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Development of Precision Rh–0.5 at%Fe Thermometers of Chinese Production: Further Tests

L. Lipinski · A. Szmyrka-Grzebyk · Peng Lin · Xing Wei Li · H. Manuszkiewicz · D. Jancewicz · A. Grykalowska · P. P. M. Steur · F. Pavese

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Abstract Following the practical impossibility to obtain new precision Rh–0.5 at%Fe thermometers over the past years, re-starting the commercial production of such thermometers in Yunnan (China) was explored by INRIM in cooperation with NIM and with the help of INTiBS for prototype characterization. The present aim is to obtain a stability of the new thermometers at the level of ±1 mK at 4.2 K. In 2008, a new batch of eight prototypes was produced. This paper reports the results of the measurements on the full characteristics of these prototypes in the range from 2.5 K to 25 K, which confirms a similarity to the typical characteristics of previous commercial RhFe thermometers, and of the effect of thermal cycling, showing for six out of eight thermometers, a stability better than ±1 mK (limited by the measurement expanded uncertainty of ≈0.8 mK) at 4.2 K and up to ≈10 K, and better than ±0.01 % T in the range from 2.5 K to 25 K. These results indicate that production problems on these commercially available thermometers are basically resolved at the aimed level of stability. Further studies are foreseen to improve production uniformity and to check if stability may actually be better by using a test apparatus of sub-millikevin uncertainty.

F. Pavese is affiliated scientist at INTiBS.

L. Lipinski · A. Szmyrka-Grzebyk · H. Manuszkiewicz · D. Jancewicz · A. Grykalowska · F. Pavese (✉)
Instytut Niskich Temperatur i Badan Strukturalnych (INTiBS), Wroclaw, Poland
e-mail: f.pavese@inrim.it

P. Lin
National Institute of Metrology (NIM), Beijing, China

X. W. Li
Kunming Dafang Science and Technology Ltd., Kunming, China

P. P. M. Steur · F. Pavese
Istituto Nazionale di Ricerca Metrologica (INRIM), Torino, Italy

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1 Introduction

Following the practical impossibility to obtain new precision Rh–0.5 at%Fe thermometers over the past years, restarting the commercial production of such thermometers in Yunnan (China) was explored by INRIM in cooperation with NIM and with the help of INTiBS for prototype characterization. We recall that the present aim (at least initial) is to obtain a stability of the new thermometers at the level of ±1 mK at 4.2 K. After the production in 2006 of 10 prototypes of the new production, the published preliminary test data [1] showed satisfactory results as to the reproducibility on thermal cycling, but the *R*–*T* characteristics with lower sensitivity was unsatisfactory, a problem attributed to the alloy composition. Further studies, concerning the alloy composition, the thermal pre-treatment of the alloy wire used in new prototypes, and some further measurements of the basic characteristics, namely, sensitivity and *R*–*T* characteristics, were performed and published in 2008 [2]. A new batch of eight prototypes was produced, showing *R*–*T* characteristics basically identical to that of the prototypes in [2]. This paper reports the results of the measurements on the full characteristics of these prototypes in the range of 2.5 K to 25 K, which confirm the similarity to the typical characteristics of previous commercial RhFe thermometers, and of the effect of thermal cycling, showing for six thermometers out of eight a stability better than ±1 mK (limited by the test uncertainty) at 4.2 K.

2 The New Chinese-Type RhFe Precision Thermometers

2.1 Specimens

In the 1980s, RhFe thermometers were produced by Yunnan Instrument Factory, which have been tested by Besley and Lin [3], using the same type of alloy (Rh with 0.5 at%Fe) launched by NPL [4] and then independently produced by Tinsley and by VNIIFTRI.

Since 2006, prototypes have been produced by Kunming Dafang Science & Technology Ltd (KDST) that has retained the initial know-how. The wire is contained in a platinum capsule of the size typical to that of the SPRTs. They were made for a room-temperature resistance of 50 Ω, as a compromise between sensitivity and a reduced wire length to be used.

In 2007, the results of the composition of the alloy wire used for the 2006 prototypes became available and obtained by neutron diffraction at INRIM. The results showed [2] that the composition was not correct, partially due to the fabrication procedure, in particular, iron depletion, but no conclusive information could be obtained from these analyses, prompting the need of further studies to get the correct *R*–*T* characteristics, aimed at being substantially equal to that obtained in 1993 and to the former commercial models.

