. T. Ewing, and R. R. Miller, "Thermoelectric Instability of Some Noble Metal Thermocouples at High Temperatures," The Review of Scientific Instruments, 33, 10 1962, page 1029-1040.
2. B. E. Walker, C. T. Ewing, and R. R. Miller, "Study of Instability of Noble Metal Thermocouples in a Vacuum," The Review of Scientific Instruments, 36, 5 1965, page 601-606.
3. A. S. Darling and G. L. Selman, "Some Effects of Environment on the Performance of Noble Metal Thermocouples," Temperature, 4, American Institute of Physics, 1972, page 1633-1644.
4. T. Gl Kollie, W.H. Christie, and Rl L. Anderson, "Large Decalibrations in Ta-Sheathed, Al_2O_3-insulated Pt/Rh Thermocouples Assemblies during Heating to 1330 °C," Journal of Less Common Metals, 57, 1978, page 9-27.
5. W. H. Christie, T. G. Kollie, R. E Eby, and R. L. Anderson, "Ion Microprobe Investigation of Large Decalibrations in Inconel-Sheathed Magnesia Insulated Platinum-Rhodium/Platinum Thermocouples," Journal of Less Common Metals, 59, 1978, page 17-33.
6. G. E. Glawe and A. J. Szaniszlo, "Long-term Drift of Some Noble and Refractory-Metal Thermocouples at 1600 K in Air, Argon, and Vacuum," Temperature, 4, American Institute of Physics, 1972, page 1645-1662.

Experimental Procedure:

A laboratory experiment was devised to compare several thermocouples of different composition to a self-verifying-temperature sensor (SVS) for an extended period of time. The experimental equipment consisted of a C&M tube furnace with temperature controller, a self verifying temperature sensor, and an INEEL designed and built data acquisition system. This equipment assembled in accordance with the schematic shown in Figure 1, heated and maintained a thermocouple bundle at a predetermined temperature schedule.

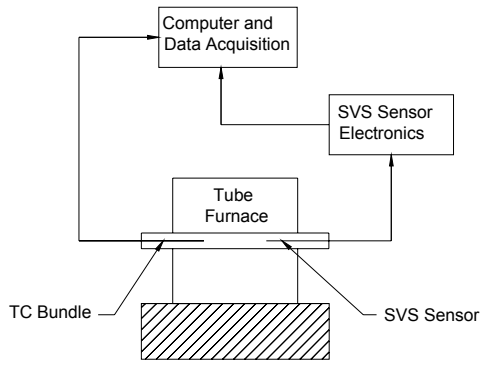


Figure 1: Schematic showing equipment setup

This furnace has temperature capabilities up to 1700 °C. It has three temperature zones, which can be independently controlled; however, in these test all zone temperature were controlled to a common temperature. The furnace uses type R thermocouple to control temperature. This particular thermocouple is not monitored for drift compensation, and is subject to drift should it occur. A 2-inch diameter ceramic tube sits in the middle of the furnace and protrudes several inches out each furnace end. Water-cooled stainless steel end caps were placed on the ends of

the ceramic tube, and act as a thermal barrier and penetration support. Five thermocouples were placed through one end of the ceramic tube end cap. The ends of these thermocouples were positioned within ½ -inch of the center of the furnace. Internal supports also kept the thermocouples radially centered in the tube. Additionally, a 5 cfh air purge was used to provide an oxidizing atmosphere inside the heating space of the ceramic tube. A picture the furnace is shown in Figure 2. Through the other end cap, a self-verifying temperature sensor (SVS) penetrated the barrier. The end of the SVS probe was positioned with in 1-inch of the ends of the thermocouple bundle. The SVS is a unique sensor in that it will not only monitor the temperature of the ceramic tubing heating space but will also adjust for temperature drift. Figures 3 and 4 shows the test thermocouples and SVS penetrations through the ceramic tube end caps. It should be pointed out that the SVS was used to monitor the temperature within the furnace and not used to adjust temperature via an automatic control loop. Any temperature adjustments based on the SVS temperatures were made manually.

