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DEVELOPMENT OF DURABLE GOLD VERSUS PLATINUM THERMOCOUPLES

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Abstract: The gold versus platinum (Au/Pt) thermocouples are very stable under long term repeated usage at higher temperature. Still there are some unsolved problems that the stress-relieving coil at the top of measuring junction is deformed after thermal cycling. In this study twist pair of thermocouple-element and U shape thin Pt wire at the measuring junction instead of the coil are tested in addition to the ordinary measuring junction. It was found that good stability and immersion characteristic is realized by a thermocouple having ordinary junction with appropriate anchoring of the thermocouple elements.

Keywords: Au/Pt thermocouple, new hot junction, stability, immersion characteristic.

1. OVERVIEW OF THE Au/Pt THERMOCOUPL

The literatures of Au/Pt thermocouples are extremely sparse. Roeser and Wensel gave a table of Themo-electro motive force (Emf) relative to Pt for Au along with other 27 metallic elements in 1941[1]. McLaren and Murdock found that Au/Pt thermocouples have superior immersion characteristic to Platinum-Rhodium thermocouples [2]. Emf variation measured in an uniform temperature zone of a silver fixed point cell corresponds to 0.1°C in the case of Au/Pt thermocouples whereas its corresponds to 0.5°C in the case of type S thermocouples which was the defining instrument of the IPTS-68 from 630.74°C to 1064°C. And then they performed extensive study on the essential thermoelectric properties of the Au/Pt thermocouple. Their results were published in 1987 including a provisional wire scale derived from a 5th degree polynomial [3]. In such pure element thermocouples as the Au/Pt thermocouple substantial differential thermal expansion occurs and mechanical stress due to it causes the strain. The strain induces parasitic Emf, which leads uncertainty of temperature measurement. McLaren and Murdock put a coil of a few windings thin platinum wire to form the measuring junction. This stress-relieving coil succeeded to reduce parasitic Emf and to improve immersion characteristic to 0.05°C at the silver point. This design is adopted by other works [4,5,6,8] since then. Thereafter, more precise reference functions based on the ITS-90 and covering the range from 0°C to 962°C or 1000°C were also published [4,5]. Bentley precisely discussed annealing process to stabilize the thermocouple [7]. Now a days a few kinds of commercial model of the Au/Pt thermocouples are available in the market.

Ripple and Burns published a textbook to provide guidance and to document the method of fabrication and calibration of the Au/Pt thermocouple [6]. They describe that Au/Pt thermocouple is more rugged but slightly less accurate compared to Standard Platinum Resistance Thermometers, defining instrument of ITS-90 in the range from 13.6K to 962°C. Relative to the highest quality industrial platinum resistance thermometers, the Au/Pt thermocouple has similar calibration uncertainties and is more resistant to loss of calibration and has a higher upper temperature limit.

The combination of ruggedness, a smaller calibration uncertainty, long-term stability of its calibration and simplicity of electronic measurement system make Au/Pt thermocouple ideal for use as a secondary reference standard. However the stress-relieving coil is very fragile and sometimes do not remain its original shape after repeated exposure to high temperature. Therefore this design is not necessary suitable for practical use. Many kinds of attempts are tried to overcome this problem in this study and results are reported in this paper.

2. THE THERMOCOUPLES

Six thermocouples were assembled and studied with various source materials. All the wires have approximately 0.5mm diameter. In the table 2 quality of the wire, insulating material and structure of the measuring junction are summarized.

2.1. Heat treatment

The thermocouples were prepared following the recommendations of McLaren and Murdock [3]. The platinum wires were electrically-annealed in air at 1300°C and cooled rapidly (quenched) to room temperature and then vacancy-annealed at about 450°C. Gold wire is too soft to be annealed by self-heating with passing electric current through the wire. Therefore they were annealed in a furnace. The gold wires, 1.5 m or 2m in length, were installed in high purity quartz tubes. These tubes (with the gold wire inside) were heated in a conventional tube furnace that has 100cm effective working length over which the temperature uniformity is within 4.6°C. This furnace was operated in the horizontal orientation. Following the first heat treatment of the first segment, the gold wire was then shifted and the second section is heated in the same way. Thus gold wires are heat-treated by repeating this process. After cooled in the furnace, they are subjected to vacancy-anneal at 450°C. In this study complete anneal (Anneal mode 1) and simplified anneal (Anneal mode 2) are tried. In the Anneal mode 1 post assembly anneal process was added in order to anneal out cold work introduced during assembly process. The annealing procedure is summarized in the Table 2.