2.2 Procedures

In 2007, attention and work were concentrated on studies concerning the thermal pre-treatment of the as-supplied wire. Previous experience had shown that without a proper thermal-treatment procedure an increase of the alloy resistivity is observed due to cold work. These studies were the object of the work published in [2]: with proper high-temperature annealing of the wire, the resistance of the wire was consistently found lowered by about 15 % by this heat treatment. The surface of the wire remained bright as before the treatment, without any color alteration. However, the wire so obtained was found to be too brittle to be handled for the thermometer fabrication. As a consequence, the procedure was modified in 2008 at the factory, and spool #8 of wire was used and then subjected to the present tests.

Initial checks were performed at NIM, according to the procedure described in [1], at three temperatures: 293 K, 77.5 K, and 4.416 K. The uncertainty of the sample comparison was about 1 mK ($k = 1$). Then, the thermometers have been more extensively tested at INTiBS according to the procedure described in [1]. We recall that the uncertainty budget of the INTiBS calibration system provides an expanded uncertainty ($k = 2$) of the calibration $U = 2.2$ mK [1], while the uncertainty in comparing samples (or the same sample after thermal cycling) is reduced to $U = 0.8$ mK, with a suspected degradation to $\pm$(2 to 3) mK above 10 K.

Two calibrations were performed of the prototypes: one after reception from NIM and one after a total of 60 thermal cycles (in two runs of 30 each) down to 4.2 K. The number of calibration points was 18 and 12 for the first and second calibration, respectively; an optimised fitting polynomial $T = \mathrm{f}(R)$ up to degree 12 with seven parameters was used in both cases.

3 Results

The initial results are reported in Table 1, with the key resistance values before shipment to and after reception at INTiBS. They demonstrate that now basically the new production has the same characteristic of the previous commercial production, including sensitivity.

Two results were obtained at INTiBS. First, the resistance values at 4.79 K were compared in three conditions: as received, after the first 30 cycles, and after the total 60 cycles. They are shown in Fig. 1. Second, the characteristics of the two full calibrations performed, one as received and one after 60 cycles, were compared. In order to have a robust comparison, considering the oscillations that affect fitting functions based on polynomials of high degree (in this case degree 10), all the calibrations points, plus the points at 4.79 K, were fitted together, considering that the deviations between the two calibrations were expected to be small. This was done for the six thermometers that did not show a large instability at 4.79 K. The results are shown in Fig. 2.

Finally, the sensitivity of the thermometers was compared with that of an equivalent Tinsley thermometer; results were only slightly lower, varying from 90 % to 92 %

Table 1 Characteristics of the 2008 RhFe Chinese prototype batch, compared with a Tinsley-type RhFe thermometer

Manufacturer and wire batch	Tinsley	Dafang #8							
Thermometer #	A19	200605	200607	200608	200609	200610	200611	200613	200615
NIM—preliminary resistance values R									
at 293 K (Ω)	63.313	57.619	57.408	57.000	57.311	57.259	57.564	57.275	57.110
at 77.5 K (Ω)	14.60	13.313	13.224	13.136	13.208	13.209	13.269	13.207	13.169
at 4.416 K (Ω)	3.894	3.545	3.497	3.479	3.502	3.499	3.510	3.498	3.493
$R(77.5\,\text{K})/R(293\,\text{K})$	0.230	0.231	0.230	0.230	0.230	0.231	0.230	0.231	0.231
$R(4.416\,\text{K})/R(293\,\text{K})$	0.0615	0.0615	0.0609	0.0610	0.0611	0.0611	0.0610	0.0611	0.0612
INTiBS—as received resistance values R at 4.416 K (Ω)		3.53775	3.49897	3.48012	3.49844	3.50184	3.51190	3.50102	3.49310
$\Delta T_{\text{INTiBS-NIM}}$ at 4.416 K (mK)		−29	8	5	−14	11	8	12	0

