

Liquid Steel Temperature Measurement

A REVIEW OF THE QUICK-IMMERSION THERMOCOUPLE METHOD

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Some 20 inches of molten steel at a temperature of about 1620°C, covered by perhaps 5 inches of molten slag at 1660°C and contained in the hearth of a furnace typically 50 × 15 × 10 feet with refractory walls and roof at temperatures up to 1650°C, and through which roar at 60 miles per hour flame and gases at temperatures of 1800°C: those are typical conditions within an open hearth steelmaking furnace and it is not surprising that the practical problem of measuring accurately the liquid steel temperature remained unsolved for many years.

The Problem and Early History

The demand from steelmakers for this information was real. It is recorded at least as early as 1917, when the late Dr. W. H. Hatfield (1) stated that "Although the temperature at which steels are cast must have an influence upon their ultimate physical properties, no ready and reliable method of measuring such temperatures from the works standpoint is available. This is a considered statement."

Not until twenty years later did this "ready and reliable" method appear to be forthcoming, when Dr. F. H. Schofield (2) of the National Physical Laboratory published his first proposals for a quick-immersion noble metal thermocouple method now so well known and well established throughout the steelmaking world. To many people these proposals must have been startling. High temperature noble metal thermocouples were seldom seen outside the

laboratory, and their use within the fierce conditions of an open hearth steelmaking furnace was not easy to visualise. A bold attempt had indeed been reported by Rogers (3) in 1917. In his arrangement the separate wires of a noble metal thermocouple terminated flush with the bottom of refractory material moulded around them, so that when inserted into the molten steel the electrical circuit was completed by the bath. Although sound in principle, various practical difficulties were not overcome and the method did not develop successfully.

It is interesting now to re-read in sequence the first Schofield paper (2) and the following paper two years later by Schofield and Grace (4) showing how by close collaboration between the steel industry and the National Physical Laboratory various possibilities were narrowed down until an acceptable practice was established.

Design of the Thermocouple Assembly

The thermo-electric method being accepted in principle, the design and development of a suitable instrument proceeded rapidly. From the early prototype numerous improvements have been made resulting in a robust, mobile and accurate instrument.

Although there are many variations in detail all types are similar in general construction. The thermocouple unit is of platinum : 13 per cent rhodium-platinum wires 0.5 mm in diameter. These are sheathed in twin fireclay insulators and led

through a steel tube with a right angle bend to the hot-junction end, where the junction is usually made by twisting. This end is normally insulated to within an inch or so of the end by small twin-bore fireclay or alumina insulators. The hot-junction is in turn protected from slag and steel by a thin-walled silica sheath which is renewed after each immersion.

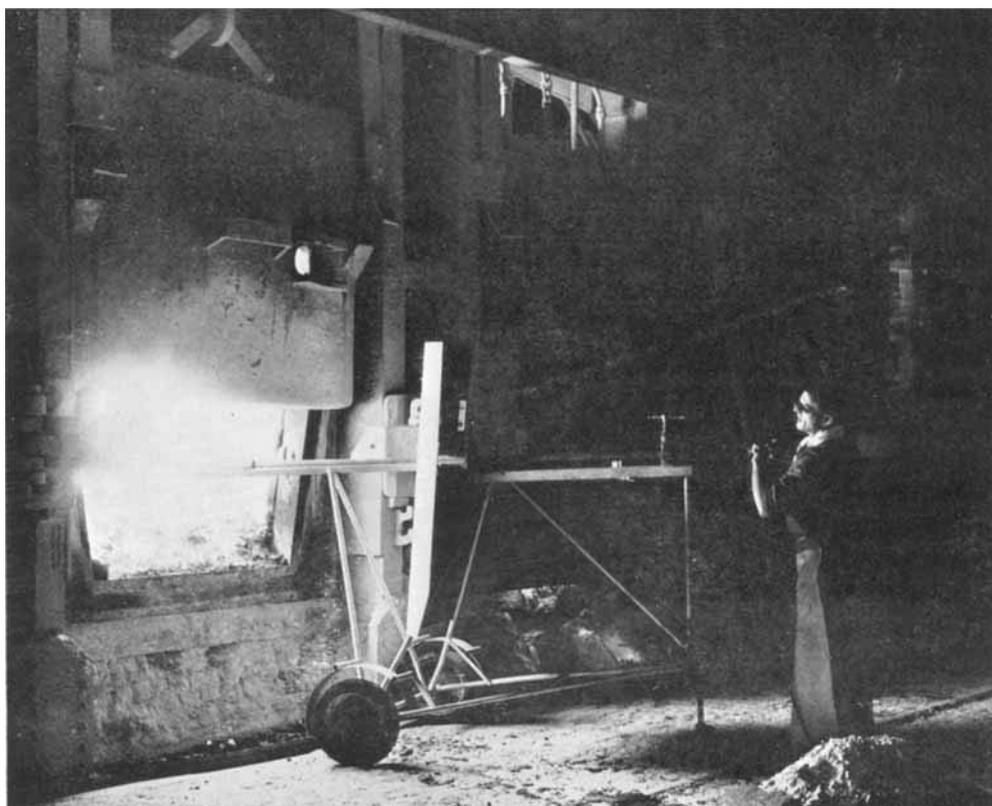
At the cool end a reserve of thermocouple wire is accommodated in a reel box. The hot-junction is renewed after about 30 immersions by cutting off the last few inches of wire, pulling through sufficient wire from the reel box and re-making the hot-junction.

