Int J Thermophys (2010) 31:1544–1553
DOI 10.1007/s10765-010-0797-6

Annealing State Dependence of the Calibration of Type R and Type S Thermocouples

F. Jahan · M. J. Ballico

Received: 31 March 2010 / Accepted: 14 July 2010 / Published online: 30 July 2010

Abstract Type R (Pt–13 %Rh versus Pt) and type S (Pt–10 %Rh versus Pt) thermocouples are widely used as reference and working standards for temperature measurements both in calibration laboratories and in industry for temperatures up to 1600 °C. Many laboratories claim that the best achievable uncertainty is 0.1 °C up to 1000 °C and 0.3 °C up to 1550 °C, and international comparisons confirm that this is achievable practically. However, due to (i) preferential Rh oxidation of the Pt–Rh alloy thermoelement and (ii) defect quenching effects, these thermocouples suffer from reversible hysteresis in their calibration. As a result, calibration laboratories usually perform some heat treatment of the wire prior to calibration to attain a specific ‘annealing state’, at which the calibration is performed. Internationally, there are two commonly used annealing states for these thermocouples: the ‘450 °C annealed state’ and the ‘1100 °C quenched state’. High-level comparisons between laboratories in the calibration of type R or type S thermocouples will rigorously specify the annealing state in the protocol, so any systematic differences due to the choice of annealing state will be masked. This article compares the calibration of several thermocouples using the two common annealing states, finding that the difference can be as large as 0.2 °C at 961 °C, larger than the best calibration uncertainties reported. The article examines the advantages and disadvantages to the user of calibrations performed in each state, and the implications for the uncertainty analysis for calibration and use of type R and type S thermocouples.

Keywords Annealing state · Hysteresis · Inhomogeneity · Pt–PtRh thermocouple

---

F. Jahan (✉) · M. J. Ballico
National Measurement Institute, Bradfield Road, West Lindfield, NSW 2070, Australia
e-mail: Ferdouse.Jahan@nmi.gov.au

M. J. Ballico
e-mail: Mark.Ballico@nmi.gov.au

1 Introduction

The platinum–rhodium thermocouple, type R (Pt–13 %Rh versus Pt) or type S (Pt–10 %Rh versus Pt), is a precision temperature sensor and is used by many laboratories as a reference standard to calibrate other industrial thermocouples. They are widely used in many industries to measure temperatures as high as 1600 °C.

As these thermocouples are known to suffer from hysteresis [1,2] due to both preferential oxidation of the Rh in the Pt–Rh thermoelement and quenched-in lattice defects, the calibration results depend on the choice of the annealing state prior to calibration. NMIA recently surveyed several of the national measurement laboratories within the Asia-Pacific region on the ‘annealing state’ used for Pt-alloy thermocouples prior to calibration. It was found that three of the laboratories use the ‘1100 °C quenched state’ as a reference state, four use the ‘450 °C annealed state’, and four of the laboratories calibrate these thermocouples in the ‘as received’ state.

Under the mutual recognition arrangement (MRA), calibration and measurement certificates issued by NMIs should be recognized as equivalent to those issued by other signatory NMIs. At present within a country, there is generally agreement between the NMI, second level calibration laboratories, and precision users about the annealing state in which such thermocouples are to be calibrated. However, at present, there is no international agreement on the reference annealing state of the thermocouple prior to calibration. Calibrations sourced internationally, thus have the potential to damage the national traceability chain, if a user familiar with calibrations performed in the quenched state now obtains calibrations in the 450 °C annealed state or vice-versa.

Although several studies [1–3] have been done on the effect of ageing or drift on Pt and Pt–Rh wires, no direct comparison was made between the effect of different annealing states on the calibration results for a thermocouple. In this article, we describe the effect of two common annealing states on the calibration results of type R thermocouples. We also suggest the advantages and disadvantages of each annealing state.

