A Rhodium-Platinum Thermocouple for High Temperatures

A REFERENCE TABLE FOR THE "FIVE-TWENTY" COUPLE

The thermocouple formed from two rhodium-platinum alloy wires containing 5 and 20 per cent of rhodium respectively, commonly known as the "Five-Twenty" couple, was used by Hanson (1), as long ago as 1927, and has in recent years gained ground at an expanding rate as a reproducible means of measuring very high temperatures.

The couple can measure temperatures up to 1700°C, it is less susceptible to contamination by rhodium—transferred either by volatile rhodium oxide or diffusion across the hot junction—than the more familiar platinum : 13 per cent rhodium-platinum thermocouple, and the readings are very little affected by quite large changes in the temperature of the cold junction.

The maximum temperature that may be measured is limited only by the melting point of the 5 per cent rhodium-platinum alloy limb, 1825°C. The exceptional stability of the couple has been, in particular, recognised by Welch (2), while Chaston (3) has given a review of its properties and advantages.

One factor that up to now has possibly discouraged wider use of this couple has been the lack of a standard calibration table prepared by one of the national standards laboratories.

A reference table for the "Five-Twenty" couple has now been established by R. E. Bedford of the Division of Applied Physics, National Research Council, Ottawa (4). In a paper that clearly reflects a most thorough and painstaking programme, Bedford describes in detail the procedure adopted. Thermocouple materials were obtained from three major manufacturers, thus ensuring a comprehensive selection from available materials and making certain that the proposed reference table is one to which all manufacturers may conform. In all, thirteen "Five-Twenty" and seven platinum : 10 per cent rhodium-platinum thermocouples were used.

Three standard methods were employed to provide calibration data, measurement of the e.m.f. generated at fixed metal melting points, comparison with platinum : 10 per cent rhodium-platinum thermocouples, and comparison with an optical pyrometer.

After pre-annealing at 1450°C all the thermocouples were calibrated by the ingot method at the freezing points of zinc (419.5°C), antimony (630.5°C), silver (960.8°C) and gold (1063°C). Palladium point determinations (1552°C) were carried out by the bridge method, and of the six furnaces used in the course of this investigation three with varying temperature profiles were used to give an estimation of the accuracy of this method of calibration. Bedford also calibrated his couples at the platinum point (1769°C) by the bridge method. Palladium point determinations were carried out in argon to prevent oxidation of the palladium while platinum points were performed in air.

A series of calibrations were then made by welding together the hot junctions of several "Five-Twenty" and platinum : 10 per cent rhodium-platinum thermocouples and locating the assemblies, suitably insulated in two- and four-bore alumina insulators, in a horizontal furnace. Direct comparisons of e.m.f.s were made over the range 0 to 1500°C at approximately 100°C intervals. Over the range 1400°C to 1750°C the outputs of the "Five-Twenty" thermocouples under review were compared with one another by the same technique. Throughout this work one plat-

Reference Table for 5 per cent Rh-Pt : 20 per cent Rh-Pt Thermocouples

(Temperature in °C (IPTS 1948); electromotive force in absolute millivolts; reference junction 0°C)

t(°C)	1000	1100	1200	1300	1400	1500	1600	1700
0	4.9121 848	5.7802 892	6.6928 937	7.6502 977	8.6378 998	9.6410 1007	10.6459 1000	11.6383 980
10	4.9969 852	5.8694 897	6.7865 942	7.7479 979	8.7376 1000	9.7417 1006	10.7459 999	11.7363 977
20	5.0821 857	5.9591 902	6.8807 946	7.8458 982	8.8376 1002	9.8423 1007	10.8458 998	11.8341 974
30	5.1678 862	6.0493 905	6.9753 951	7.9440 985	8.9378 1002	9.9430 1006	10.9456 995	11.9315 971
40	5.2540 866	6.1398 911	7.0704 956	8.0425 987	9.0380 1003	10.0436 1005	11.0451 994	12.0286 969
50	5.3406 870	6.2309 915	7.1660 959	8.1412 989	9.1383 1005	10.1441 1006	11.1445 992	12.1255 964
60	5.4276 875	6.3224 919	7.2619 965	8.2401 991	9.2388 1005	10.2447 1004	11.2437 990	12.2219 962
70	5.5151 879	6.4143 924	7.3584 968	8.3392 994	9.3393 1005	10.3451 1004	11.3427 988	12.3181 957
80	5.6030 883	6.5067 928	7.4552 973	8.4386 995	9.4398 1006	10.4455 1002	11.4415 985	12.4138 954
90	5.6913 889	6.5995 933	7.5525 977	8.5381 997	9.5404 1006	10.5457 1002	11.5400 983	12.5092 950
100	5.7802	6.6928	7.6502	8.6378	9.6410	10.6459	11.6383	12.6042

inum : 10 per cent rhodium-platinum couple was kept for reference purposes and was frequently checked at the gold point to record any change in e.m.f. output.