Figure 2: CM Furnace Assembly

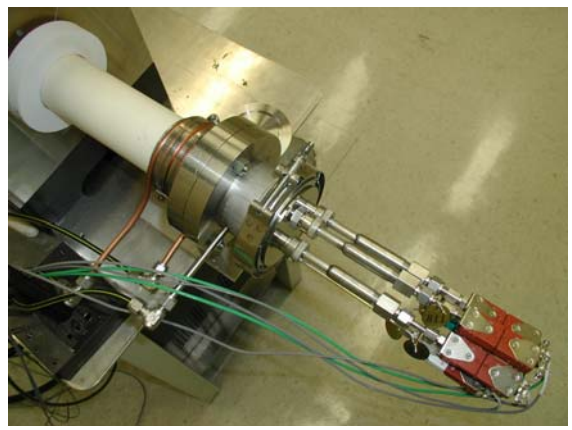


Figure 3: Test thermocouple end cap penetration

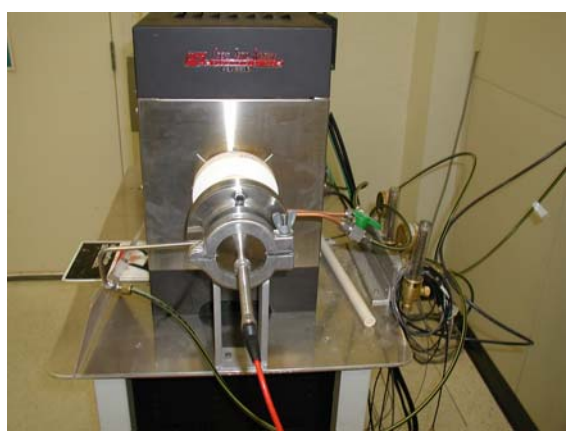


Figure 4: SVS end cap penetration

Five thermocouples were received and placed into the furnace for testing. All of the thermocouples were sheathed in platinum and had identification permanently attached to the head. The compositions, identification, and thermocouple sizes are shown in Table I. Filtered dry air was injected into the furnace at a rate of 5 cfh during testing. The thermocouples were heated from ambient room temperature to 1399 °C in 24 hrs, held for 759 hours, heated from 1399 °C to 1610 °C in 8 hours, and held at 1610 °C for 295 hours. The furnace run was then terminated and the thermocouples were allowed to cool to room temperature. Time and temperature of each thermocouple, including the SVS thermocouple, were recorded using computerized data acquisition.

The thermocouples were removed, sectioned, and analyzed. Thermocouples #693, #694, #810, and #812 were transversely sectioned through the center of the thermocouple junction. Energy dispersive x-ray analyses were run to

determine if any noticeable changes in the chemical composition were present. All samples were saved for later if warranted.

Table 1: Thermocouple Identification

ID Tag #	Type	Diameter (in.)	Composition
693	S	0.125	Pt-10%Rh vs Pt
694	B	0.125	Pt-30%Rh vs Pt-6%Rh
810	S	0.346	Pt-10%Rh vs Pt
811	B	0.346	Pt-6%Rh vs Pt-30%Rh
812	B	0.346	Pt-30%Rh vs Pt-40%Rh

Experimental Results and Analysis:

The SVS sensor monitored the furnace temperature during the testing. Figure 5 shows the SVS temperature trace of the furnace temperature for the duration of the experiment. The data indicates approximately a 1 °C/min temperature rise from ambient room temperature (25 °C) to the first step temperature (1397 °C). The furnace was held at this step temperature for 759 hours with a variation that was less than 0.5 °C. The furnace was then increased to the second step temperature (1605 °C) at a rate of approximately 0.5 °C/min and held for 295 hours. The temperature variation during this hold was less than 0.5 °C. Analysis of this data shows that the furnace system maintained the temperature as programmed, and the variation from the programmed temperature was very low. The triangular data points indicate major changes in the furnace programming/operation.