2 Experimental Details

Several type R thermocouples purchased from Sigmund Cohn Corp. (USA) and Pyrosales (Australia) were examined in this study. Reference grade 0.5 mm diameter platinum and platinum–13 % rhodium wires were used. The insulators used were high purity alumina, purchased from Ceramic Oxide Fabricators (Australia) and baked at 1200 °C for 6 h. The thermocouple wires were bare wire annealed at 1400 °C for 1 h, at 1100 °C for 1 h, and then quenched. After being assembled into the prebaked insulator, a further 1 h anneal at 1100 °C and more than 16 h at 450 °C were applied. The thermocouple wires emerging from the alumina tube were insulated with PVC sleeves.

The thermocouples were calibrated in two different reference states:

(i) 1100 °C quenched state—thermocouples were annealed in a horizontal tube furnace (1000 mm long and uniform to ±10 °C for the central 700 mm) at a temperature of 1100 °C for at least 1 h and quickly removed to be cooled in air. This reference state will be referred to as the 'quenched state' in this article.

(ii) 450 °C annealed state—after 1100 °C annealing and quenching, thermocouples were annealed at 450 °C for more than 16 h in a long tube furnace. This reference state will be referred to as the 'annealed state' in this article.

The thermocouples were calibrated using NMIA's normal test procedure [4], which involves calibration up to 550 °C against a standard platinum resistance thermometer using a salt bath and then at the Au point using the 'melt-wire' technique [5] and/or Cu mini-fixed point [6], with appropriate anneal applied after measurements in each enclosure.

In order to understand the causes of the shifts in calibration, the inhomogeneity of the thermocouples was measured by scanning in an oil bath at 200 °C [7,8]. As there is no effect on the Seebeck coefficient of a Pt-based thermocouple at this low temperature, this is a useful diagnostic tool to study changes in the Seebeck coefficient along the length of the thermocouple wires due to various heat treatment effects.

The effect of the annealing state on 'fixed point' type calibration of type R thermocouples was also examined. Finally, the short-term drift of thermocouples in each of the two annealing states was examined by recording the measured emf with time after inserting in a slow freezing plateau of the Ag point.

3 Results and Discussion

It is well known that type R and S thermocouples suffer hysteresis during use, mainly due to the Pt–Rh alloy thermoelement. The Seebeck coefficient along each thermocouple wire changes as it experiences high temperatures. The thermoelectric changes within each segment of wire depend on the temperature it experiences and also on the duration at that temperature. Figure 1 shows a thermoelectric signature of a thermocouple after it had been used for about 100 h in an oven to measure temperatures of 900 °C and clearly shows that the thermocouple has become inhomogeneous. As the thermocouple emf is mostly generated in the temperature gradient zone of the enclosure, an inhomogeneous thermocouple will give an emf strongly dependent on the position of the temperature gradient zone of the enclosure. To obtain the most meaningful calibration, a thermocouple should thus be in a reasonably homogeneous state. As most of the changes in the Seebeck coefficient up to 1100 °C are reversible, after an appropriate annealing, the thermocouple can return to a more homogenous state as shown in Fig. 1. The thermocouple is then in a more suitable state for calibration.

To see the effect of the annealing state on the calibration results, several thermocouples were calibrated in both the '450 °C annealed state' and the '1100 °C quenched state'. Figure 2 shows typical calibration curves of a same thermocouple in these two different states. The calibration was done against an SPRT using a salt bath up to 550 °C and then at the Ag and Au fixed points. The thermocouple was annealed to the same annealing state before measurement in each enclosure. The figure clearly shows that the calibration results differ between 2 μV and 3 μV, for the temperature range of 400 °C to 1100 °C, which is equivalent to errors of 0.2 °C to 0.3 °C. The measured emf, and hence $E - E_{\mathrm{ref}}$, of the 'annealed' thermocouple is higher than that