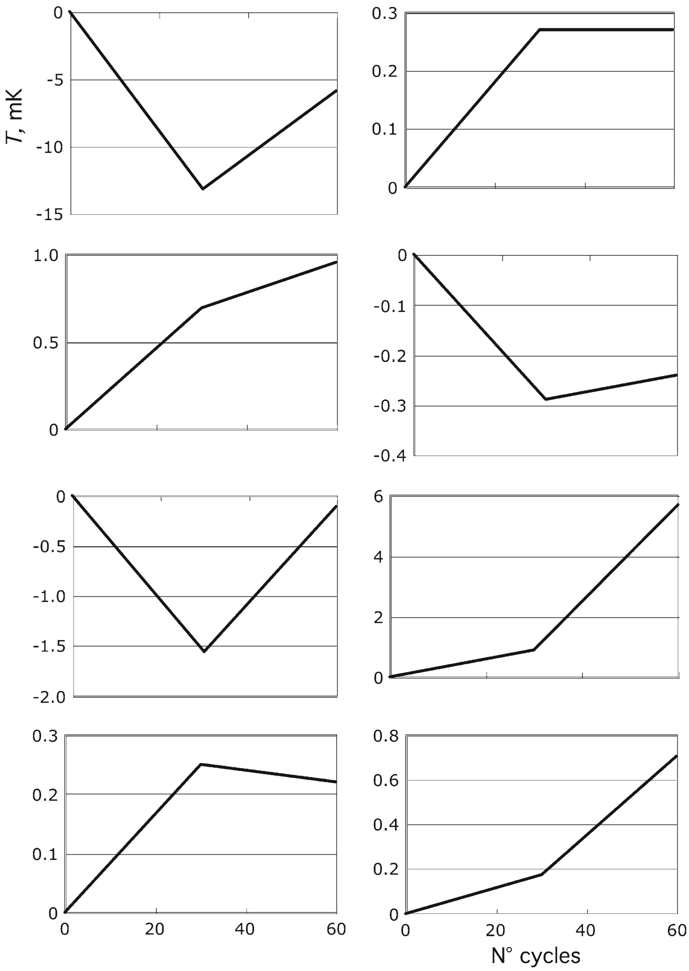

Fig. 1 Reproducibility (*ordinates*) close to 4.79 K for the new prototypes as received, after 30 cycles and after 60 cycles (*abscissas*) ($U_{\text{test}} = 0.8\,\text{mK}$)

of the Tinsley one (Fig. 3a). Figure 3b shows much smaller differences from thermometer to thermometer; the maximum in the worst case is less than 2 %. Figure 4 shows the relative sensitivity of the thermometers, very close to previous commercial production.

4 Discussion and Conclusions

Six of the eight prototypes had *R*–*T* characteristics very close to those of the Tinsley-type and were observed to be stable within ±1 mK or better at 4.79 K, over 60 thermal cycles down to 4.2 K, i.e.. within the test-facility precision. When

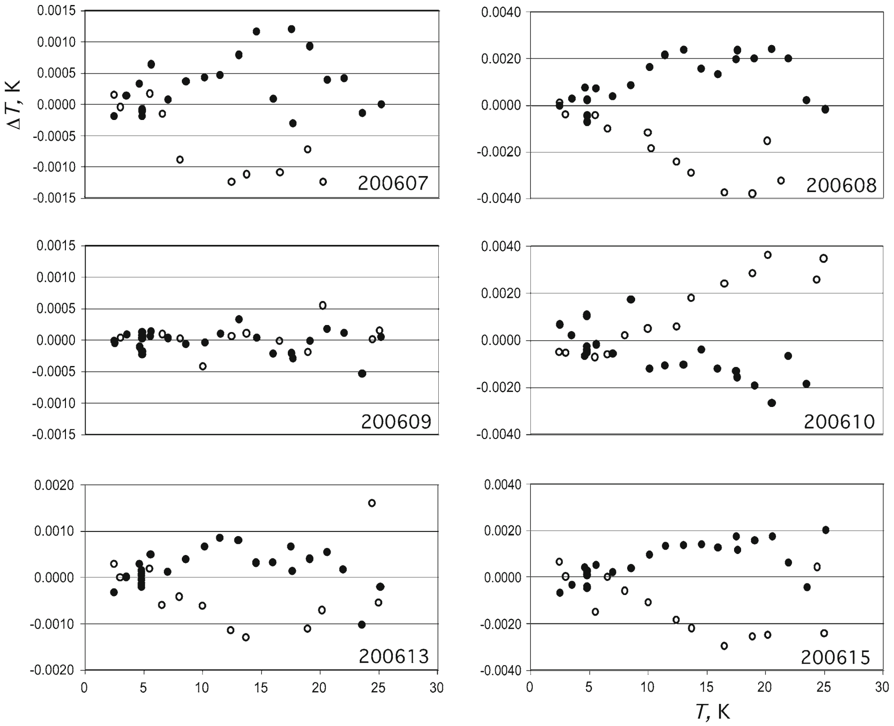

Fig. 2 Reproducibility of calibrations in the range 2.5 K to 25 K, for the six stable prototypes. *Closed circles* as received; *open circles* after 60 cycles down to 4.2 K

