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APPLICATION OF SELF-CALIBRATING THERMOCOUPLES WITH MINIATURE FIXED-POINT CELLS IN A TEMPERATURE RANGE FROM 500 °C TO 650 °C IN STEAM GENERATORS

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Abstract - Using integrated miniature fixed-point cells, a measuring uncertainty of < 1 K can be reached under operating conditions in the superheated steam range of power plants by a periodic recalibration of the thermocouples, with operating times of > 20000 h. The fixed-point materials used for a temperature range from 500 °C to 650 °C are technically pure metals and binary alloys.

Keywords: temperature measurement, measuring uncertainty, self-calibration, fixed-point, superheated steam

1. INTRODUCTION

In case of convent ional steam generators in power plants equipped with thermocouples of the K or N type, a drift of their characteristics and of the error limits, increasing with the time of operation, of the subsequent elements of the measuring sequence m ust be expected due to their permissible tolerances, with the uncertainty being up to 5 K.

Fig. 1: Schematic representa tion of the connection between temperature measurement uncertainty and adjustable temperature desired value

The aim is to reduce the necessa ry safe distance between the controlled steam temperature and the maximum permissible temperatures for pipelines and plumbing controls by a considerably lower uncertainty, thus permitting a higher efficiency ratio and lower am ounts of emissions to be reached.

2. BASIC PRINCIPLE

The basic principle of self-calibrating thermocouples consists in integrating a suitable fixed-point material encapsulated in a miniature fixed-point cell into a thermocouple. When the temperature around the melting or also freezing

temperature T_{FP} of the fixed-point material changes, the thermoelectric voltage undergoes charact eristic temporal variations due to phase transformations. From these characteristic temporal changes, a calibration value U (T_{FP}) for the thermocouple or also for the entire measuring sequence can be obtained at the fixed-point temperature [1].

Fig. 2: Temperature and thermoelectric voltage profiles of a thermocouple in a miniature fixed-point cell during m elting and freezing proces ses

To make this principle usable on an industrial scale for the automatic in-situ recalibration of thermocouples under operating conditions such as in power plants, the following preconditions had to be fulfilled [2]:

- long-term stability of the miniature fixed-point cells also in case of temperatures and temperature cycles far above the phase transformation temperature,
- availability of small and metrologically optimum fixed-point cells which permit the integration into industrial gauge inserts,
- availability of fixed-point materials with well reproducible phase transformation temperatures at a small distance to the normal operating temperature of the thermocouple to guarantee an as low as possible measuring uncertainty after a single-point calibration.

3. TECHNICAL REALIZATION

When selecting suitable substances as fixed-point materials, four aspects should particularly be considered:

- phase transformation temperature at normal pressure of about 20 to 50 K above the normal operating temperature,
- material available at sufficient purity $(> 99.99\%)$,

ratio between enthalpy and latent heat during phase transformation

In cooperation with several large power plants, test probes which fulfilled these requirements were developed and tested under practical application conditions. In doing so, a total of 7 different technically pure metals and binary alloys whose phase transformation temperatures lie in the tem perature range of the superheated steam were successfully employed.

Table 1: Usable fixed points in the temperature range of the superheated steam [3]

Alloy	T_{FP}	Alloy	T_{FP}
Cu23Sb	523,3 °C	Al17In	638,4 °C
Al67Cu	548,2 °C	Cu ₃₀ Ge	642,4 °C
Ag71Al	567,6 °C	Ag90Ge	652,4 °C
Al ₈₇ Si	578,7 °C	Al	660,3 °C
Al75Pd	616,5 °C		

Fig.3: Various designs of ceram ic miniature fixed-point cells

The miniature fixed-point crucible to be integrated into the complete thermocouple shall contain the fixed-point material and prevent permanently foreign substances from penetrating, or also any chemical changes. The crucible m aterial shall meet the following requirements:

- temperature stability in the air at working temperatures,
- chemical long-term stability against metal melts,
- availability and processability at high purity,
- high thermal conductivity and low thermal capacity.

Thus, various ceramic materials such as aluminium oxide, silicon nitride, boron nitride, and aluminium nitride have proved to be suitable crucible mate-rials.

The geometry and the material of the crucibles are decisive for the shape and the evaluability of the measurable fixedpoint plateaus, and thus, also for the calibration uncertainty that can be achieved.

A novel design of miniature ceramic crucibles including the corresponding filling and seali ng technologies were developed. This design is characterized by a far more efficient

encapsulation, which offers a better protection of the fixedpoint material against long-term pollution.

Furthermore, through detailed FEM model calculations, it was possible to increase the filling volume of the new design by 50 %, with the external dimensions remaining unchanged, thus extending the time duration of the phase transformation processes whi ch can be used for calibration.

Fig. 4: Melting plateaus of two designs of a miniature fixedpoint cell with Al filling

A controllable heating element additionally integrated into the thermocouple makes it possible to calibrate the entire measuring sequence from outside also in case of constant medium temperatures.

Fig. 5: Freezing plateaus of two designs of a miniature fixedpoint cell with Al filling

During practical application, a calibration uncertainty at the fixed-point temperature of about 0.2 K and measuring uncertainties at the operating tem perature of $\langle 1 \rangle$ K are obtained.