Anneal Mode	Pt Step 1 Wire Anneal	Pt Step 2 Wire Anneal	Au Step 1 Furnace Anneal	Au Step 2 Furnace Anneal	Post Assemble Furnace Anneal	Post Assemble Vacancy Anneal
1	1300˚C, 10hours	450˚C, 20hours	960˚C, 10hours	450˚C, 20hours	960˚C, 1hours	450˚C, 20hours
2	1300˚C, 10hours	450˚C, 5hours	970˚C, 10hours*	none	none	none

Note*: The Au wire was traveling through a tube furnace having effective heating length 30cm at 970˚C at a speed of 3cm/hour.

Table 2. Annealing procedure

2.2. Stress-relieving coil

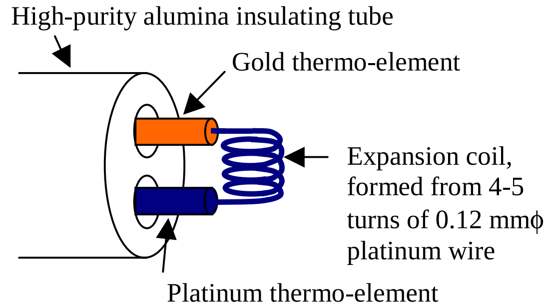
The stress-relieving coil recommended by McLaren and Murdock [3] is easily deformed after heat cycles and in an extreme case it is tangled and does not functions properly. In order to improve the problem, three types of measuring junction were tried in this study in addition to the stress-relieving coil. In every type both of the insulating tubes and the capillaries were heated at 960°C for 5 hours prior to assembly.

Type 1: The same stress-relieving coil as the one reported by McLaren and Murdock is attached to the top of the measuring junction. A thermocouple with this junction was tested as a reference.

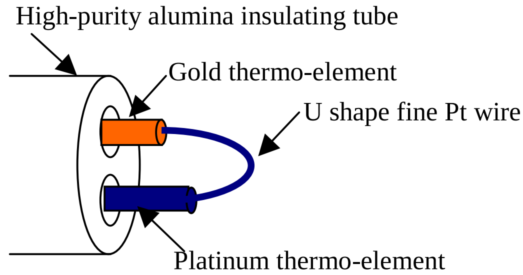
Type 2: The structure is the same as Type 1 except that a U shape thin Pt wire bridges the end of Au wire to the end of Pt wire to form the measuring junction. It is expected that the thin platinum wire relieves stress effectively enough to prevent parasitic Emf.

Type 3: Measuring junction is formed at the top of thermocouple by direct welding together. Twisted quartz capillary is used for the insulator of the thermo-elements. It is expected that the twisted capillary accounts for the differential thermal expansion and prevents stress induced parasitic Emf.

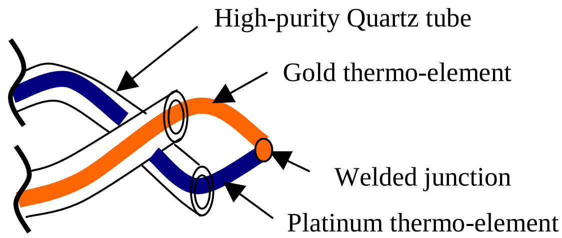
Type 4: At the top of the measuring junction Au and Pt wire is directly welded together. This simplest structure was tried in this study again. In the course of our study it was found that stability and immersion characteristic depend not only on the structure of the measuring junction (stress-relieving coil or U shape thin wire bridge) but also on the anchoring methods of the thermometer elements.



