BEHAVIOR OF EUTECTIC MELTING CURVES

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Abstract. Melting curves of binary eutectic substances are compared with those of pure metals. If eutectic substances are melted by conventional methods then their melting curves are far less reproducible than those of metals are. However, if they can reach their equilibrium states during melting curve determination then their reproducibility can be much improved.

1. INTRODUCTION

Melting and freezing point of metals are conventionally realized by keeping the furnace temperature higher or lower than the melting point of the samples respectively. If the furnace cools a liquid sample then, at the freezing point the sample solidifies. During most of solidification, the sample temperature remains very stable. Similarly, if the furnace warms a solid sample once the temperature reaches the melting point then, during most of the melting, the temperature remains very stable. Both the melting and the freezing curves are highly reproducible. Their high reproducibility and stability are the main reasons for using freezing and melting points of pure metals as defining fixed-points of the temperature scale.

Figures 1, 2 and 3 show examples of the temperature stability of Tin, Zinc and the Aluminum points realized for calibrating thermometers, while keeping the furnaces a few degrees Celsius above the melting points of these substances. These temperatures are reproducible within 1/4 mK.

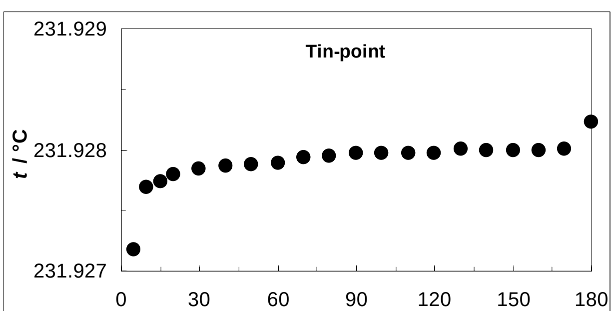

Figure 1

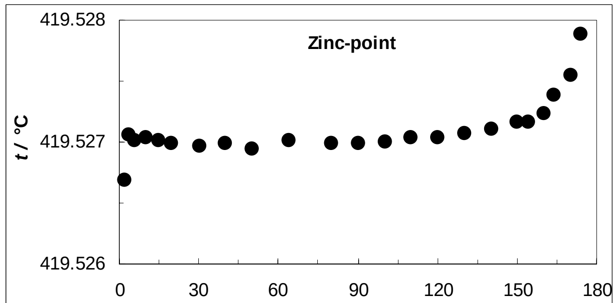

Figure 2

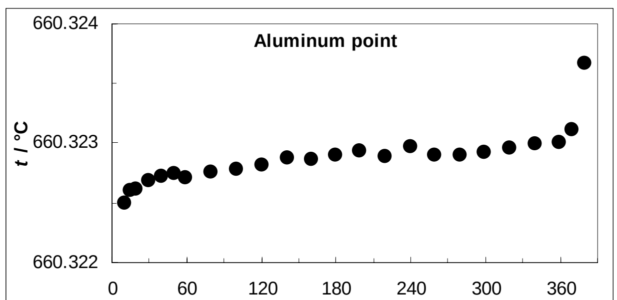

Figure 3

Figures 1, 2 and 3. Examples of stability of the Tin, Zinc and the Aluminum point temperatures realized for calibrating thermometers.

There are occasions when additional fixed-points are needed between the above temperatures. It turns out that eutectic alloys, a mixture of two metals, provide a great number of additional fixed-temperatures. However, if one melts or freezes eutectic substances the same way as if they were pure metals then both, the melting and the freezing curves are much less reproducible than those of pure metal samples. Figure 4 shows examples of melting curves of an eutectic substance (Al-Cu) obtained when it is melted, by keeping the furnace temperature above its melting point. As seen in this figure, the reproducibility of the melting temperatures spans several mili kelvins, which is much more than that of pure metals.

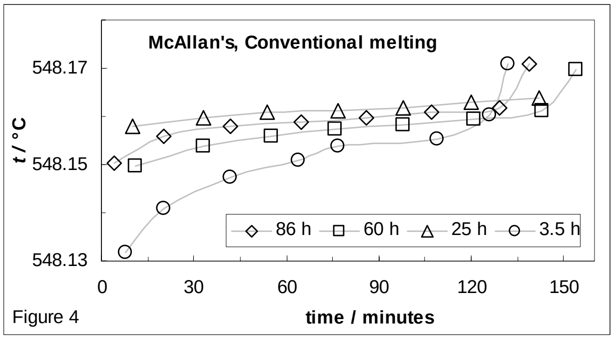

Figure 4. Reproducibility of Al-Cu eutectic melting curves obtained by keeping the furnace above the melting temperatures of the sample (from reference [1]. The temperatures were converted from IPTS-68 to ITS-90 values.)