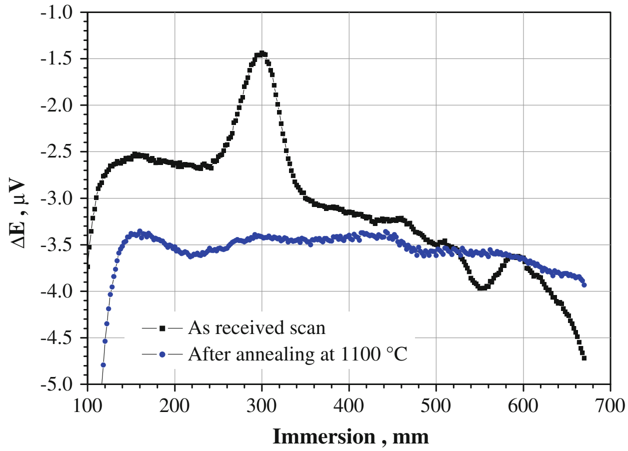

Fig. 1 Thermoelectric scans of a typical 'used' type R thermocouple at 200 °C, showing the improvement in homogeneity after performing a '1100 °C quench'

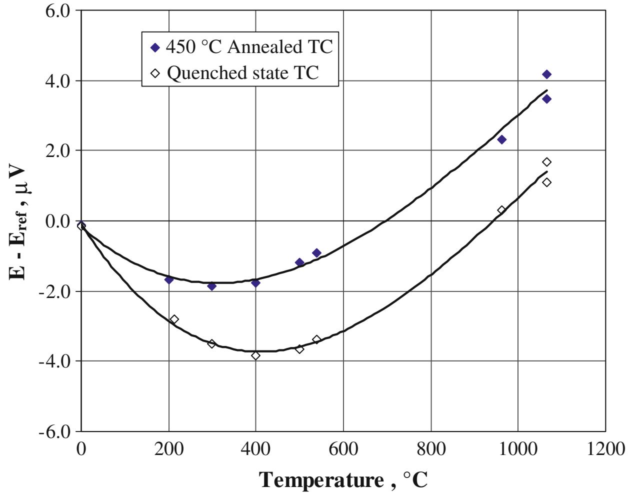

Fig. 2 Calibration graph of a type R thermocouple (13-0295) when calibrated in (a) the '450 °C annealed' state and (b) the '1100 °C quenched' state, showing differences of up to 2 µV

for the 'quenched' thermocouple at all temperatures. Previously it has been observed [2,3] that the 'annealed' Pt wires are more negative than the 'quenched' Pt wires and 'annealed' Pt–Rh wires are more positive than the same wires in the 'quenched' state. As a result at a particular temperature, a thermocouple generates more emf in the 'annealed state' than in the 'quenched state'. Figure 3 shows the thermoelectric signature of a thermocouple in the two different reference states at a temperature of 200 °C. There is no significant difference in the structure of the thermoelectric signatures of the thermocouple in the two different states (they are both relatively homogeneous),

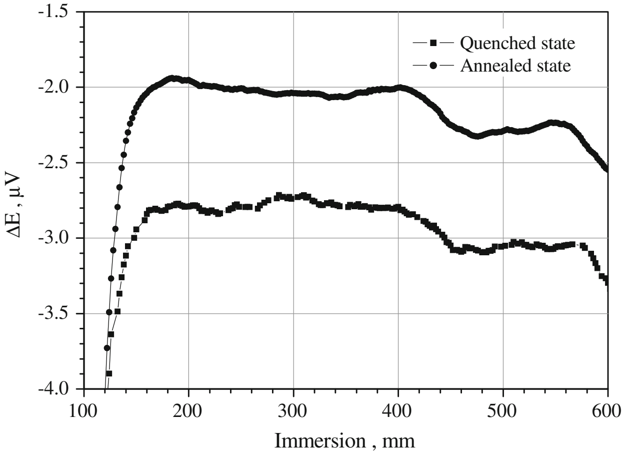

Fig. 3 Thermoelectric scans of a type R thermocouple (920101) at 200 °C in the annealed and quenched states, showing similar level of inhomogeneity

