Solidification Behaviour of Rapidly Quenched Cu–Sn Alloys

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A series of solidification experiments using DTA furnace were performed on different Cu–Sn alloys. The undercooling, cooling rates of the liquid and the solid states, solidification times and temperatures were evaluated from the curves. The cooling curves for different samples and alloys were simulated using a FEM solidification program. The heat transfer coefficient and the heat of fusion were evaluated. The calculated fraction of solid formed before quenching has been compared with the experimental result. It was found that the calculated values of the heat of fusion were much lower than the tabulated ones. The fraction of solid was also found to be much higher than those calculated theoretically. It is proposed that a large number of vacancies form during rapid solidification and that they condense during and after the solidification. The influence of these defects on the thermodynamics and solidification of the alloys has been evaluated.

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1. Introduction

In a casting process, the mechanical and other physical properties depend upon the microstructure. The microstructure is formed during solidification and the heat extraction rate during cooling processes determines the scale of the microstructure.

There are several methods for studying phase transformations during a solidification process. Quenching during unidirectional solidification is often very useful since it gives good information about the complete transformation process. However, a major drawback is that the experiments have to be compared with previously not quenched solidified cast materials. Another possibility is to make use of differential thermal analysis, DTA, in which one measures the temperature difference between a sample and a reference in a furnace, which usually has a constant cooling rate. In this kind of experiment, it is important that the sample reaches a thermodynamic equilibrium before starting the cooling process.

The probability of formation of lattice defects such as vacancies during a cooling process were studied earlier. It has been observed that the structure and properties of rapidly solidified alloys are influenced by the cooling rate during solidification. A supersaturation of vacancies can also be formed in a metal by quenching, mechanical deformation or by energetic particle irradiation. The energies for the formation of vacancies have been studied before. These vacancies can migrate and coalesce to form microscopic clusters at temperatures where the vacancies are mobile, generally T > 0.3T_m, where T_m is the melting temperature. It has earlier been proposed that during a solidification process a large number of lattice defects such as vacancies are formed and then condensed. The thermodynamic properties of metals are changed by the lattice defects. The concentration of vacancies in the solid depends on the cooling conditions. When the alloy is rapidly quenched from a high temperature, there will be insufficient time for the new equilibrium concentration to be established and the high concentration of vacancies will be trapped. The increase in the concentration of vacancies will have an influence on the solidification process. The results have also been discussed in connection with formation of lattice defects.

On the other hand, lots of research groups and industries all over the world have already found the simulation of solidification process interesting and profitable to work on. The casting process is very complex and there is a need of making numerical solidification modelling of the process based on experimental results.

This paper is intended to study the formation of lattice defects during a solidification process, and also to analyse the effect of lattice defects (vacancies) on the thermodynamic parameters as well as on the solidification behaviour. The study is concentrated to Cu–Sn alloys with a Sn content up to 12% Sn.

2. Experimental Procedure

A series of quenching experiments with two different cooling rates were performed for pure copper and copper-tin alloys containing 2, 4, 6 and 11%Sn. All the alloys were made by melting pure elements in a vacuum induction or an arc-melting furnaces under argon atmosphere. The purity of the elements was more than 99.95 wt. The experiments were based on quenching of a four g sample (placed in an alumina crucible) inside a heat resistance DTA furnace which was constructed in a way that quenching could be done from a determined temperature. The temperature of the samples was recorded by a "S" type thermocouple positioned in the centre of the sample. The furnace temperature and the cooling rate were measured and controlled by another thermocouple placed at the walls of the furnace. The process is described in details elsewhere. The sample was heated up to 60°C above the melting point and kept constant at that temperature for some minutes, to achieve thermal equilibrium. The furnace was then cooled at a rate of 0.018 or 0.17 K s^{-1}. The solidification process was interrupted by quenching the sample in water in order to analyse the fraction of solids formed at the moment of quenching the samples. The experiments were performed under an argon
atmosphere and all measurements were calibrated with a pure copper sample. The temperature data were recorded and plotted as a function of time by using a data acquisition system connected to a computer, which gives a cooling curve as a result. Typical cooling curves obtained from DTA experiments are plotted in Fig. 1. Samples were metallographically prepared using conventional methods. The metallographic analyses of the area close to the tip of the thermocouples were performed by optical microscopy.

3. Thermal Analysis for Estimation of Thermodynamic Properties

The heat entering the crucible comes from the heat of fusion during the solidification process as well as from the heat capacity during cooling of the sample. Thus,

$$\left( \frac{dQ}{dt} \right)_{\text{sample}} = \rho \cdot V \cdot C_p \cdot \frac{dT}{dt} + \rho \cdot V \cdot (-\Delta H) \cdot \frac{df_s}{dt}. \quad (1)$$

Here $\rho$ is material density, $C_p$ is specific heat, $V$ is volume, $T$ is temperature, $dT/dt$ is the cooling rate of the sample and $\Delta H$ is the latent heat released during solidification when the fraction of the solid phase, $f_s$, increases from 0 to 1.

The first term on the right hand side of eq. (1) describes the heat released from the sample due to the heat capacity when changing the temperature. The second term describes the rate of heat generating due to latent heat of fusion during a solidification reaction.

