PHASE TRANSFORMATION TEMPERATURES OF BINARY ALLOYS IN MINIATURE FIXED-POINT CELLS

S. Augustin, D. Boguhn

Technical University of Ilmenau, Germany

ABSTRACT

This paper describes some special features found during phase transformations of binary alloys which may exert an influence on the potential utilization of those alloys as reproducible fixed-point temperatures. Furthermore, it reports some experiences made when using alloys as phase transformation materials in miniature fixed-point cells, and presents a number of results obtained by using AgAl alloys. For those alloys, extensive investigations into the influence of the mixing ratio on the solidus temperatures determined by means of miniature fixed-point cells as well as on the shape of the measured phase transformation plateau were carried out.

1. INTRODUCTION

For a long time already, the principle of the miniature fixed-point cells has been known. Small, closed crucibles containing little amounts of a high-purity material will directly be integrated into a thermometer. The phase transformation processes in this fixed-point material caused by temporal temperature changes can directly be detected by the temperature sensor and, thus, used for self-calibration [1-3].

Originally, this principle of the miniature fixed-point thermometers was applied as an alternative to the use of conventional fixed-point cells in the calibration laboratory and as precision calibration standard [4]. In doing so, high-purity metals, whose solidification temperatures are defined as primary or secondary temperature fixed points of the ITS-90, were mostly used as phase transformation (fixed-point) materials [5, 6]. Thus, it was possible to realize fixed-point calibrations with a calibration uncertainty of less than 20 mK within a large temperature range (150…1085 °C) [7].

Recent research work is being carried out with the aim to apply the principle of the miniature fixed-point cells for self-calibrating thermocouples also for industrial purposes [8]. Hence, the scientific research activities are focused not only on the thermal and mechanical long-term stability of the cells, on methods for inducing phase transformation processes at nearly constant application temperatures and on the automatic recognition and evaluation of the fixed-point plateaus measured, but also on investigations into potential fixed-point materials.

Calibrations at miniature fixed-point temperatures are, in general, single-point calibrations. Under laboratory conditions, however, it is possible to realize a recalibration of the temperature sensor at several temperatures by replacing the miniature cell and, thus, the fixed-point material, which is nearly impossible in the case of industrially applied miniature fixed-point thermometers. On the other hand, the recalibration of the entire sensor characteristic at several points does not seem to be necessary in most cases. Many industrial processes are taking place at temperatures which are either nearly constant or changing within a restricted range only. Here, also an in-situ recalibration at only one fixed-point temperature may result in a sustained diminution of the uncertainty during temperature measurement.

A prerequisite for this, however, is a reproducible fixed-point temperature which is either as close to the application temperature range as possible or lying within this range. This cannot always be realized by utilizing the phase transformations of high-purity materials. Therefore, the phase transformation processes of some binary alloys were investigated in more detail with regard to the suitability of those alloys as potential fixed-point temperatures.

2. PHASE TRANSFORMATIONS OF BINARY ALLOYS

Phase transformations taking place in alloys can be compared only partially can the melting and solidification processes in high-purity materials. Not only pressure and temperature, but also the concentration ratio of the single components exert an influence on the thermodynamic equilibrium conditions of multi-component systems. Their liquefaction or also solidification processes are mainly determined by the mutual solubility of the alloying constituents as a function of temperature and concentration. In general, the melt-down or also solidification process of a certain alloy does not take place at a fixed temperature, but rather within a temperature range which is bounded by the solidus and the liquidus temperatures. Above the liquidus temperature, the entire sample is liquefied, whereas below the solidus temperature, it is completely solid. Only in the case of special mixing ratios – eutectic or monotectic compositions – the solidus and the liquidus temperatures are nearly identical as in the case of high-purity metals.

However, the spatial and the temporal inhomogeneities in the composition of alloys represent a big disadvantage to the realization of reproducible phase transformation temperatures. In a liquid state, the different densities of the metals involved lead to the diffusion of one constituent in the direction of gravity and, thus, to a concentration gradient within the solution. It is true that convection effects can counteract this segregation process, but, for example, a desirable eutectic mixing ratio within the sample can be encountered only locally in most cases. Theoretically, the differences in concentration are evened out during the cooling down of this eutectic solution by the segregation of that constituent that is locally "overconcentrated" in comparison with the eutectic ratio. In the case of real alloys, however, those compensation processes depend on the cooling-down regime as well as on the deviation of the global mixing ratio from the eutectic value.

However, it was shown that reproducible temperature fixed points can be realized when eutectic alloys are utilized in an appropriate way [9-12]. Investigations carried out with eutectic alloys so far prove the relatively good reproducibility of the melting temperatures (≤ 30 mK). On the other hand, they also show that the solidification temperatures greatly depend on the cooling-down regime due to the diffusion and segregation processes taking place within the liquid phase.