Table 1 Summary of measured emf at various fixed points with two different annealing states

Fixed point	ITS-90 temperature (°C)	Thermocouple serial number	Measured emf (μV)		Difference (μV) (annealed state–quenched state)
			Annealed state	Quenched state	
Aluminium	660.323	APMP-08	6279.31	6276.80	2.51
Aluminium	660.323	APMP-02	6279.25	6276.70	2.55
Silver	961.78	APMP-08	10005.28	10002.54	2.74
Silver	961.78	APMP-11	10005.20	10002.57	2.63
Gold	1064.18	APMP-08	11365.70	11362.80	2.90
Gold	1064.18	APMP-11	11365.00	11362.70	2.30
Copper	1084.62	APMP-04	11638.70	11636.30	2.40
Copper	1084.62	APMP-02	11639.30	11637.36	1.94

but there is about 1 μV difference between the emfs produced. In both conditions, the thermocouples should be oxide free, but after quenching from an 1100 °C anneal there should be a higher level of trapped vacancies and lattice defects, which lowers the Seebeck coefficient of the thermocouple. After annealing at 450 °C for more than 16 h, the number of trapped vacancies and dislocations is reduced and some short-range reordering of lattices occurs, which increases the Seebeck coefficient [1,2].

Table 1 gives the values of emf measured at the fixed points of Al, Ag, Au, and Cu in two different annealed states. Each thermocouple was annealed to the same annealed state before doing the fixed-point measurements. The difference in the measured emf between the 'annealed' and 'quenched' states is in the range of 1.9 μV to 2.9 μV. This difference is consistent with the difference obtained in the calibration curves (Fig. 2) of a thermocouple in two different annealing states.

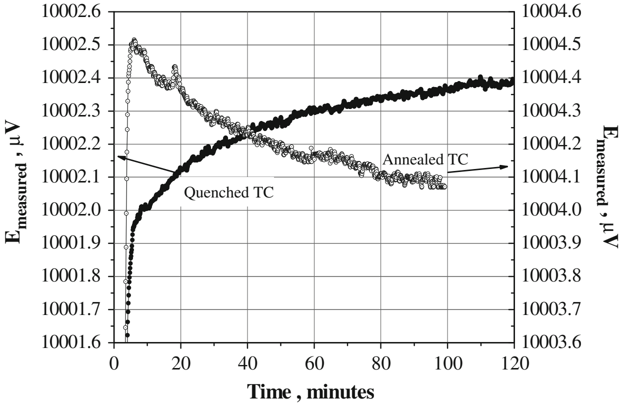

Fig. 4 Short-term drifts in the measured emf of a type R thermocouple in the 'quenched state' and 'annealed state' during Ag freezing-point measurement

Figure 4 shows the variation in the measured emf of a thermocouple with time in two different annealing states after being placed in the Ag freezing point. For the 'annealed' thermocouple, it can be observed that after reaching thermal equilibrium from ambient temperature to the Ag point temperature (961 °C), the emf started to *decrease* with time. After about 80 min, the emf became stable at a value of about 0.4 μV less than the maximum value. This is attributed to the changes in the section of the wire, which is above 450 °C due to the formation of Rh oxide and establishment of a higher equilibrium value of the vacancy concentration appropriate to that of the Ag-point temperature [1,2,9]. For a 'quenched' thermocouple, after reaching thermal equilibrium at the Ag-point temperature, the measured emf started to *increase* and after about 90 min attained a stable value of 0.4 μV above the initial value. This is attributed to the short-range reordering of lattice defects and annealing out of the trapped vacancies from the section of the wire that experienced temperature below 500 °C. Note, however, that the final stable emf for the 'annealed' thermocouple is still 2 μV lower than the 'quenched' thermocouple.