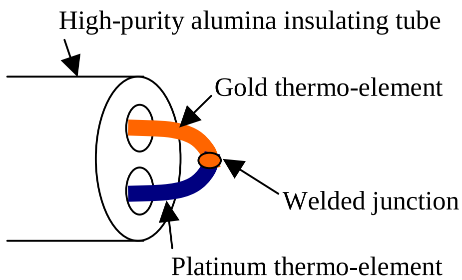
(a) Type 1



(b) Type 2



(c) Type 3



(d) Type 4

Fig.1 Four types of measuring junctions of the thermocouples

2.2. Assembly of thermocouples

In the preliminary study it was found that long-term stability and immersion profile depends in some way on how thermocouple wire is anchored. In the pioneer work by McLaren and Murdock, they succeeded to get very good performance of stability with a bar clamp attached to the harness just beyond the alumina insulator. The bar clamp presses the thermocouple wires over electrical insulator tube and protect the measuring junction from mechanical damage. On the other hand movement of thermocouple wire due to the differential thermal expansion can be prevented with it and stress induced Emf causes instability of the thermocouple. These phenomena are studied by testing two kinds of thermocouples with anchors and without anchors. Anchors were realized with a lock nut (Fig.2) installed in the handle of the thermocouple. The lock nut squeezes the thermo-element by pressing the wire over electric insulator of the wire (thermocouple G61). Thermocouple G51 has exactly same bar clamp as those of McLaren's work.

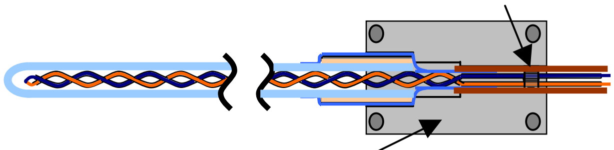


Fig.2 Thermocouple G61 that has a lock nut and twist pair quartz insulating tube.

As is mentioned in section 1 of this paper, stress-relieving coil is easily deformed after thermal cycling. In order to solve this problem many attempts are made in this study.
Actual differential thermal expansion is calculated in the case of temperature profile of our furnace for silver fixed-point cell. In the furnace closed type sodium heat pipe is installed. To calculate precisely enough thermocouple wire is divided into 10mm segments in order to take temperature dependent linear thermal expansion coefficient into account. The distance from the bottom of fixed-point cell to the top of the furnace is 50cm and thermocouple wire expands as follows when it is inserted into the cell at 962°C.

Thermal expansion of gold wire: 8.6mm
Thermal expansion of platinum wire: 4.6mm

U shape fine platinum wire is expected to relieve the stress caused by 4mm differential expansion in addition to pre-equalization of Platinum wire illustrated in the Fig. 1(b).

Another consideration against the differential thermal expansion is the use of insulation tube made of twisted pair of quartz capillary (Fig.1(c)). The twisted pair of capillary has made of high purity quartz straight tube having outer and inner diameter 2.7mm and 1.5mm respectively.

It is expected that considerably large inner diameter spiral tube moderates thermal expansion and reduces stress induced Emf.

In the table 2 summaries of studied thermocouples are tabulated with various design features and heat treatments.
Except thermocouple G61, 99.7% purity alumina two bore insulating tubes are used for all the thermocouple. The size of them is 4.7mm outer diameter and 1.5mm bore.

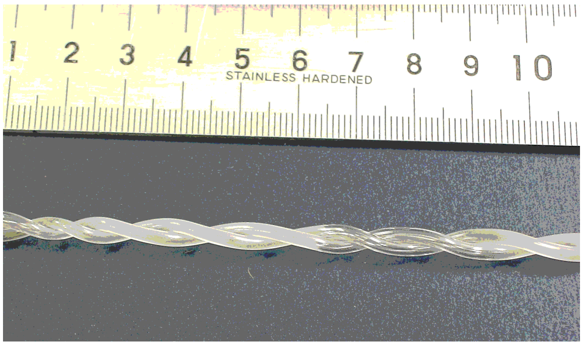


Fig.3 Twist pair of quartz insulating tube. Sand blast is applied.

