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THE THERMAL ANALYSIS OF Sn-RICH Cd–Sn ALLOYS

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ABSTRACT

Thermal analysis represents a most effective technique for determining the constitution of alloys. However, when using the conventional analytical procedure of slow-cooling the alloy from above the liquidus, non-equilibrium structures can be generated via coring reactions. The structures may persist through subsequent heat-treatments with the result that spurious thermal effects may be observed not only during the initial cooling run but also in subsequent heating and cooling runs. This study of Cd–Sn alloys shows that the spurious effects can largely be avoided by the use of a technique in which the DTA specimen is initially quenched from above its liquidus. After a relatively short homogenising treatment, the sub-solidus phase changes are first defined before reactions involving the liquid phase are investigated. This technique should considerably simplify the study of the very many other systems which would be expected to be vulnerable in this way. The solidus temperatures measured with this improved technique were confirmed using tensile tests.

INTRODUCTION

Despite its long history, differential thermal analysis (DTA) still remains a most effective and economical technique for determining the constitution of alloys. It is therefore tempting to use it as the main method for investigating phase equilibria. In most cases, the results obtained are unambiguous. However, experimental data may be produced with some alloy systems which, although consistent and reproducible, nevertheless are incorrect with perhaps little internal evidence to suggest that this is the case. Under certain circumstances, therefore, DTA can produce results that are misleading and this obviously reduces the confidence with which the technique can be used.

An example of a system of this type is Cd–Sn. The constitution of Sn-rich alloys as critically reviewed by Hansen and Anderko [1] is illustrated by Fig. 1. This shows that the β-phase is generated by a peritectic reaction at 223°C and decomposes in a eutectoid reaction at approximately 130°C. Superimposed on this diagram are the original thermal analysis results of

Hanson and Pell-Walpole [2] on which the phase diagram was mainly based. A feature is the spurious thermal effects at 158–167°C and at approximately 176°C which persist into the single-phase β and the $\beta + \alpha$-Sn regions of the diagram. These are attributable to inhomogeneity generated within the alloys when they are cooled slowly.

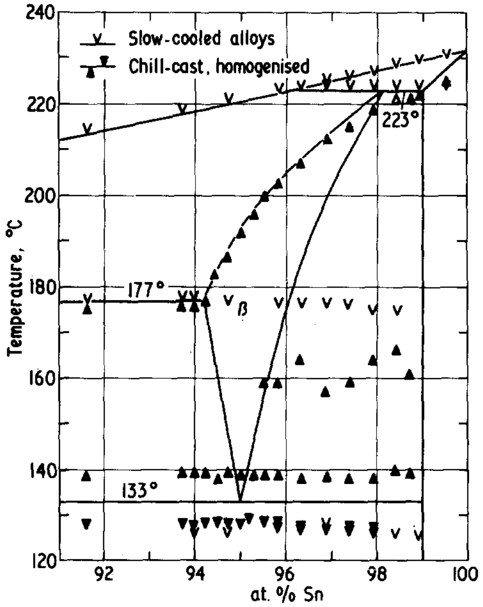

Fig. 1. Part of the Cd–Sn system. The phase boundaries are due to Hansen and Anderko [1]; the thermal analysis results are those of Hanson and Pell-Walpole [2].

In the case of binary alloys, it is often possible to deduce the correct form of the phase diagram despite spurious effects of this type. Nevertheless, even in this case it must be recognised that the inhomogeneity responsible for these effects implies that the constitution of other parts of the alloy sample also is atypical: the thermal effects associated with the latter must therefore also be suspect.

For ternary and higher order alloys, the equilibria are almost always more complicated and the elucidation of its correct form when confused by spurious results can become most difficult and time-consuming. With these alloys, it becomes all the more worthwhile to avoid generating the spurious data in the first place. The conventional approach is to use prolonged heat-treatments to homogenise the alloys. However, these treatments in themselves may represent considerable effort and delay, and usually pre-suppose some knowledge of the constitution of the alloys in order that suitable homogenising conditions can be specified.

The ideal technique would, of course, be one in which spurious results simply would not be generated. However, should this not be possible, it would be most desirable to be able to at least readily identify and eliminate the spurious results and for this to be done within the time-scale of a single examination of the specimen and using essentially standard DTA techniques. Experiments to examine this possibility, using Cd–Sn as a simple model system, are described below.

EXPERIMENTAL PROCEDURE

Cd–Sn alloys containing 92–100 at.% Sn were prepared using Johnson Matthey Grade 1 pure metals having total metallic impurities of less than 15 p.p.m. The alloys were melted in silica crucibles under a hydrogen atmosphere. The constituents were weighed out to specific compositions to within 0.01–0.1%: as the weight changes on melting were also within these limits, the nominal compositions have been used to describe the alloys.