To see the change in the thermoelectric signature along the length of a thermocouple after measurement in the Ag point, the thermocouple was scanned in the oil bath at 200 °C. Figure 5a shows a thermoelectric scan of a 'quenched' thermocouple after Ag point measurement. No change was observed in the section of the wire exposed to 961 °C, as this wire was already in the high-temperature state. However, the length of the wire which was in the throat region of the Ag-point furnace (temperature below 500 °C) shows a peak of about 0.5 μV, as this section of the wire was originally at the '1100 °C quenched state' and slowly attained its new equilibrium state at ∼ 500 °C. The figure also shows the effect on the thermoelectric signature of an 'annealed' thermocouple after measurement at the Ag point. In this case, it is the segment of wire exposed to 961 °C which changed, showing a decrease of about 1.0 μV. These changes were reversible and were quite reproducible in magnitude.

A similar effect on the thermoelectric signature was observed after measurement in the Cu point (Fig. 5b). The magnitude of changes in the emf for 'annealed' and

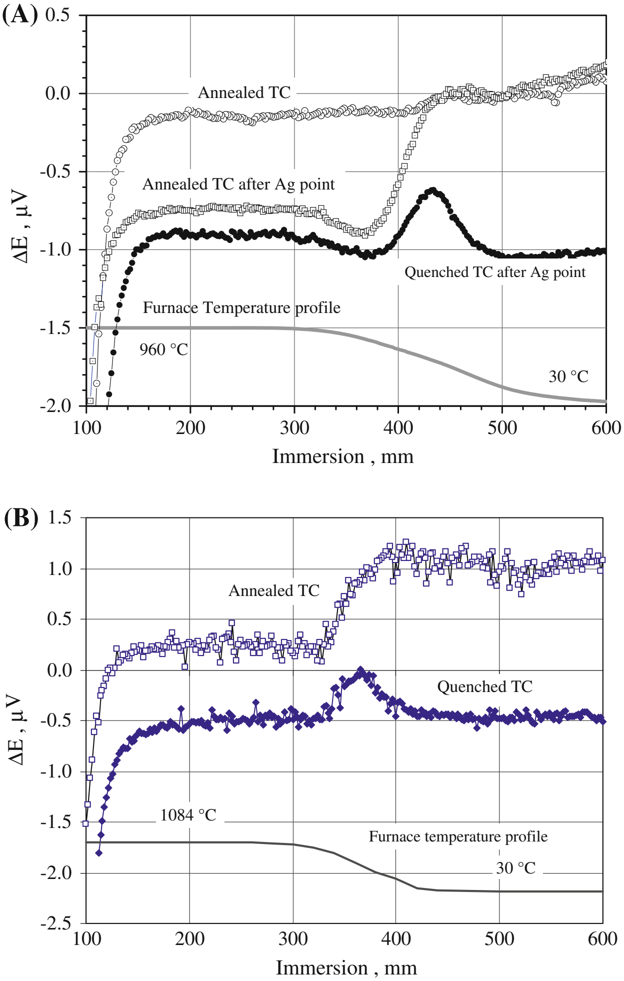

Fig. 5 (a) Effect of measurement of the Ag point on the homogeneity of a type R thermocouple in the 'quenched' and 'annealed' states and (b) effect of measurement of the Cu point on thermocouple homogeneity. The furnace temperature profile is also indicated schematically. Note that the curves have been shifted vertically for clarity if needed: only the shape of the curves is important

'quenched' thermocouples was in the same range as those observed after measurement in the Ag point.

Figure 6 shows the change in the thermoelectric signature after calibration in a salt bath up to 550 °C. As expected, there was no significant change in the thermoelectric signature of an 'annealed' thermocouple; however, for a 'quenched' thermocouple, the section of the thermocouple wire immersed into the salt bath changed by about 1 μV. This is consistent with the salt bath annealing-out the lattice defects and vacancies trapped by the 1100 °C quench. This is also evident in the magnitude of the hysteresis shown in the calibration curve (Fig. 7) where it is evident that the emf at 300 °C is 2 μV higher after exposure to 550 °C.