Thermocouple designation	Gold wire	Platinum wire	Insulating Tube	Measuring Junction type	Anneal Mode	Anchor
C2	99.999%	99.999%	High purity ceramic	1	1	Yes
G51	99.999%	1.3924(Note)	High purity ceramic	2	2	Yes
G61	99.99%	99.99%	Twisted quartz capillary	3	2	Yes
C1	99.999%	99.999%	High purity ceramic	4	1	No
C5	99.999%	99.999%	High purity ceramic	4	1	No
C6	99.999%	99.999%	High purity ceramic	4	1	No

Note; Resitance ratio at 100°C to 0°C

Table 2. Studied thermocouples

3. THE MEASUREMENT SYSTEM AND TESTS

Emf is measured with a high precision digital voltmeter. In this study an Agilent technology model 3458A and a Fluke model 8508A are used with a Data proof model 160B low thermal scanner. By reversing the polarity with the scanner parasitic Emf generated in the wiring system is canceled.

Two types of the tests are performed. (a) Drift measurement after long-term exposure to nearly 960°C and (b) immersion profile measurements in the silver fixed point cell while freezing plateau is realized. Measurement procedure of immersion profile is as follows. Waiting until the temperature is stabilized after super-cool test thermo-couple is inserted to the bottom of the fixed-point cell. Once it attains equilibrium the thermocouple is moved by 2 cm step after taking the Emf value. This process is repeated until the thermocouple reaches to 12 cm from the bottom of the cell. Then the same process is repeated by inserting the thermometer.

The thermometers are exposed to nearly 960°C in a vertical conventional furnace and from time to time it is calibrated at Ag fixed point for drift measurement.

4. RESULTS AND DISCUSSIONS

Generally speaking uncertainty of Au/Pt thermocouples is an order of magnitude smaller than that of Platinum-Rhodium thermocouples. In most cases Au/Pt thermocouple is used as a secondary standard thermometer. Once it is calibrated the temperature is calculated with the calibration equation. Therefore deviation of Emf at the fixed point is not so significant but drift is more important factor for its uncertainty estimation. So deviation from the initial value is discussed in the following data analysis.

4.1. Drift test

In the following two figures Fig.4 and Fig.5 drift measurement results are shown. Thermocouples C1, C5 and C6 prove to be stable within 7mK up to 800 hours as is shown in the Fig.4. All of those have are Type 4 measuring junction (without stress-relieving coil) and have no anchor. Namely the gold and platinum wires are routed to the reference junction without any clamp. At the top of the reference junction these wires are fastened together to a stainless tube. This structure allows thermocouple wire to expand with heating. Up to 200 hours exposure C2 deviates significantly. However after this point deviation decreased. At this time 0.12mm diameter platinum stress-relieving coil was installed instead of 0.2mm diameter coil. Finer coil brought better performance. This proves that fine coil relieves the stress even thermocouple wires are clamped at the handle. This result is consistent with the former works [3,4,5].

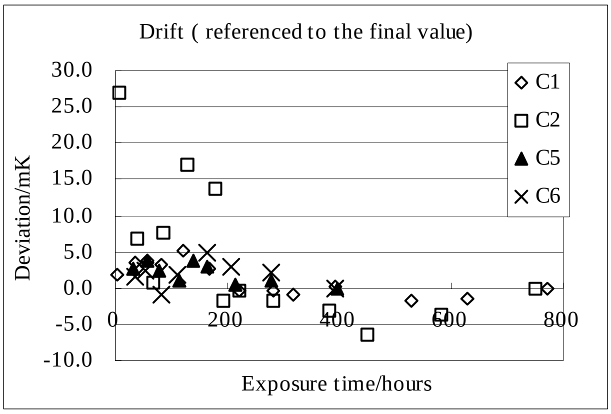


Fig.4 Drift test for the thermocouple C1, C2, C5 and C6.

In the Fig.5 results of the drift test for thermocouple G51 and G61 are shown. These two thermocouples received simplified heat treatment (Anneal Mode 2) and also have different measuring junction type (Type 2 and 3 respectively). Therefore G51 exhibits larger initial drift. But after 500 hours it is stabilized within 5mK.