Alloys for thermal analysis weighed approximately 5 g and were contained in silica crucibles of 9 mm internal diameter and having a wall thickness of 0.8 mm. A conventional DTA apparatus capable of detecting temperature differences of 0.005°C was used for this work. Temperatures were measured using Chromel–Alumel thermocouples which had been calibrated against the melting points of pure In and Sn. The overall accuracy of temperature measurement is considered to be generally within ±1°C. When using the conventional DTA procedure, the alloy was heated to approximately 25°C above its liquidus and analysed during slow-cooling at 1°C min^{-1}. Supercooling was minimised by stirring the alloy until nucleation of the solid phase had occurred. In some cases, alloys were homogenised in situ at intermediate temperatures for periods up to 100 h before further analysis.

In an alternative analysis technique, the alloy was heated to 25°C above the liquidus and thoroughly stirred to ensure its homogeneity. With the silica thermocouple sheath held in position in the liquid, the alloy was then quenched by immersing the crucible in water. The high resistance of silica to thermal shock enabled this to be done without risk. The cooling rate in each quench was estimated using a thermocouple set in the alloy and was typically 250°C min^{-1} in the solidus/liquidus gap, increasing to 700°C min^{-1} when the alloy had solidified.

The normal procedure used in examining quenched alloys was to hold the alloy at a temperature approximately 10°C below or above a phase change, usually the one at the lowest temperature of interest, and then to repeat heating and cooling runs as necessary to define the phase change as regards both temperature and size of the thermal effect. The holding time usually was 0.5–1 h, although up to 100 h in some cases. Other phase changes at higher temperature were then investigated in turn.

To provide a basis for comparison, the solidus of the alloys was measured using a tensile testing technique. The alloys used weighed 10–15 g and were prepared in a similar manner to that described above. After thorough stirring of the melt, the silica crucible containing the alloy was tilted to produce an ingot 40–50 mm long which was then rapidly cooled by pouring water over the crucible. The alloys were cold-worked and homogenised for at least one week at 20°C below the estimated solidus and finally were cold-rolled and drawn to wire 2 mm in diameter. Tensile specimens of 20 mm gauge length were stressed using weights of up to 2 kg and were heated at 1 °C min^{-1} until failure.

Samples of alloys for metallographic examination were prepared by first quenching the alloys as for DTA specimens. The specimens were sectioned longitudinally and one half was treated for 24–100 h at temperatures within the β-region. The second half was remelted and cooled at 1°C min^{-1} to room temperature. The alloys were polished using standard techniques except that the final stage used alumina with a 1% solution of HNO_3 in ethanol as an etch/polish.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental work was divided broadly into the study of slow-cooled alloys and of quenched alloys. It is convenient to consider these separately.

Slow-cooled alloys

The main features of the earlier work shown in Fig. 1 are the persistence in alloys containing more than 95 at.% Sn of what appears to be the eutectic reaction at approximately 176°C, and of other arrests at 158–167°C, when the alloys would be expected from other evidence to consist solely of the β-phase or of the $\beta + \alpha$-Sn phases. Similar arrests were observed in the present work, examples of which are shown in Fig. 2. The DTA curve obtained on slow-cooling a Cd–95.5 at.% Sn alloy shown in Fig. 2(a) indicates a strong spurious arrest at 177°C, which unfortunately is also detected as a strong reaction in the subsequent heating curve, as is shown in Fig. 2(b). The curves also show the different reaction temperatures obtained on heating and cooling characteristic of a eutectoid reaction.

The generation of the spurious thermal effects in slow-cooled alloys can be explained in terms of a coring reaction associated with the precipitation of the β-phase: the β-phase is unable to change in composition at a rate