2. EQUILIBRIUM STATES

The main reason for the poor reproducibility of the eutectic melting curves relative to those of pure metals is the way they reach their equilibrium states during melting.

For pure metals the time to reach a stable thermal equilibrium at any solid/liquid fraction depends only on its heat conductivity. The higher the heat conductivity the faster it can reach a uniform temperature throughout the entire sample. Of course, there will be some temperature gradients within a melting pure metal sample because the furnace constantly heats it. However, due to the high heat conductivity of metals and the relatively slow heating rates these temperature gradients will be negligibly small.

To reach equilibrium states in eutectics however, it is not only the temperature gradients that have to be minimized but also an equilibrium distribution must be reached between the two different metals that make up the eutectic.

In the liquid state, at equilibrium the Al and the Cu atoms have uniform distribution. Concentration gradients in general tend to gradually disappear if the density of the components is not too different. If there is substantial density difference as in the case of Al-Cu eutectic (the density of Al and of Cu is 2.7 g/cc and 8.9 g/cc respectively) then there will be some gravitational segregation. The light Al atoms will tend to rise toward the top and the heavy Cu atoms will tend to settle toward the bottom of a liquid sample. The two tendencies, to segregate and to achieve uniform distribution will come to a dynamic equilibrium. Of course if the liquid is stirred, then uniform distribution can be quickly achieved.

If a eutectic liquid of uniform component distribution is rapidly solidified then the solid phase will also have near uniform component distribution. However, in the eutectic solid phase, uniform component distribution on atomic scale does not correspond to equilibrium.

The diffusion of the Al and of the Cu components toward equilibrium states will take much longer than eliminating only the temperature gradients. Figure 5 shows how slowly a partially melted sample, insulated within the furnace, drifts toward its equilibrium state after a brief heating period.

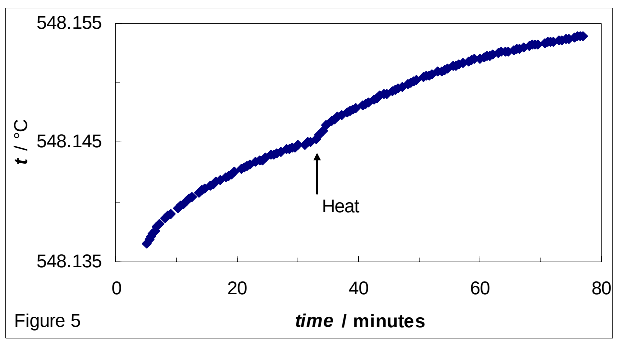

Figure 5. This figure shows the drifting of a partially melted sample towards its state of equilibrium.

As seen in Figure 5, after heating a partially melted sample for a short time its temperature drifts. The drift will continue until the Al and the Cu atoms reach their equilibrium locations.

If the eutectic is heated all the time during melting as in Figure 4, then the sample will never be able to reach its equilibrium state. Instead, it will be forced to melt through transient states. During each melting the sample is likely to be in a different transient state than it was during any other melting. Hence, repeated melting curves show considerable irreproducibility.

In order to improve the reproducibility of eutectic melting temperatures one should try to obtain eutectic equilibrium states in both the liquid and the solid phases. This can be achieved if the sample is kept insulated within the furnace in order to stop it from either gaining or from loosing heat. The sample could then gradually drift and eventually reach its state of thermal and of component equilibrium without being influenced by its surroundings.

After the sample reached its equilibrium state at a given solid / liquid fraction, its temperature will stop drifting. The temperature can be recorded and then it can be melted some more. Then, again, if left undisturbed, i.e. keeping it from gaining or from losing heat, it will be able to reach its new equilibrium state that corresponds to this solid / liquid fraction. In this way the sample can be melted in steps until the entire equilibrium melting curve is realized.

Figure 6 shows a set of equilibrium melting curves thus determined.