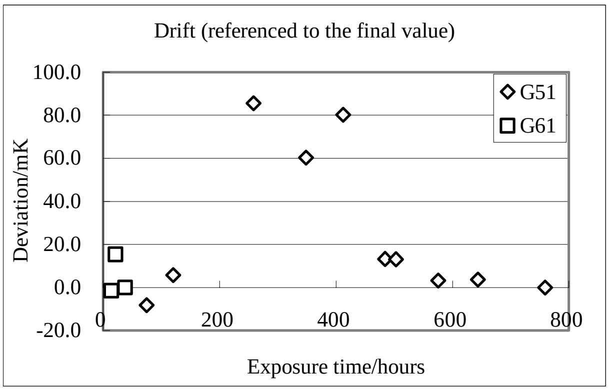


Fig.5 Drift test for the thermocouple G51 and G61.

4.2. Immersion characteristic

Measurements of the immersion profile were repeated 9 times at most during the exposure to 800 hours. Every time the measurement concluded one cycle of insertion and withdrawal. Results are shown in the figures 6, 7, 8 and 9 for thermocouples C1, C5, C6 and C2. The first three thermocouples have the same design (Type 4 junction, no anchor). Width of scattering at 6cm level corresponds approximately to 5mK for C5 and C6 and 8mK for C1.

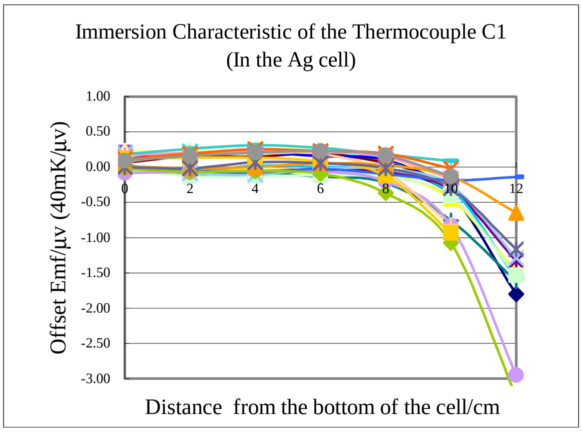


Fig.6 Immersion characteristic for the thermocouple C1

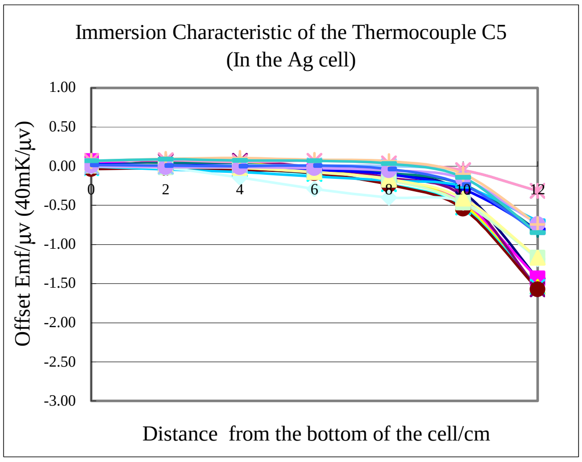


Fig.7 Immersion characteristic for the thermocouple C5

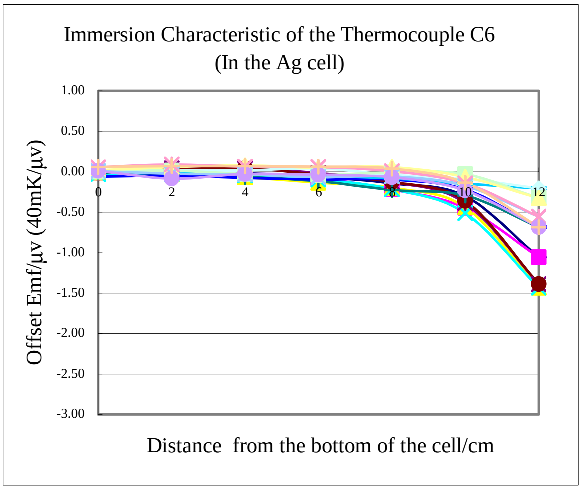


Fig.8 Immersion characteristic for the thermocouple C6

Among the thermocouple group of C1, C5, C6 and C2 only C2 has anchor mechanism. This difference is demonstrated in the immersion profile of the Fig. 9. Width of scattering at 6cm level corresponds approximately to 13mK for C2. Because this is slightly worse than C5 and C6 anchoring the wire at the handle possibly disturb stress-relieving mechanism.