3. BINARY ALLOYS AS PHASE TRANSFORMATION MATERIALS IN MINIATURE FIXED-POINT CELLS

Most of the precision measurements published so far concerning phase transformation temperatures of binary alloys within a temperature range of 500…800 °C (AlCu, AgAl, AgCu) were made by means of comparatively large crucibles or also conventional fixed-point cells. In the case of this method, the shape and the temperature of the phase transformation plateau measured are determined by the local material composition of the alloy around the position of the temperature sensor.

The segregation and diffusion processes influence the local composition of the alloy in an almost unforeseeable way, which is also due to the dimensions of the crucibles. A purposive control of the phase transformation boundaries, as it is practised in the case of fixed-point calibrations with high-purity metals in large fixed-point cells [13], is nearly impossible.

Even when miniature fixed-point cells, whose dimensions are pretty small, are used, concentration gradients can develop within the phase transformation material. However, the advantage of employing this method is that – due to the small dimensions of the rotationally symmetrical miniature crucibles – the temperature gradients developing within the fixed-point material are low. The temperature sensor is able to directly register the phase transformation processes of the whole fixed-point material. Therefore, the plateaus measured will not essentially be influenced by the local properties of the alloy. Here, not only the static and dynamic temperature gradients represent some certain factors of uncertainty in the reproducible determination of the phase transformation temperatures, which is mainly due to externally existing temperature fields and to the structure of the thermometer, but so also does the reliable evaluation of the comparatively short fixed-point plateaus [14].

For a number of binary alloys, such as Cu24Sb (eutectic transformation at 526 °C), Al67Cu (548 °C), Ag70Al (567 °C), Al87Si (577 °C), Al75Pd (619 °C), Al17In (639 °C), Cu60Ge (614 °C, 644 °C) or Ag28Cu (780 °C), investigations concerning the reproducibility of their phase transformation plateaus were carried out using miniature fixed-point thermocouples. Regarding the characteristic parameters of the plateaus measured and the reproducibility of the fixed-point temperatures ascertained through straight line approximation [8, 14], the plateaus measured (see, for example, Figure 1) are very similar to those found when using high-purity metals. It is true that the plateau lengths measured vary between the different alloys as expected, but the rise in the melt-down plateaus of all samples is very slight only, which permits to determine the values of the solidus temperatures in a reproducible way and with low uncertainty (< 0.1 K). A significant dependence of these temperatures values on the heating-up rate (≤ 1 K/min) was not established.

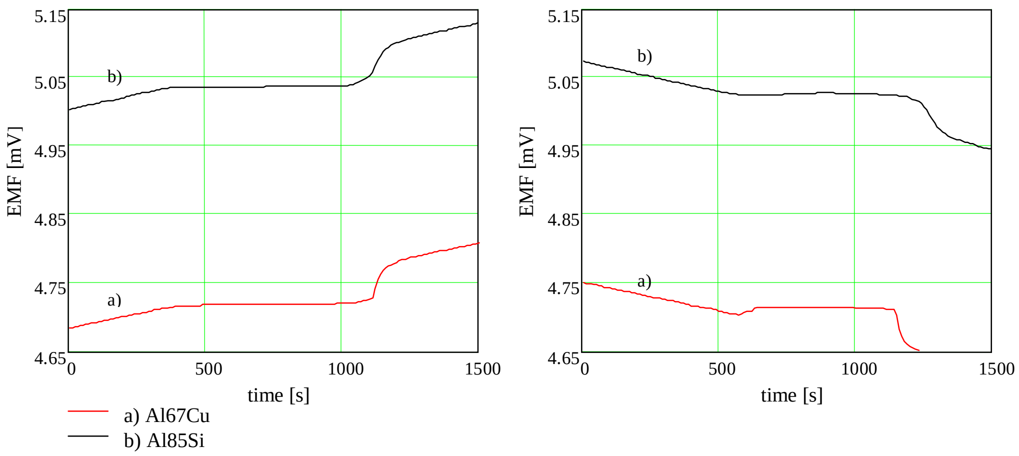

Figure 1: Phase transformation plateau of an Al67Cu alloy and an Al85Si alloy, respectively, mea s-ured by means of a thermocouple (PtRh10/Pt) with integrated miniature fixed-point cell (external diameter 4 × 20 mm) at a heating-up or also cooling-down rate of 0.5 K/min

While during heating-up processes, phase transformation plateaus are detected only at the solidus temperatures, short recalescence points can also be found in the temperature-time-curve measured during cooling-down processes in some off-eutectic alloys at the respective liquidus temperatures. The appearance of those points as well as the shape and the temperature values of the solidification plateaus measured at the solidus temperature are greatly dependent on the material composition, the preceding maximum temperature, the cooling-down rate, etc. Hence, they are hardly usable for miniature fixed-point calibration [8]. Only the evaluation of the melt-down plateaus is profitable as it is much better reproducible.