the full range of 2.5 K to 25 K is considered, the reproducibility remains at the same level for the six thermometers below ≈10 K, degrading to ±3 mK from 10 K to 25 K for some of the six thermometers. For the latter range, it is presently believed that the degradation is apparent and arises from a lower precision of the test apparatus; this explanation might be supported, by the fact, that most calibrations converge again within ±2 mK at the end point, ≈25 K, but no firm evidence is presently available. In all instances, a relative reproducibility, $\delta T/T$, within 0.01 % is ensured in the whole range of 2.5 K to 25 K. The remaining two prototypes (#605 and #611) were found anomalous and unstable (±15 mK in the full 2.5 K to 25 K range).

Overall, the characteristics and the stability on thermal cycling of the new production of RhFe thermometers are within the expected aimed stability bounds. Minor improvement may still be desirable concerning the uniformity of the production. Further studies are foreseen, also to check if stability may actually be better by using a test apparatus of sub-millikelvin uncertainty, or if more development is necessary toward the more ambitious goal of approaching a ±0.1 mK stability limit.

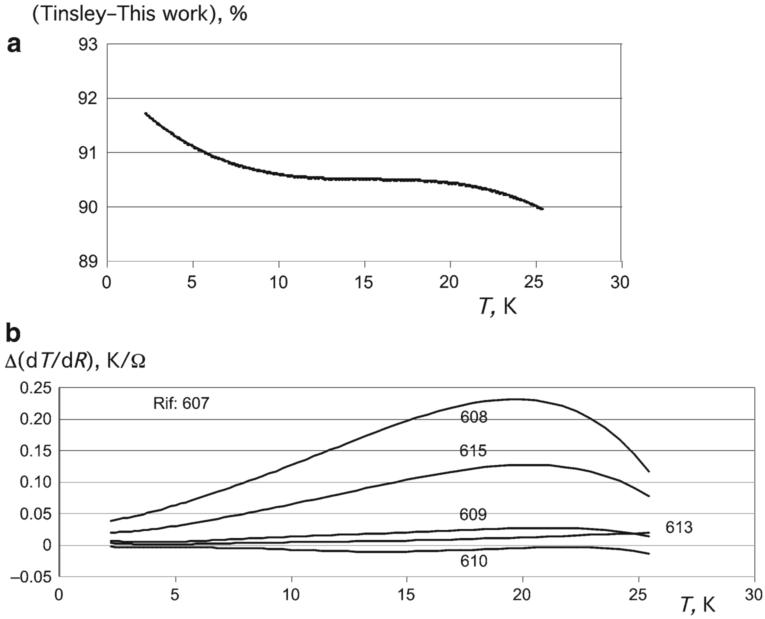

Fig. 3 (a) Sensitivity dR/dT of the new prototypes relative to Tinsley-produced RhFe thermometer B256 and (b) sensitivity differences Δ(dT/dR) between the six stable prototypes (reference #200607)

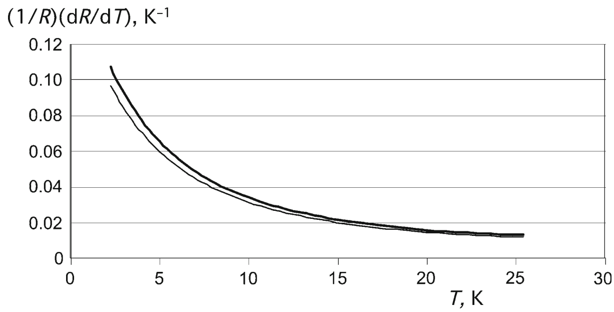

Fig. 4 Relative sensitivity (1/R)(dR/dT) of the new prototypes (*thick line*) compared with Tinsley-type (B256) (*thin line*)

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