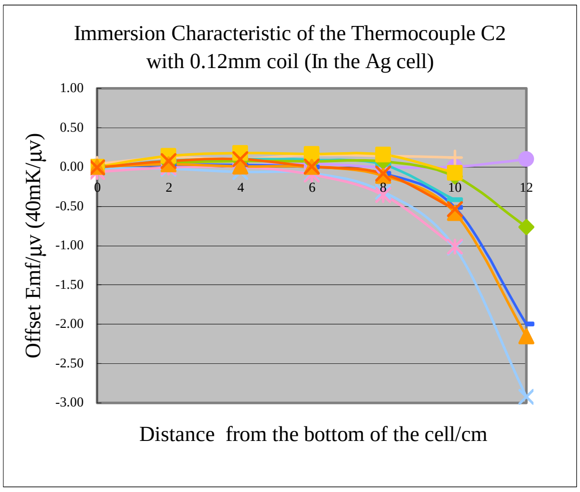


Fig.9 Immersion characteristic for the thermocouple C2

G51 has U shape fine platinum wire to form the measuring junction (Type 2 Junction). Fig.10 is immersion profile of the thermocouple. Width of scattering at 6cm level corresponds approximately to 50mK. Although profile is getting better with exposure time it is suspicious that the U shape junction properly relieves differential expansion.

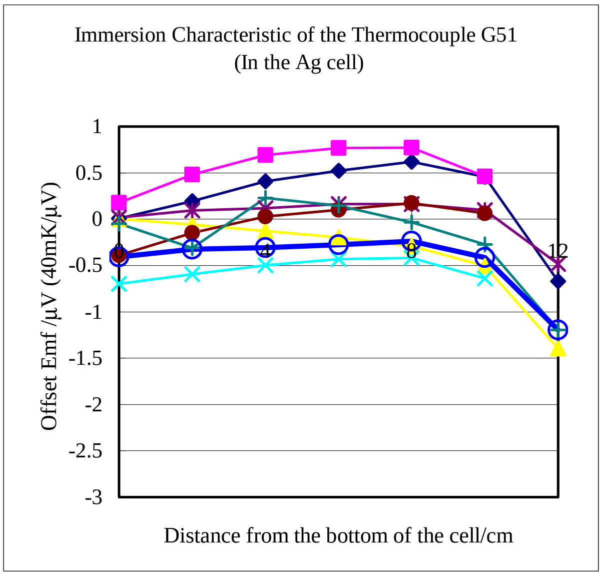


Fig.10 Immersion characteristic for the thermocouple G51

5. CONCLUSIONS

(1) Without stress-relieving coil good long time stability and good immersion characteristics is attainable by not anchoring the thermocouple wire (Thermocouple C1, C5, and C6). To fabricate the proper reference junction is necessary to prevent any movement of the thermocouple wire through reference junction side (Fig.11). Thus we have succeeded to remove fragile stress- relieving coil without any degradation of the performance of the thermocouples. They are stable within 7mK. Immersion characteristic is within 5mK for C5 and C6

Fig.11 Picture of the thermocouple. In the handle of Ice point probe, thermocouple wire is anchored. Flexible stainless bellows connecting thermocouple and reference junction protects thermocouple wire from any stress for the thermocouple.

(2) Thermocouple C2 has the same stress-relieving coil and anchoring construction. This behaves exactly same as the one reported in the other studies [3,4,5] in

terms of immersion characteristics and drift. Drift is within 5mK after initial aging. Immersion characteristic is within 13mK.

(3) Validation of Type 2 and Type 3 junction has not yet completed (Thermocouple G51 and G61). For practicality and further mechanical ruggedness it is preferable that thermocouple wires are anchored in the handle. Further study is necessary to prove Type 2 and Type 3 junction to work properly.

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