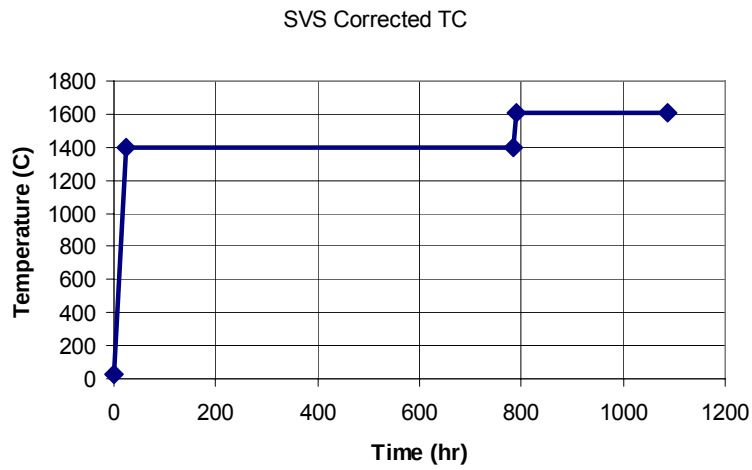


Figure 5: SVS temperature trace of furnace temperature

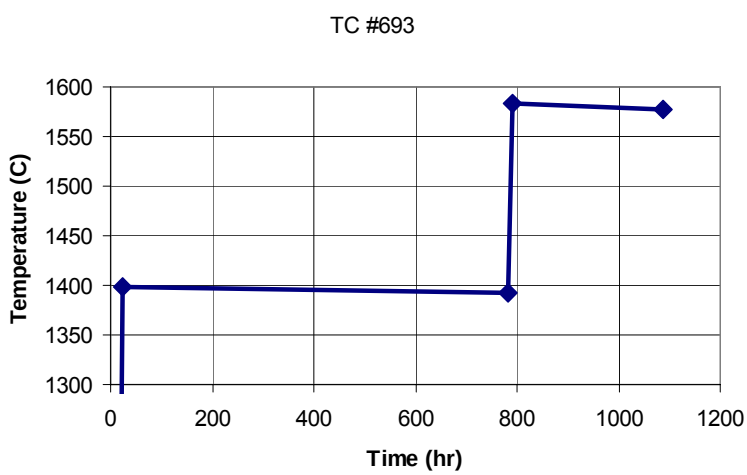


Figure 6: Test thermocouple #693 temperature trace

Figures 6 through 10 indicate the temperatures of all the test thermocouples. The Pt-10%Rh vs Pt thermocouple with swaged high purity MgO insulation (Enclad®) construction (#693) exhibited drift at the lower and upper temperatures. At the 1399 °C hold temperature, the thermocouple drifted -6 °C over 759 hours, or at an average calculated rate of -0.008 °C/hr. At the 1610 °C hold temperature, the thermocouple drifted -7 °C over 295 hours, or at an average calculated rate of -0.024 °C/hr.

The Pt-30%Rh vs Pt-6%Rh thermocouple with swaged high purity MgO insulation (Enclad®) construction (#694) did not exhibit drift at the lower holding temperature; however, at the higher

temperature (1610 °C) the thermocouple drifted -3 °C over 295 hours, or at an averaged calculated rate of -0.012 °C/hr.

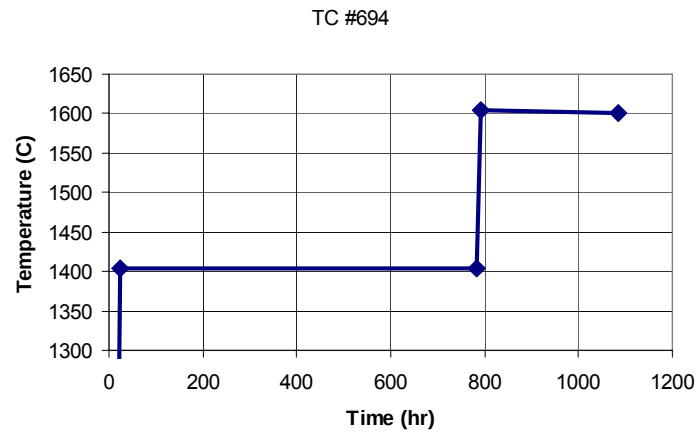
The Pt-30%Rh vs Pt-40%Rh thermocouple with high purity Al_2O_3 insulation construction (#812) failed as the furnace temperature was increased from 1399 °C to 1610 °C. However, at the lower holding temperature, the thermocouple exhibited a drift of +4 °C over 759 hours, or at an average calculated rate of 0.005 °C/hr.

The Pt-10%Rh vs Pt and Pt-6%Rh vs Pt-30%Rh thermocouples with high purity Al_2O_3 insulation construction (#810 and #811) did not exhibit drift at any of the holding temperatures.

The scanning electron microscope proved to be inconclusive. Energy dispersive x-ray analyses verified that thermocouples Pt-10%Rh vs Pt and Pt-30%Rh vs Pt-6%Rh (#'s 693 and 694, respectively) were sheathed with platinum and filled with magnesium oxide and that the union was nominally the chemical composition of the two legs. Similarly, thermocouples Pt-10%Rh vs Pt and Pt-30%Rh vs Pt-40%Rh (#'s 810 and 812, respectively) were sheathed in platinum and filled with aluminum oxide and that the union was nominally the chemical composition of the two legs. However, energy dispersive x-ray analyses for chemical variation across the section thermocouple unions proved to be inclusive at this time.