Fig. 6: Structure of a miniature fixed-point thermocouple with integrated heating

4. TEST RESULTS

During test runs over more than 15000 operating hours performed in various power plants under different application conditions, it was possible to prove the serviceability and the long-term stability of the miniature fixed-point cells developed, as well as the excellent reproducibility of their phase transformation temperatures and the sufficient therm al and mechanical load capacity of the miniature fixed-point sheathed thermocouples equipped with these fixed-point cells.

Figure 7 shows calibration cycles measured under application conditions for a thermocouple with Al fixed-point cell in a power plant at a steam temperature of 630° C.

Fig. 7: Typical calibration cy cles in the temperature range of 630 °C (steam temperature) and 660 °C (fixed-point temperature of Al)

After an operation time of more than one year, this test thermocouple was checked i n the calibration laboratory. The results are illustrated in Figure 8 and Figure 9. It can be seen that the measured fixed-point plateaus can still be evaluated without any problems. The fixed-point temperature which can be found has changed by < 100 mK. The visible difference between the two cu rve shapes is caused by the drift of the thermocouple to be corrected.

Concerning the freezing tem perature of the material (aluminium) in the miniature fixed-point cell, one can start out from the assumption that it has changed onl y slightly during

the long-term measurements under power plant conditions. Comparative measurements of the miniature fixed-point thermocouple made in a standard reference al uminium fixed-point cell yielded, from the thermoelectric voltage profile, a difference of about –70 mK between the short miniature fixed-point freezing plateau (Fi gure 10, right-hand part of the curve) and the long reference freezing tem perature plateau (Figure 10, left-hand part of the curve).

Fig. 8: Melting plateaus before and after long-time application under power plant conditions

Fig. 9: Freezing plateaus before and after long-tim e application under power plant conditions

Fig. 10: Freezing plateaus of a reference alum inium fixed-point cell (T_{FP} = 660.323^oC) and of the aluminium miniature fixed-point cell in the MFP thermocouple afte r long-term operation at steam temperatures of 630 $^{\circ}$ C

Further long-term measurements were carried out in several power plants also using metal alloys as fixed-point material [4].

Table 2: Steam temperatures und fixed-point materials used during long-term experiments at fixed-point temperatures above the steam temperature

By means of the miniature heatings integrated into the MFP thermocouples, it was possible to achieve temperature variations, which were time-linear on average, of the fixed-point cell of up to 30 K at temperature variation rates between 0.1 K/min and 1 K/min. The phase transformation plateaus thus induced proved to be extremely reproducible both with regard to their shapes and the fixed-point temperatures approximated from them. No significant dependence of t he fixed-point temperatures on the heating or cooling rate was stated (Figure 11 and Figure12).

Fig. 11: Typical measuring cycle when using an integrated m iniature heating at steam temperatures of about 565° C and varying heating power

Fig. 12: Individual calibra tion process from Fig. 11

Also during these test measurements made over more than one year at steam temperatures of 535 $^{\circ}$ C and 565 $^{\circ}$ C, no significant changes of the miniature fixed-point plateaus of Al67/Cu measured at a temperature of 548.2 °C or also of Al87/Si at a temperature of 577.2 °C (Table 2) were stated. The miniature cells, heating system s and thermometer designs used showed a hi gh thermal and mechanical long-term stability.

5. AUTOMATIC RECOGNITION AND EVALUATION OF CALIBRATION SIGNAL PROFILES OF MFP THERMOMETERS

The aim of an automatic recognition is $-$ in case of thermoelectric voltage profiles with interfering temperature variations and other disturbances - to detect those signal profiles which are typical of the phase transformations of the fixedpoint material.

The determination of typical search patterns of the thermoelectric voltage profile before, during and after phase transformation, which are typical of a concrete thermocouple design and a special fixed-point material, constitutes the basis for a suitable computer program.

Fig. 13: Schematic representati on for straight-line approximation and the calculation of the intersection point

For the evaluation of the calibration processes found (m elting process), the thermoelectric voltage profile is approximated by a straight line before and after calibration.

Afterwards, a straight-line approximation is carried out for the increase in the therm oelectric voltage (tem perature) during the plateau phase with a time-limited search window between the starting and the and point of the plateau.

For both approximation straight lines, the two coefficients and their variability are determined. Thus, the coordinate of the intersection point of the two straight lines $U(T_{FP})$ can be calculated, and its uncertainty can be evaluated.

The data for the slope of the straight lines as well as their ratio and the uncertainty values can be used for filtering useless or wrongly interpreted processes.

Before a newly calculated intersection point is accepted as calibration value, its plausibility is verified.

Fig. 14: Fixed-point temperatures determined in a power plant by means of an AlSi fixed-point th ermocouple (without characteristic correction)

Figure 14 shows the temperatures calculated from the measured thermoelectric voltages according to the standard characteristic. Compared with the actual temperature profile, they are shifted in ordinate direction due to a characteristic deviation of the non-calibrated thermocouple and to an offset error of the AD convert er used for these measurements. In the course of 80 days of operation, which was not interrupted by any intermediate calibrations, a continuous characteristic drift by about 0.2 K was stated. The reproducibility of the fixed-point temperatures found lies in the range of < 50 mK.

5. SUMMARY

As a result, prototypes of miniature fixed-point thermocouples presenting a therm al and mechanical long-term stability under power plant conditions as has been proved are available whose reproducible measuring uncertainty of the livesteam temperature is < 1 K. Thus, an essential prerequisite for reducing the necessary safe distance between steam temperature and material limit values and for increasing the efficien cy is fulfilled .

At present, this novel measuring system is being introduced in industrial practice.

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