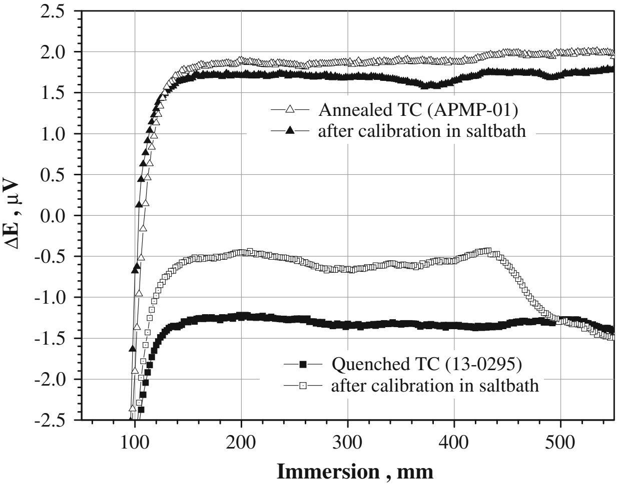

Fig. 6 Effect of measurement in a salt bath (up to 550 °C) on the thermoelectric scans of a 'quenched' and an 'annealed' type R thermocouple

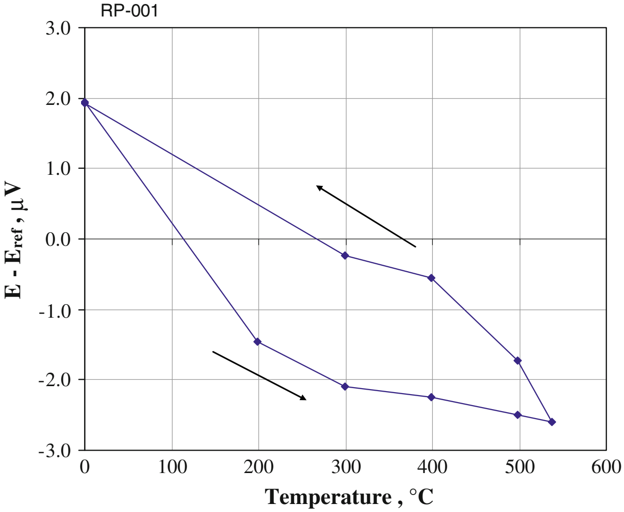

Fig. 7 Calibration in a salt bath of a type R thermocouple in the '1100 °C quenched' reference state, showing the hysteresis due to annealing effects in the bath

At NMIA, thermocouples are always re-annealed to their reference state prior to immersion in any given enclosure, because the immersion depths in the enclosures are different and the heat treatment the thermocouple experiences in one enclosure affects the calibration in the next. Figure 8 shows thermoelectric signatures of an 'annealed state' thermocouple at different stages of its calibration, *when no intermediate annealing was applied*. The initial scan after a 450 °C anneal is relatively homogeneous, and after the salt-bath measurement, the thermocouple is still homogeneous

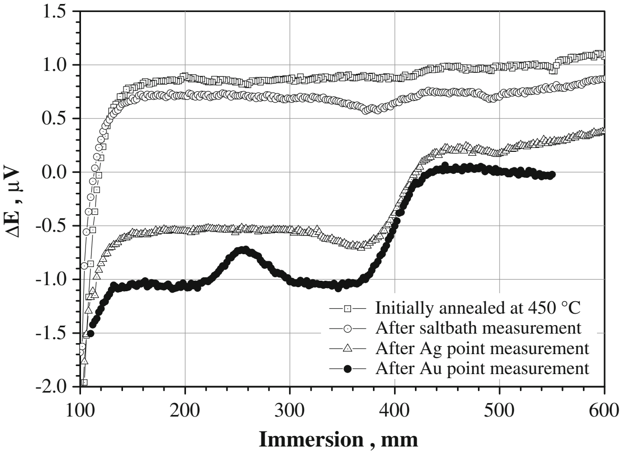

Fig. 8 Thermoelectric scan of a type R thermocouple in the '450 °C annealed' state at different stages in its calibration, when no additional annealing is performed between measurements in the different enclosures. Note that the curves have been shifted vertically for clarity if needed; only the shape of the curves is important