For the smaller electric furnaces the steel tube can be of heat-resisting steel with no external protection. A typical thermocouple arm is shown in the illustration on page 112.

For larger electric furnaces and for open hearth furnaces some external thermal protection of the arm is necessary. The hot-junction end which is immersed in the slag and steel is protected by a graphite or mild steel end-block. For electric or acid open hearth furnaces a graphite end block is more suitable but a mild steel one is used successfully in basic open hearth. Also for open hearth work the main arm is protected by insulating cylinders, usually of diatomaceous brick.

This assembly is conveniently mounted on a wheeled trolley with a protecting screen for the operator as shown in the illustration below.

A further type was developed which was attached to the furnace back wall (5). This consists of an all-steel hollow arm through



A quick-immersion platinum thermocouple assembly for an open hearth furnace in use at the Lackenby Works of Dorman Long & Co. Limited. The trolley was designed and produced by Amalgams Co. Limited



A typical thermocouple assembly for small electric furnaces

which the insulated thermocouple wires pass to the hot-junction end which is protected by a replaceable silica sheath in the usual manner. By means of a light winch this can be inserted into and retracted from the furnace bath and can be swung back parallel to the furnace wall when not in use. This type is illustrated on the facing page.

The application of the thermocouple method of temperature measurement to the Bessemer converter presents some difficulties, but these are not insuperable. For example the acid Bessemer slags are often hard and crusty and a special steel prong can be fixed alongside the silica sheath to protect it and to pierce the slag.

Nowadays the measurement of the thermocouple reading is usually by means of a high speed recorder or combined indicator and recorder. Formerly, manual potentiometric measurement was widely used for this purpose and still is used to some extent.

General Use and Development

There is now a great deal of easily available literature on liquid steel quick-immersion pyrometry and it is proposed here to indicate the general scope and to give a selection of references.

Early Applications

By 1942 the British iron and steel industry was already able to give a comprehensive account (6) of early applications of the quick-immersion technique, and since it is clearly desirable that the temperature of a liquid steel bath can be measured from a single representative position it is understandable that much of the early work was concerned

with studying temperature distributions in metal baths. Explorations were made in three dimensions and variations at different times during steelmelting processes were examined. In a joint report (7) figures for large and small arc furnaces were given by three steelmaking companies (United Steel Companies Ltd., English Steel Corporation Ltd. and William Jessop & Sons Ltd.). A paper by Oliver and Land (8) reported on acid open hearth furnaces and a small high frequency furnace as well as giving further data concerning arc furnaces, and additional information on similar furnaces was provided by Hatfield (9). A little later Manterfield (10) helped to complete the picture with information on the larger type of basic open hearth furnaces. The general conclusion from these surveys was that in most types of steelmaking practice, and at the times of greatest interest to the steelmaker, it is possible to select a single position which within acceptable limits gives a representative temperature for the whole of the bath.

Comparison with the Optical Pyrometer

Prior to the development of the immersion method, attempts to measure liquid steel temperatures had been chiefly by means of optical pyrometers, and the early joint report (6) contained two sections in which comparison of the two methods was made. Thomas Firth and John Brown Ltd. reported on a "comparison of thermocouple and optical pyrometer on acid open hearth furnaces" and Hadfields Ltd. reported on "emissivity and optical pyrometry of liquid steel streams."