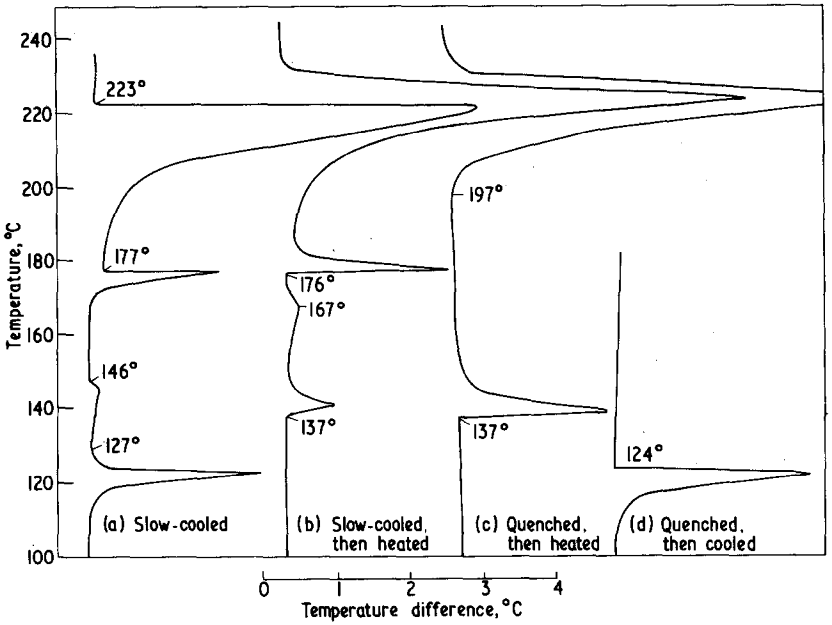

Fig. 2. DTA curves for the Cd–95.5 at.% Sn alloy in the slow-cooled and quenched conditions.

sufficient to maintain near-equilibrium conditions within the time-scale of the tens of minutes set by the normal DTA procedure. One of the consequences is that liquid is present in alloys above 177°C which otherwise would be entirely solid. The melting and freezing of this liquid on subsequent heating and cooling is consistent with the spurious thermal effects observed at that temperature.

Having generated what is known in this system to be a non-equilibrium structure, the question arises of whether it can be eliminated using procedures which are compatible with the DTA technique. To study one approach, alloys were cycled through the spurious 177°C phase change in a number of consecutive heating and cooling runs. The results for the Cd–95.5 at.% Sn alloy given in Fig. 3, are typical of slow-cooled alloys: the size of the arrests decreased with each cycle indicating a slow but progressive approach to equilibrium. Similar data on the size of the 177°C arrest in other alloys that previously had been slow-cooled is summarised in the Tamman-type plot shown in Fig. 4. This relates the heat change associated with a reaction (as approximately indicated by peak height) with composition and therefore provides the basis for determining by interpolation the range over which a reaction occurs.

In further experiments, alloys which had previously been slow-cooled were held in the DTA apparatus at temperatures either 20°C above or below 177°C for periods up to 100 h. After even these treatments, strong spurious arrests were still obtained. These latter observations are consistent with the

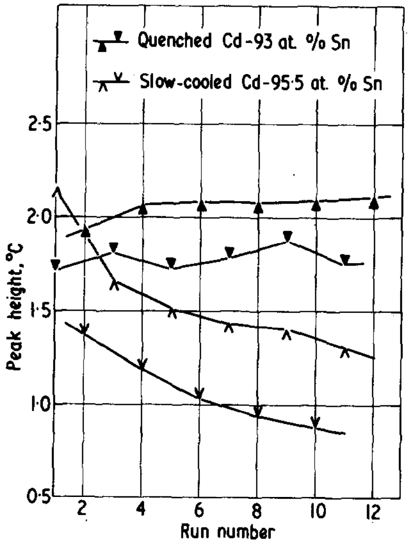

Fig. 3. Peak height of the 177°C reaction for a quenched Cd–93 at.% Sn alloy and a slow-cooled alloy Cd–95.5 at.% Sn as affected by thermal cycling.

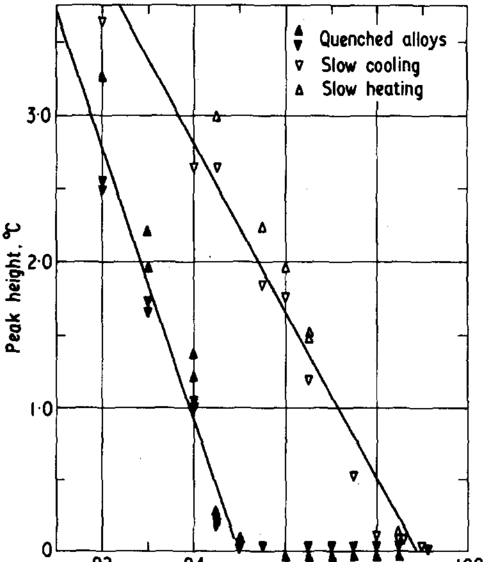

Fig. 4. Peak height for the 177°C reaction in slow-cooled and quenched alloys containing 92–99 at.% Sn.

extended homogenisation times suggested by Hanson and Pell-Walpole [2], especially for alloys which had not been chill-cast. It was concluded from these experiments that neither cycling the alloys through the spurious arrest nor prolonged heat-treatment represented a practical method for obtaining results corresponding to near-equilibrium conditions within the time-scale of routine DTA.