(as expected, as the 550 °C bath does little to the 450 °C state of the thermocouple). However, after the Ag-point measurement, the section of wire in the Ag-point furnace (tip to 400 mm) is now clearly in a different condition. The thermocouple was then calibrated at the Au point in another furnace with a somewhat shorter immersion. After the Au-point measurement, the thermoelectric scan shows a small additional peak at about 250 mm, which is around the throat region of the Au-point furnace (400 °C to 500 °C) partially annealing-out the high-temperature changes caused by the Ag point. The key observation is that the thermocouple emf value measured at the Au point immediately following the Ag point will not be the same as if the thermocouple had been annealed just prior to the Au point. A similar effect would occur with a 'quenched' thermocouple; a Au-point calibration of the quenched thermocouple in Fig. 6 will be affected by the exposure to the salt bath. The calibration will depend on the order in which the measurements are taken, unless the thermocouple is annealed to the same annealing state prior to each measurement.

4 Conclusions

By carefully ensuring that the annealing state of the section of wire immersed in each enclosure is well-defined, calibration repeatability as low as 0.03 °C can be achieved in both the '1100 °C quenched' and the '450 °C annealed' states [10,11]. However, if the thermocouple is to be used below 700 °C, the '450 °C annealed' state will offer better homogeneity and, hence, less sensitivity to subsequent changes in immersion. Above 700 °C, the '1100 °C quenched' state thermocouple is more suitable as it is then less sensitive to subsequent changes in immersion. In either case, the highest accuracy can only be achieved by re-annealing the thermocouple to the specified annealing state prior to measurement.

If thermocouples are calibrated without regard to the annealing state of the thermocouple prior to measurement at each calibration temperature, the measurement results will vary by up to 2 μV from 400 °C to 1100 °C, and proportionally less in the region from 0 °C to 400 °C. In use, unless the thermocouples are re-annealed, an additional uncertainty term for these hysteresis effects should be included.

We further recommend that thermocouple calibration reports issued by NMIs should clearly identify the annealing state of the thermocouple used to perform the calibration, to reduce the possibility that errors as large as 0.2 °C are introduced due to ambiguity in the annealing state.

References

1. R.E. Bentley, T.P. Jones, High Temp.–High Press **12**, 33 (1980)
2. E.H. McLaren, E.G. Murdock, in *Temperature: Its Measurement and Control in Science and Industry*, vol. 4, ed. by H.H. Plumb (Instrument Society of America, Pittsburgh, 1972), pp. 1543–1560
3. E.H. McLaren, E.G. Murdock, in *Temperature: Its Measurement and Control in Science and Industry*, vol. 5, part 2, ed. by J.F. Schooley (Instrument Society of America, Pittsburgh, 1972), pp. 953–975
4. F. Jahan, *NMI Quality System PM–EADA–8.2.25* (National Measurement Institute, Australia, 2001)
5. R.E. Bentley, Meas. Sci. Technol. **11**, 538 (1980)
6. F. Jahan, M.J. Ballico, in *Temperature: Its Measurement and Control in Science and Industry*, vol. 7, part 1, ed. by D.C. Ripple (AIP, New York, 2002), pp. 469–474
7. F. Jahan, in *Proceeding of 8th Biennial Conference of MSA* (Metrology Society of Australia, Queensland, 2009), pp. 69–74
8. F. Jahan, M.J. Ballico, in *Temperature: Its Measurement and Control in Science and Industry*, vol. 7, part 1, ed. by D.C. Ripple (AIP, New York, 2002), pp. 523–528
9. R.E. Bentley, Measurement **23**, 35 (1998)
10. F. Jahan, M.J. Ballico, Metrologia **44**, Tech. Suppl. 03004 (2007)
11. F. Jahan, M.J. Ballico, Int. J. Thermophys. **28**, 1832 (2007)