The possibility of a two-point calibration is offered by the use of special alloys presenting several usable phase transformations. An example of this is the Cu60Ge system. At a temperature of about 614 °C, it presents an eutectoid phase transition, whereas at a temperature of 644 °C an eutectic phase transition can be found. Both transitions can be recognized as strongly defined, reproducible plateaus in the temperature curve measured.

4. MINIATURE FIXED-POINT TEMPERATURES OF THE AG-AL-EUTECTIC

Phase transformation processes in alloys depend on the mixing ratio of the pure single constituents. Therefore, particularly those alloys having defined compositions – eutectic and monotectic mixing ratios – present themselves as potential fixed-point materials. However, their global material compositions are mostly known with a precision of ≥ ±0.1 weight-% only. If only small quantities of an alloy are used as it is the case for miniature fixed-point cells, the reproducible realization of a well-defined global mixing ratio will require comparatively big efforts.

In order to determine the influence of the composition of the alloy in the range from –4.5…+10.5 weight-% of aluminium around the eutectic ratio on the miniature fixed-point plateaus measured, investigations were carried out with an eutectic Ag70Al system (marked region in Figure 2). For these investigations, a number of miniature fixed-point cells were filled with this alloy (5N purity of the single constituents) and then inserted in a PtRh10/Pt thermocouple.

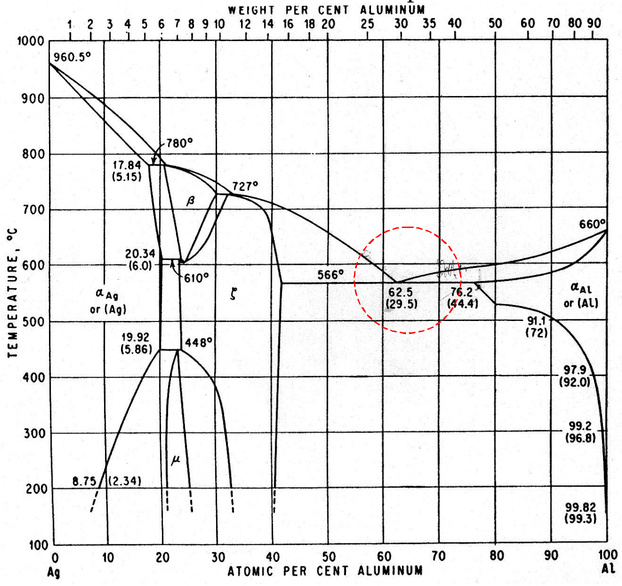

Figure 2: Phase diagram of the AgAl system according to [15]

The phase transformation plateaus of the various alloys were registered at a heating-up or also cooling-down rate of 0.5 K/min. Then, their solidus temperatures were determined through comparative measurements. As reference, we used the solidification temperature of a conventional closed aluminium fixed-point cell (purity of 6N, 660.323 °C) inserted in a heat pipe furnace type Hart Scientific 9115, where the miniature fixed-point thermocouple was located during the repeated heating-up and cooling-down processes between 540 and 680 °C.