Conclusions and Recommendations:
Evaluations of the results of this experiment indicate the following:

1. That the Pt-10%Rh vs Pt thermocouple with swaged high purity MgO insulation (Enclad®) construction (#693) showed drift at 1399 °C and 1610 °C. The magnitude of the drift was slightly more at the higher temperature.
2. That the Pt-30%Rh vs Pt-6%Rh thermocouple with swaged high purity



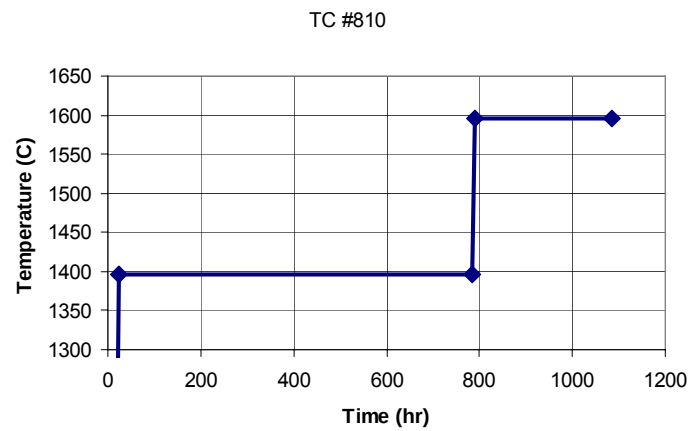


Figure 8: Test thermocouple #810 temperature trace

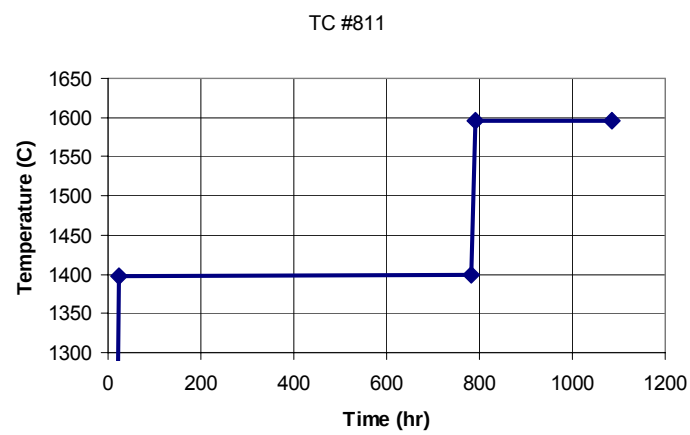


Figure 9: Test thermocouple #811 temperature trace

MgO insulation (Enclad®) construction (#694) exhibited drift at the 1610 °C.

3. That the Pt-30%Rh vs Pt-40%Rh thermocouple with high purity Al_2O_3 insulation construction (#812) failed as the furnace temperature was increased from 1399 °C to 1610 °C and exhibited drift at the lower holding temperature. Evaluation of drift at the higher holding temperature was not evaluated because of the failure.
4. That the Pt-10%Rh vs Pt and Pt-6%Rh vs Pt-30%Rh thermocouples with high purity Al_2O_3 insulation construction (#810 and #811) did not exhibit drift at any of the holding temperatures.

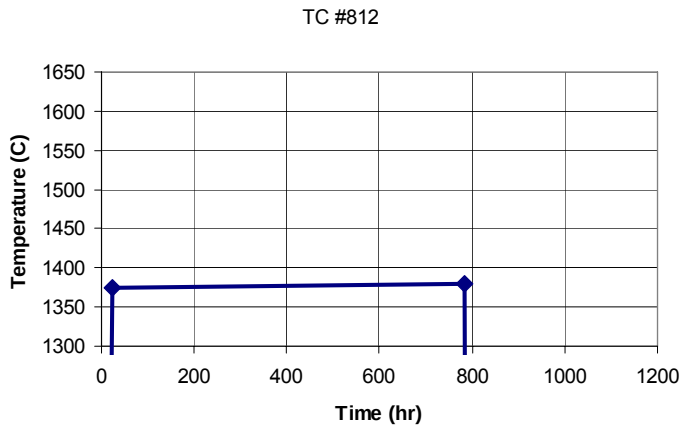


Figure 10: Test thermocouple #812 temperature trace

5. That the energy dispersive x-ray analyses verified the materials of construction; however, verification of chemical composition variations was inconclusive.
6. A follow up experiment to expose another set of thermocouples to a single elevated temperature for an extended period of time (6 to 12 months) is recommended, as it will allow drift characterization of a timeframe that is consistent with the expected period of use in the glass industry.