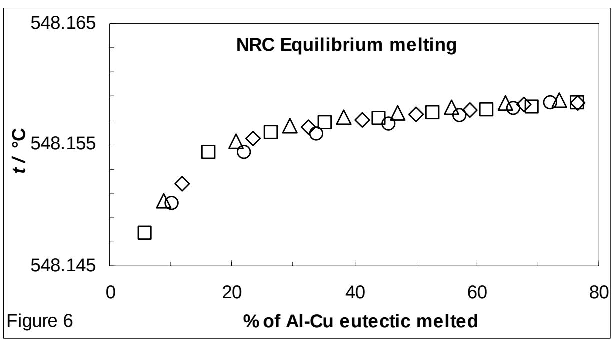

Figure 6. Equilibrium melting curves obtained by keeping the sample insulated within the furnace. The sample was melted using a separate sample heater. Different symbols along the melting curve indicate different experiments in order to show reproducibility of the equilibrium melting curves.

As seen in this figure the reproducibility is much improved compared to Figure 4. In fact such melting curve can be used as a fixed-point for accurate calibration of thermometers.

3. THE FURNACE

The eutectic melting curves of Figure 6 were realized in a homemade adiabatic furnace shown in figure 7. The outer dimensions of the furnace (a rectangular box of 67 cmx67 cmx90 cm high, filled with high density Fiberfrax insulation) are large enough that it can be used without water cooling.

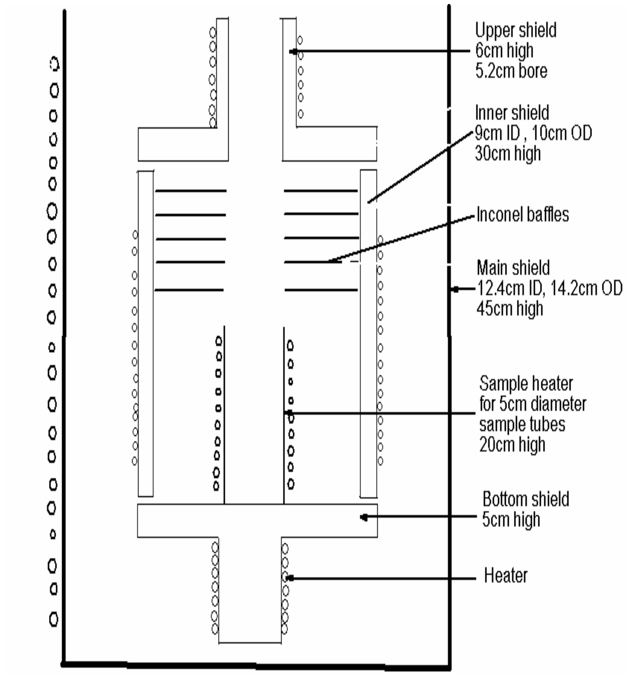

Figure 7. High temperature adiabatic calorimeter used for obtaining equilibrium melting data.

The main shield is insulated from all the other shields. Within the inner shield the sample heater (wound on a, thin, 20 cm high and 5.4 cm I.D. ceramic tube) is insulated from the inner shield but the space between the upper shield and the top of this heater is un-insulated. This space is filled with a set of horizontal baffles to provide a thermal window for preheating the thermometer near the sample. There are a number of "S" thermocouples sensing the temperature of the various components.

It has no temperature control. Instead, high stability DC power supplies are used. Tuning the furnace is a rather lengthy process due to the high heat capacity and low heat conductivity of the shields (made of Inconel) but if it is done well then quite uniform temperature profile can be obtained along the samples. Because the furnace is well insulated its temperature remains stable within about 0.1ºC for several hours. The slow drift is well behaved (monotonic, rather than fluctuating), thus, it can be adjusted if necessary. The inner shield heater is used only when relatively rapid and substantial furnace temperature changes are required as for instance during heat capacity measurements.

The sample housing has already been described in details in [2]. The sample itself is in the form of a cylindrical shell, surrounding the thermometer well, of 1.9 cm O.D., has 0.33 cm wall thickness and is about 15 cm high.

4. CONCLUSION

If eutectic samples can reach their equilibrium states during solid-liquid phase transformation then their melting curves become sufficiently repeatable for using them as high quality fixed-points.

REFERENCES

[1] McAllan J.V., *Temperature: Its Measurement and Control in Science and Industry*, Volume Four: proceedings of the Fourth International Temperature Symposium (1972, Washington, D.C) pages 265-274.

[2] Ancsin J, Metrologia, 2001, **38,** pages 1-7