Finally the joint report (6) contained contributions from Hadfields Ltd., Thomas Firth

and John Brown Ltd., English Steel Corporation Ltd. and William Jessop & Sons Ltd. on early experience and thoughts on the possibilities of applying liquid steel temperature measurement to steelmaking control. That casting temperature should have an effect on casting properties (fluidity) is obvious, but it was also established that there was a real influence on ingot quality.

Outside the actual steelmaking furnaces, thermocouples were used quite early on by William Jessop & Sons Ltd. (6) for measuring temperatures in the trough, and modified techniques were developed by Oliver and Land (11) for measuring in liquid steel casting streams.

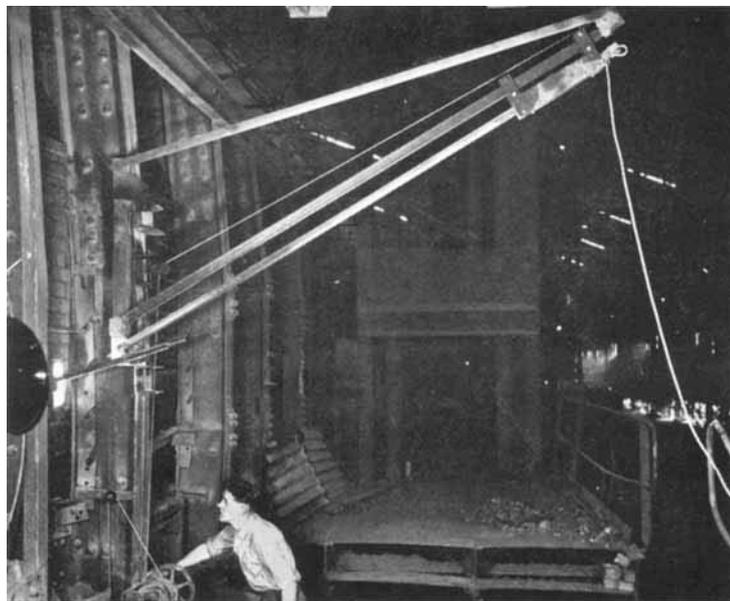
Further Development

In the years immediately following many papers appeared both at home and abroad describing constructions and techniques, and at the instigation of the B.I.S.R.A. Pyrometry Sub-Committee (now the Steel-making Instruments Sub-Committee) Manterfield and Cresswell (12) published in 1952 a summary of accepted British practice which can still be taken as authoritative.

This was accompanied by papers by Herne (13) and Cresswell (14) respectively describing theoretical and laboratory studies of the effect of various factors on thermocouple response time. These factors included (i) thermocouple wire diameter, (ii) wire insulation near the hot-junction, (iii) method of making the hot-junction, (iv) condition of the thermocouple wires, e.g., shape, and bright versus black surfaces, (v) thickness and opacity of the thermocouple sheath, and (vi) slag adhesion to thermocouple sheath. One of the theoretical conclusions was that heat transfer from bath to thermocouple occurs approximately equally by radiation and by conduction, and both the theoretical and practical work showed the importance for quick response of having thin wires with bare junction in a thin walled silica sheath. Practical considerations of course demand a compromise between fast response time and robustness to withstand furnace conditions.

Some of the problems to be faced when applying quick-immersion pyrometry on a large scale in the modern steelworks have been described by Goodall (15) who comments on

Jib mounting for an immersion pyrometer operating through the back wall of an open hearth furnace





A platinum thermocouple in use to determine the temperature of liquid steel in a Bessemer converter at the Ebbw Vale Works of Richard Thomas & Baldwins Limited

the organisation of the work and the training of operators, and on practical features that have been found important to minimise maintenance.

A present-day assessment of the metallurgical value of the application of quick immersion pyrometry is made at the end of this article.

Extension to Higher Temperatures

For normal liquid steel immersion pyrometry the platinum: 13 per cent rhodium-platinum combination is quite satisfactory, being capable of use up to about 1700°C or even higher with care (melting point of platinum 1769°C). In certain special cases, however, considerably higher temperatures than this occur during steelmaking, a particular case being oxygen-blown stainless steel in an electric furnace. Some success has been achieved both with tungsten-molybdenum

thermocouples (16) and with platinum-rhodium thermocouples of high alloy content. The addition of rhodium progressively raises the melting point (solidus) of platinum-rhodium alloys, and Chaston (17) has recently described the development of a 5 per cent rhodium-platinum : 20 per cent rhodium-platinum thermocouple which can with care be used up to about 1800°C. While this combination is proving most useful in other applications it is not sufficient for the oxygen-blown stainless steels and an even more highly alloyed thermocouple, 20 per cent rhodium-platinum : 40 per cent rhodium-platinum has been developed (18) for use up to 1900°C. Refractory protection at these high temperatures becomes a very real problem. It is outside the range of silica, and alumina sheaths have been used, usually coated with some cement and pre-heated before immersion to reduce the chance of spalling.