It is obviously a better approach to prevent the formation of the non-equilibrium structures in the first place. One method for achieving this would require alloys to be cooled at a rate such that adequate time is available for the solid phase to change its composition to maintain equilibrium conditions. However, the above experimental results suggest that this rate would have to be very much slower than the 1°C min^{-1} already in use, which is therefore hardly a practical possibility. On this basis, attempting to obtain DTA results which correspond to near-equilibrium conditions using the conventional slow-cooling DTA technique would seem to be a basically unsound approach with systems of the type under discussion.

Quenched alloys

An alternative method for avoiding the gross inhomogeneity associated with slow-cooling through the liquid/solid reactions is simply to quench the alloy from above the liquidus. It was envisaged that the rapidly cooled alloys would be free from large-scale segregation and therefore more readily converted into a near-equilibrium structure by a minimal heat-treatment. Sub-solidus phase changes could first be investigated before moving on to the problems associated with liquid/solid reactions.

Experiments to check this approach were done on alloys which had been quenched using the technique described above. Examples of heating and cooling curves obtained are shown in Figs. 2(c) and 2(d), which indicate the elimination of the 177° arrest and other spurious effects present in the corresponding slow-cooled alloy as shown in Figs. 2(a) and 2(b). In some alloys containing more than 95 at.% Sn, small spurious arrests were still observed at 177°C despite quenching. However, their transient nature was emphasized by their disappearance from the following cycle through the phase change. After allowing for these, the thermal effects obtained represented accurately the established form of the constitution of the Cd–Sn system with no spurious results. The reaction temperatures measured agreed well with those obtained on slow-cooling for the liquidus, peritectic, eutectic and eutectoid temperatures: these temperatures, of course, would not be affected by coring reactions. It was concluded that the examination of quenched alloys need not be any the less comprehensive than that on slow-cooled alloys.

Normally, quenched alloys were analysed after holding at intermediate temperatures only for the time required for the specimen and the DTA furnace to come into thermal equilibrium, and this was typically 0.5 h. However, whenever possible, the opportunity was taken to homogenise the alloys for longer periods, for example overnight or over weekends, to better establish the equilibrium structure. In practice, the thermal arrests observed in the two cases rarely differed. These observations emphasize that, when only short-range segregation is present, then the alloys homogenise rapidly. Similar conclusions were drawn by Homer and Plummer [5] who showed that a heat-treatment for 15 min at 170°C proved as effective as one for 14 days in improving the fracture strength of chill-cast Cd–Sn alloys. It is to be noted that the temperature of the lowest reaction of interest in the present work, namely 130°C, exceeds 0.8 of the absolute melting point of the alloys under examination and this factor, coupled with the small scale of the structure in quenched alloys, would be expected to result in the rapid homogenisation observed.

The difference between quenched and slow-cooled alloys can be demonstrated in other ways. Figure 4 compares the 177°C peak height as measured in initial heating and cooling runs in a Tamman-type plot with the corresponding arrest in slow-cooled alloys already referred to. The plot shows the disappearance of the eutectic reaction in quenched alloys at approximately 95 at.% Sn, which corresponds to the established minimum value at which the β-phase is stable under equilibrium conditions. By contrast, the same reaction in slow-cooled alloys persists to Sn contents up to 99 at.% Sn. This is the maximum composition at which the β-phase is stable, and is additional evidence that little homogenisation takes place on slow-cooling during thermal analysis. This picture was confirmed by metallographic examination of β-phase alloys: quenched alloys homogenised for 24–100 h consisted of a single phase, whereas slow-cooled alloys contained significant proportions of non-equilibrium eutectic.

A further advantage of analysing quenched alloys was the relative ease with which the β-phase solidus was detected on heating as compared with alloys which had previously been slow-cooled. Typical curves are compared in Figs. 2(b) and 2(c). In the case of slow-cooled alloys, the coring reaction results in the β-phase having a wide range of composition. The "solidus" of this graded structure therefore extends over a wide temperature range producing ill-defined thermal effects. By contrast, the β-phase in quenched alloys is essentially homogeneous, and the solid/liquid reaction therefore begins at a specific temperature. This leads to the relatively sharply defined thermal effect at 197°C shown in Fig. (2c). The solidus values obtained with quenched alloys were confirmed by tensile tests, examples of the results for which are given in Fig. 5. In these, the solidus value is given by the point of inflexion of each curve. The values obtained by the two methods agree within the experimental error of 1–2°C.