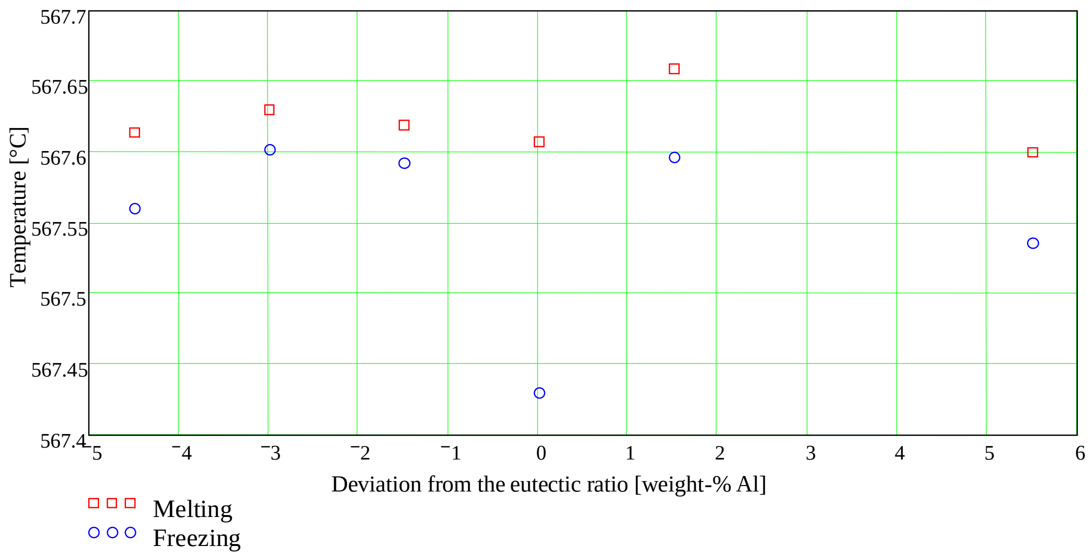

Figure 3: Approximated melting and solidification temperatures of AgAl alloys presenting different mixing ratios

In an unexpectedly large range of about ±5 weight-% around the eutectic mixing ratio, no significant differences in the solidus temperatures were observed, with the measuring and evaluation uncertainties being taken into consideration. The temperature values obtained for the various compositions of the alloys are lying in a range from ±35 mK around 567.62 °C, thus slightly below the temperature value published in [12] for the eutectic equilibrium of the AgAl system of 567.81 °C.

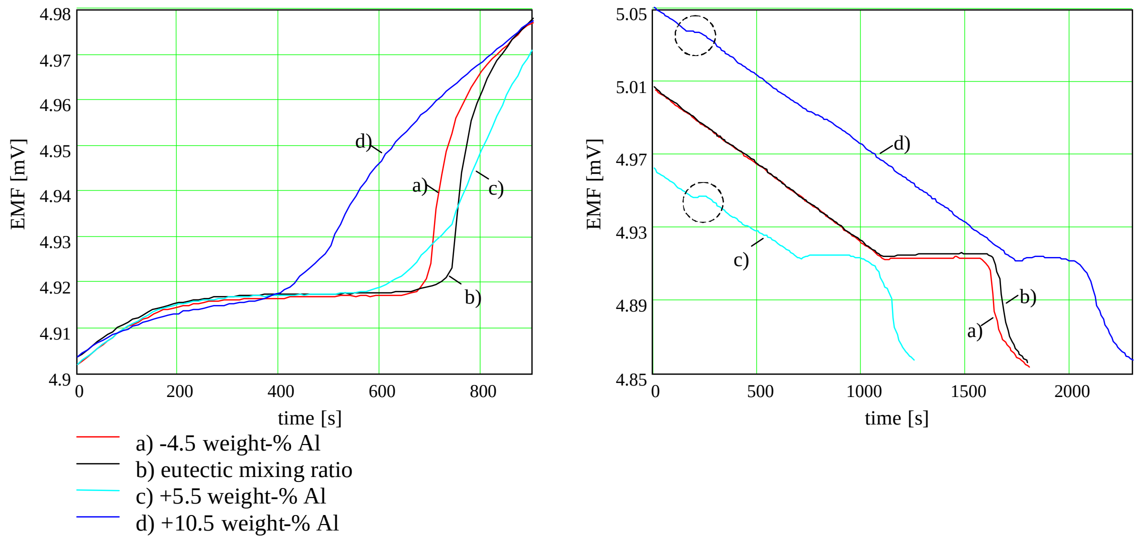

Figure 4: Phase transformation plateaus of AgAl alloys presenting different mixing ratios, related to the eutectic ratio, measured by means of a miniature fixed-point thermocouple (PtRh10/Pt)

Only in the case of larger deviations from the eutectic ratio, some significant shifts of the solidus temperatures were observed (e.g. 566.96 °C at +10.5 weight-% of Al). With increasing deviation of the composition of the alloy from the eutectic mixing ratio, changes in the shapes of the plateaus measured (Fig. 4) lead to ever shorter analysable phase transformation plateaus.

Similar statements can be made concerning the solidification plateaus measured. The solidus temperatures determined from these plateaus were always lower than those determined on the basis of the melt-down plateaus and presented a larger degree of scatter (Figure 3). Hence, they are only partially suitable for miniature fixed-point calibrations. In addition, their shape and also the possibility of evaluating them depend strongly on the diffusion and segregation processes which become evident, for example in the case of hypereutectic (rich-in-aluminium) alloys, through short recalescence points in the temperature curve measured of the liquidus temperatures (marked regions in Figure 4, right-hand side).