Checking and Calibration

The accuracy of a thermocouple can be checked at any time by simultaneous (or immediately consecutive) dips with a standard couple using the same measuring instrument. In the laboratory the precision check can conveniently be made at the melting point of palladium (1552°C) by the wire method. In this the separated wires of the thermocouple hot-junction are bridged by a short length of palladium wire and the e.m.f. continuously read while the assembly is slowly heated. The calibration e.m.f. is that when the palladium melts and breaks the circuit. A typical procedure has been described in detail (19, 20) as has also a modified differential method (21).

Measuring instruments are nearly always of potentiometric type and these should periodically be checked against a standard potentiometer. Commercial recorders for quick immersion pyrometry are usually provided with internal devices for checking calibration at one or two points.

Maintenance of the Thermocouple

The expendable parts of the assembly include the thermocouple wires, the protecting sheath, the graphite or mild steel end-block into which the refractory sheath fits, and the protecting graphite or diatomaceous sleeves along the arm of the assembly. The last two items normally have extensive lives so that their cost per dip is small; it is the first two items that warrant closest consideration, although for somewhat different reasons. The two most expensive items in the total cost per dip are the cost of the protecting sheath and the cost of labour. Good thermocouple life without having to re-make the hot-junction results in lower maintenance and operating costs. Thus it is that considerable attention has been given to improved thermocouple and sheath performance.

Thermocouple Wires

The scrap value of platinum is high, with the result that the net cost of thermocouple wire

is not great if good housekeeping principles are observed by operatives carefully collecting all bits for return to the supplier. A good life before having to cut back and re-make the hot-junction is, however, a great advantage in reducing maintenance time and instilling confidence in readings.

At normal steelmaking temperatures by far the chief cause of deterioration of the thermocouple wires is by contamination resulting in embrittlement and/or loss of calibration, although grain growth can also have some effect in causing embrittlement. Loss and migration of rhodium from the rhodium-platinum wire can occur, but the practical effect of this on the thermocouple reading is usually negligible because of the depth to which the thermocouple is immersed in use. A concerted effort was made by the Liquid Steel Temperature Sub-Committee (22) to study the causes and effects of contamination and the results are briefly reviewed below. The summaries are given in the same order as the papers in the Symposium, which should be read as an historical series covering work extending over some years prior to publication.

(i) Land (23) investigated the embrittlement of platinum thermocouples experimentally by exposing new thermocouple wires to different combinations of materials normally in proximity to the wire in the pyrometer, and concluded that oil or other carbonaceous materials in the steel tube of the thermocouple assembly is the cause of embrittlement. Embrittlement was pronounced with a new tube, but did not occur after the tube had been thoroughly burnt out.

(ii) Reeve and Howard (24) described a laboratory test which simulated practical conditions by heating a short length of wire in a graphite block in the presence of lubricating oil, the wire being placed in a silica insulator. It was shown that attack was less marked on fully annealed or fully cold worked wire than on wire which has been only partially annealed, and a separate series of tests confirmed the conclusions of Chaston

and his co-workers that the presence of silica and sulphur is essential for attack to occur. Reeve and Howard also confirmed that thorough baking at a dull red heat of the iron pipes used for carrying the thermocouple assembly, with a current of air drawn through them, results in almost complete freedom from this type of intercrystalline failure in practice.

(iii) Goldschmidt and Land (25) examined by X-ray diffraction thermocouple wires contaminated and embrittled in service or by laboratory exposure to oil and graphite in the presence of silica. Three phases additional to the matrix were found. Two were identified as silicides and it seems that one of these is relatively strong and ductile, whereas the other silicide and the third phase (unidentified but quite possibly a further silicide) are weak and brittle. The presence of greater proportions of the latter two phases may account for more severe embrittlement of platinum-rhodium as compared with pure platinum wire.