It is to be noted that coring may occur in any of the very many systems in

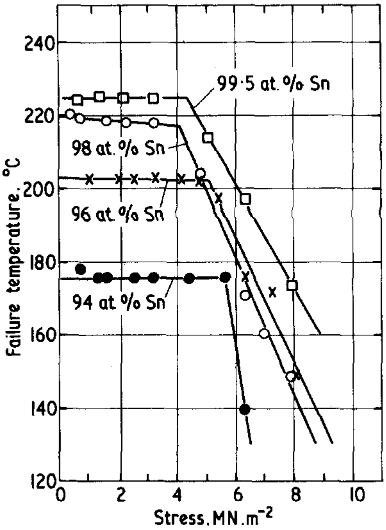

Fig. 5. The tensile strength of Cd–Sn alloys as a function of temperature.

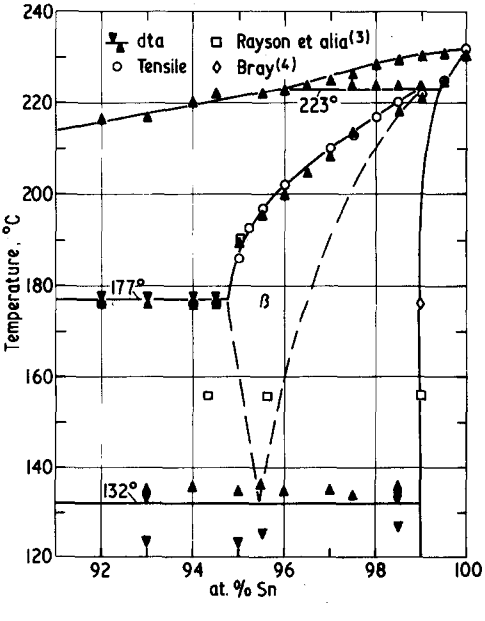

Fig. 6. The Cd–Sn system: present work using quenched alloys.

which the solidus changes progressively with composition. The liquidus is, of course, unaffected by coring and the slow-cooling technique can be used to detect this reaction. Since the examination of quenched alloys clearly has advantages where this type of system is involved, and no obvious fundamental disadvantages, there would seem to be good reasons for adopting this procedure as a matter of routine. If the alloys are also examined during slow-cooling, then the combination should produce results corresponding to near-equilibrium conditions, and also an indication of those reactions which generate non-equilibrium structures.

The data obtained using quenched alloys are summarised in Fig. 6, and in many cases are the mean of several determinations. For clarity, liquidus data obtained on slow-cooling has been omitted. Figure 6 also includes some results due to Rayson et al. [3] and Bray [4]. Although an important objective in the present work was the study of the DTA technique itself, significant constitutional data were obtained. In general, there was excellent agreement with the liquidus, peritectic and eutectic temperatures previously summarised by Hansen and Anderko [1]. However, the present results displace the range of stability of the β-phase to Sn levels higher by approximately 0.5 at.%, with the solubility of Cd in Sn somewhat lower at 0.6 at.% compared with 1 at.%. The present solidus results are almost identical to those obtained by Homer and Plummer [5] who employed a high temperature bend test. It is concluded that the constitution of this part of the system must be regarded as well established.

CONCLUSIONS

The conventional DTA procedure of slow-cooling alloys from above the liquidus can generate persistent non-equilibrium structures in Cd–Sn alloys. These can produce spurious results during subsequent differential thermal analysis (DTA).

Once the cored structure is formed, neither prolonged homogenisation nor cycling through the 177°C spurious phase change will eliminate it within a time-scale even very much greater than that normally available for routine DTA.

However, the coring reaction and the associated spurious thermal effects can be eliminated, or at least very considerably reduced, by first quenching the DTA specimens from above the liquidus. For the Cd–Sn alloys investigated, a cooling rate of a few hundred degrees per minute was adequate. Each of the solid-state reactions could then be defined in heating and cooling runs before the more complicated solid–liquid reactions were investigated.

In general, the minimum homogenising time required to establish the equilibrium structure after quenching, as indicated by the size of the thermal arrests, was in the region of an hour, and therefore could conveniently be incorporated in the routine DTA examination itself rather than as a separate heat-treatment.

The effectiveness of studying alloys when in the quenched condition, and the apparent lack of disadvantages of this technique, suggests its wider use as a routine procedure, especially for the very many other systems in which there is a risk of the coring effects such as observed in Cd–Sn alloys.

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