5. SUMMARY

A number of binary eutectic and monotectic alloys can be used as fixed-point materials in miniature fixed-point cells. Particularly their solidus temperatures measured during melt-down processes are sufficiently reproducible so that they could be used as fixed-point temperatures for the single-point self-calibration of industrial miniature fixed-point thermocouples around a certain process temperature. Furthermore, special alloys (e.g. Cu60Ge) presenting several reproducible phase transitions offer the possibility of performing two-point calibrations [14].

For the Ag70Al eutectic, it was shown that its solidus temperatures in a range from ±5 weight-% around the eutectic composition are reproducible within ±35 mK and, thus, largely independent of the mixing ratio. However, alloys presenting an almost eutectic composition should preferentially be used for fixed-point calibrations. The phase transformation plateaus realized with them permit to determine the fixed-point temperatures with the comparatively lowest uncertainty.

ACKNOWLEDGEMENTS

The authors' thanks are due to the Technical Association of Large Power Plant Operators (Vereinigung der Großkraftwerksbetreiber e.V., VGB), to the German Federation of Industrial Cooperative Research Associations (Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V., AiF) and to the German Federal Ministry of Economics and Technology (Bundesministerium für Wirtschaft und Technologie, BMWi) for giving financial support when carrying out the research projects (No. 0327066B/7 and No. 196/12132B/1).

REFERENCES

1. Lehmann, H. and Bernhard, F., *tm - Technisches Messen 64*, 1997, **3**, 91 - 99.
2. Lehmann, H., Boguhn, D., and Bernhard, F., In *Temperatur '98*, Berlin, VDI Verlag Duesseldorf, 1998, 77 - 84.
3. Boguhn, D., Lehmann, H., Bernhard, F., and Tegeler, E., In *Temperatur '98*, Berlin, VDI Verlag Duesseldorf, 1998, 25 - 34.
4. Tischler, M. and Korembit, M. J., In *Temperature, Its Measurement and Control in Science and Industry*, Vol. 5 (Edited by J. F. Schooley), New York, American Institute of Physics, 1982, 383 - 390.
5. Preston-Thomas, H., *Metrologia*, 1990, **27**, 3 - 10.
6. Bedford, R. E., Bonnier, G., Maas, H., and Pavese, F., *Metrologia*, 1996, **33**, 133 - 154.
7. Tischler, M. and Neubert, W., In *Temperature, Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 1992, 1055 - 1060.
8. Augustin, S., Bernhard, F., Boguhn, D., Donin, A., and Mammen, H., "Miniature Fixed-Point Thermocouples Applicable for Industrial Purposes", In *8th International Symposium on Temperature and Thermal Measurements in Industry and Science TEMPMEKO*, Berlin, 2001.
9. McAllan, J. V., In *Temperature, Its Measurement and Control in Science and Industry*, Vol. 4 (Edited by H. H. Plumb), New York, American Institute of Physics, 1972, 265 - 274.
10. McAllan, J. V., In *Temperature, Its Measurement and Control in Science and Industry*, Vol. 5 (Edited by J. F. Schooley), New York, American Institute of Physics, 1982, 371 - 376.
11. Ancsin, J., In *Temperature, Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 1992, 349 - 351.
12. Ancsin, J., In *5th International Symposium on Temperature and Thermal Measurement in Industry and Science TEMPMEKO '93 : Prague*, Prague, Tech-Market Praha, 1993, 46 - 54.
13. Mangum, B. W., Bloembergen, P., Chattle, M. V., Fellmuth, B., Marcarino, P., and Pokhodun, A. I., (Edited by Editor), Sèvres Cedex, France, Bureau International des Poids et Mesures (BIPM), Consultative Committee for Thermometry, 2000.
14. Boguhn, D., Augustin, S., Bernhard, F., and Mammen, H., "Phase transformations of technically pure metals and two-component alloys in miniature fixed-point crucibles", *High Temperature - High Pressure*, 2001, **33**, expected issue 4.
15. Schenectady, N. Y., *Constitution of binary alloys*, 2. ed., 3. print., Genium Publ. Corp., 1991, 1305 p.

Addresses of the Authors:

Dipl.-Ing. Silke Augustin, Technical University of Ilmenau, Institute of Process Measurement and Sensor Technology, P.O. Box 100565, D-98684 Ilmenau, Germany, E-mail: Silke.Augustin@MB.TU-Ilmenau.de, Internet: http://www.tu-ilmenau.de

Dipl.-Ing. Dirk Boguhn, Technical University of Ilmenau, Institute of Process Measurement and Sensor Technology, P.O. Box 100565, D-98684 Ilmenau, Germany, E-mail: Dirk.Boguhn@MB.TU-Ilmenau.de, Internet: http://www.tu-ilmenau.de