(iv) Manterfield (26) had met some unusual cases of bad contamination and failure of thermocouples during an investigation concerning the solidification of molten ingots. Examination by visual, X-ray, microscopic and spectroscopic methods showed this failure to have been due to the reduction of

silica to silicon and the alloying of this silicon with platinum to form a new phase of platinum silicide.

(v) Chaston, Edwards and Lever (27) investigated the mechanism of the embrittlement of platinum thermocouple wires when heated in various environments. They confirmed the findings of other workers that platinum is not embrittled by heating in contact with carbon, with hydrocarbon vapours or with sulphur alone, and went on to show that if platinum is heated in, and not necessarily in contact with, a siliceous refractory enclosure in the presence of small amounts of sulphur and carbon (as can be provided for instance by traces of oil) then embrittlement may occur. The authors suggest that under these conditions and at temperatures above about 1100°C the volatile compound silicon sulphide SiS_2 can be formed and that it is this that attacks the platinum to form platinum silicides at crystal boundaries.

(vi) Jewell (28) studied three cases of embrittlement microscopically but supported by spectrographic examination. Two different silicides were identified and one type of failure appeared to be due to the formation of a eutectic between the respective silicide phases and platinum, possibly also with 13 per cent rhodium-platinum. The silicide

Typical Liquid Steel Temperatures for Carbon Steels

Melting C%	Temperature Required Before Feeding °C	Finish C%	Refining Range °C	Tapping Range °C
0.10	1600	0.10	1590/1610	1600/1620
0.20	1590	0.20	1580/1600	1590/1610
0.30	1580	0.30	1570/1590	1580/1600
0.40	1575	0.40	1565/1585	1575/1595
0.50	1570	0.50	1560/1580	1570/1590
0.60	1565	0.60	1555/1575	1565/1585
0.70	1560	0.70	1545/1565	1555/1575
0.80	1555	0.80	1540/1560	1550/1570
0.90	1550	0.90	1535/1555	1545/1565
1.00	1545	1.00	1530/1550	1540/1560
1.20	1530	1.20	1515/1535	1525/1545

operating in the alloy wire was found to be more brittle than the other. A second type of failure was due to intercrystalline cracking of the alloy wire and was associated with the presence of a dark unidentified constituent. The two silicides and the unidentified constituent appeared to correspond with those reported by Goldschmidt and Land.

The practical significance of all this work is the paramount importance of cleanliness. Both of the first two components of this harmful trio of carbon, sulphur and silica can arise from oil and grease. It is vital that traces of oil in the steel assembly tube (remaining from drawing and screwing operations in manufacture) should be removed by thorough baking in a current of air, and that scrupulous cleanliness be maintained when making up the thermocouples or handling the wires in any way.

Refractory Sheaths

The chief advantage of a silica sheath as normally used is its freedom from spalling when suddenly subjected to steel-making temperatures. A disadvantage is its tendency to devitrification which, even though the sheath is still whole after an immersion, makes it hazardous to use more than once.

Sheaths of other refractory materials have been tried, e.g., zircon, alumina, and graphite, but none has achieved the overall success of silica. Metal ceramics appear to offer more hope. It is not clear that an early American claim (29) that a chromium-alumina material could be used for about 20 dips has been substantiated but it is understood that molybdenum-alumina combinations are in use in Germany. Research work in progress in this country has indicated that chromium-

alumina sheaths are unsuitable because of their contamination effects on noble metal thermocouples at liquid steel temperatures. Molybdenum-alumina shows more promise but the use of metal ceramic sheaths in this country is not yet established.

Metallurgical Value

Liquid steel temperature measurement has now been applied for many years for purposes of routine control, and a fair estimate is that between one and two million dips are made annually in this country alone.

A typical practice is to take the temperature at melting, an intermediate temperature during refining, and a final one just before tapping. Temperature ranges for these periods are fixed and control exercised. Some typical working ranges for carbon steels are shown in the table on the facing page.

Too low a temperature at melting can result in chilling the metal when additions of refining materials (lime and ore) begin. Too high a temperature can also retard the refining process as the slag metal reactions proceed more rapidly and effectively in given temperature ranges.

Temperature control will also minimise attack on the furnace structure, the ladle and casting pit refractories, and have a beneficial influence on the life of ingot moulds. It also has a profound effect upon steel quality. Cracking can be caused by a high temperature, and non-metallic inclusions and sluggish metal can result from a low temperature.

There is no doubt that liquid steel temperature measurement and its attendant control are of great benefit to the science of steel making.

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