An attempt was made to check some of the "Five-Twenty" couples using an optical pyrometer but the degree of accuracy obtainable was found to be much lower than from the fixed melting-point and comparison methods.

To produce a reference table the data obtained at the fixed melting points and by comparison with platinum : 10 per cent rhodium-platinum were averaged out to give e.m.f.s at the six fixed points and at sixteen temperatures over the range 0 to 1500°C. The final table of e.m.f.s corresponding to twenty-two temperatures was processed by using an IBM 1620 computer. An attempt to find a single polynomial by the least squares method was unsuccessful, even a sixth degree function being insufficient to represent the data. In consequence the temperature range 0 to 1769°C was divided into three intervals 0 to 960.8°C, 960.8° to 1300°C and 1300° to 1769°C. Equations were found for each interval and from these equations the reference table was constructed.

Bedford goes on to discuss the accuracy of the fixed-point determinations, the platinum: 10 per cent rhodium-platinum comparisons, the optical pyrometer comparisons and their effect on the accuracy of the reference tables. He concludes that after taking these into account plus instrument errors and errors due to ceramic conduction the calibration is probably accurate to ± 1°C below 1063°C, to ± 2°C from 1063 to 1552°C and to ± 3°C above.

Finally he gives some interesting results of stability tests. He found that the palladium point e.m.f. decreased by up to 50 microvolts (about 5°C) after soaking four "Five-Twenty" couples for 200 hours at 1700°C in air. After allowing for the scatter of results in these tests the e.m.f. decrease was roughly linear on either a semi-logarithmic or linear plot, a result which Bedford claims to be in broad agreement with Walker, *et al.* (5) and also Chaussain (6).

A comparison between the proposed table and the results previously reported by other

workers shows a rather erratic scatter within ±10°C of the new values.

Summing up, it is stressed that this study indicates that temperature measurements above 1000°C may be made every bit as accurately with the "Five-Twenty" couples as with platinum : 10 per cent rhodium-platinum couples, and that the former have a considerably higher range. They can be used continuously in air up to 1700°C with only a relatively slow and easily monitored change in calibration and cold junction compensation can normally be neglected.

Bedford's work is broadly confirmed by recent unpublished work in the Johnson Matthey laboratories. There are slight but systematic differences between the curves and the explanation of these most probably lies in the variation in composition of the alloys which although nominally 5 and 20 per cent rhodium-platinum naturally tend to vary slightly from these exact values. The real value of Bedford's work is that it proposes an acceptable table to which all manufacturers may conform, thus ensuring that matching characteristics are obtained. This has been done very successfully with the platinum versus 10 per cent and 13 per cent rhodium-platinum thermocouples where tables originally proposed by the National Physical Laboratory, London, and the National Bureau of Standards in Washington, U.S.A., are now the international standards.

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References

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Crystallisation of Glasses Containing Platinum

A STUDY OF THE MECHANISM OF NUCLEATION

Glass of high strength can be produced by suitably controlling the process of crystallisation (1). Its formation can be better understood by studying the mechanism of the nucleation and crystallisation of glass.

Work has been carried out recently on this problem by R. L. Thakur of the Central Glass and Ceramics Research Institute of India with K. Tazikawa, T. Sakaino and T. Moriya, of the Tokyo Institute of Technology (2). They chose for their studies a eutectic composition glass of lithia-alumina-silica melting at 975°C, which is reasonably homogeneous after melting at 1400°C. Platinum was introduced as dilute platinum chloride solution. Tests were made on glasses with and without platinum as nucleating agent.

Differential thermal analysis was used to determine the transformation temperature, the nucleation and crystallisation temperatures, and the heat treatment necessary for the samples. The crystals were studied by electron microscopy and X-ray diffraction.

Glasses containing no platinum always commenced to crystallise from the surface inwards and there was no phase separation except at the interface with the part already crystallised. The crystals were much larger than when platinum was present.

The appearance of crystals in the platinum-containing glass was always preceded by phase separation, and crystallisation then took place throughout the whole mass. Heat treatment at 550°C produced complete nucleation within eight hours but nucleation remained incomplete at this temperature when no platinum was present even after eleven days.

A series of electron micrographs was produced that clearly indicated the phenomena described. The ability of platinum to act as a nucleating agent for the controlled crystallisation was fully confirmed and the paper is a valuable contribution to studies of the platinum metals for this purpose.

References

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