In this study, the heat transport in the crucible and the sample during the solidification process is calculated by solving Fourier’s heat equation. The principal features are outlined below.

$$\rho \cdot C_p \cdot \frac{dT}{dt} = \text{div}(k \text{ grad } T) + \dot{q}, \quad (2)$$

where $k$ denotes heat conductivity. The source term, $\dot{q}$, is described as:

$$\dot{q} = \begin{cases} 0 & \text{when } T > T_L \\ \rho \cdot \Delta H \cdot \frac{df_s}{dt} & \text{when } T_S < T < T_L \\ 0 & \text{when } T < T_S \end{cases} \quad (3)$$

The model is supplemented by suitable boundary conditions, expressing heat flow by radiation and heat exchange. Heat extraction from the sample to the surroundings can be obtained from the following relation:
\[ \frac{dQ}{dt} = -K \left( \frac{\partial T}{\partial n} \right) = h(T_S - T_0) + \sigma \varepsilon (T_S^4 - T_0^4) \quad (4) \]

where \( \partial T/\partial n \) is the outward normal derivative, \( \sigma \) is the Boltzmann constant, \( \varepsilon \) is the emissivity of the radiating surface, \( T_0 \) is the ambient temperature, \( h \) is heat transfer coefficient and \( T_S \) is the temperature of the sample.

It was assumed that a constant heat transfer coefficient exists at the interface of sample/crucible. However, the heat conductivity in the metal is very high compared to the heat transport to the crucible and compared to the heat conductivity in the crucible. This results in a very small temperature gradient in the sample. (i.e., the Nusselt’s number for the sample is much less than one). \( dQ/dt \) for the sample is thus described by eq. (1) which gives the indata for the heat transport to the crucible. Equation (2) is solved together with eq. (4) for the heat transport through the crucible. The ambient temperature is, in this case, the furnace temperature.

Moreover,

\[ T(x, y, 0) = T_{\text{max}} \quad \text{at} \quad t = 0, \]

where \( T_{\text{max}} \) is the initial temperature at the starting point of the solidification process.

It is in general impossible to find an analytical solution to this problem. Solutions must be obtained by numerical methods.

### 3.1 Numerical treatment

The partial differential eqs. (2)–(4) of heat transport with phase change in two dimensions can be combined and solved with a finite element method. The FEM base program, CASTFEM,\(^{29}\) which has been modified to describe the case studied here, was used to evaluate heat transfer from the sample to its surroundings. The pre and post-processor for the program, FEMGV4\(^{23}\) was used to generate the mesh. Equation (2) is discretized by conventional finite elements, three nodes triangles in two-dimensional models of the material in the sample and in the mould for the DTA furnace experiments. A mesh consisting of four-noded quadratic elements, was used to define the gap between the sample and crucible.

Due to the symmetry of the samples for the DTA experiments, only one quarter of the specimens needed to be modelled. Suitable time steps and element sizes were determined by a series of preliminary computations. Typical FEM model used for the numerical analyses, for the DTA furnace equipment, is shown in Fig. 2. Appropriate relationships, which describe the initial temperature conditions of the different materials, in the sample and in the crucible have been considered. The boundary conditions including the heat transfer coefficient, \( h \), as a constant value during the solidification process, the emissivity factor, \( \varepsilon \), and the boundary temperature were added. Material data for the sample and crucible included heat conductivity, \( k \), the specific heat for both solid and liquid zones, the latent heat of fusion, the liquidus and the solidus temperatures were also considered. The thermophysical data of the crucible and the metal were obtained from the literature,\(^{22-26}\) and carefully adapted to the experimental conditions for each case. In order to find the proper range of values for different operating condition such as emissivity of the radiating surface and heat transfer coefficient, a series of numerical computations with different \( \varepsilon \) and \( h \) was carried out. It was found that the contribution of variation of \( \varepsilon \) is negligible. The heat transfer coefficient was determined by fitting the data prior the solidification.

### 4. Results

Typical cooling curves of the samples in the temperature ranges of the solidification for pure copper and Cu–4%Sn and two different cooling rates of 0.018 and 0.17 K s\(^{-1}\), were earlier shown in Fig. 1. The furnace cooling curves are also shown in Fig. 1.

The cooling curve often contained a plateau temperature. Some experiments did not show any plateau temperature, but instead contained a fairly small undercooling followed by a recrystallization. The plateau temperature or the maximum recrystallization was chosen as the solidification temperature.

The cooling rate in the liquid region was measured on the undisturbed part of the cooling curve just before the start of the solidification process. Start and end of solidification were chosen as the point where the slope of the temperature-time curve of the sample was changed.

The solidification range and the actual solidification time in each experiment were preliminary determined by an experiment without any interruption. The cooling rates in the liquid and in the solid state, the solidification temperature, the solidification time and the undercooling temperature were evaluated from the curves. However, it was often difficult to determine the time for the end of the solidification. In order to study the development of the microstructure during the solidification process, samples were quenched at certain times after the start of the solidification process. After metallographical preparation, all samples were studied under the microscope for measuring the fraction of solid.

### 4.1 Simulation of solidification

The calculations were performed in the following way. The latent heat for the total solidification process was first evaluated by simulating the total solidification process. Then this value was used to evaluate the fraction of solid in the quenched sample by simulating the cooling curves. Figure 3 shows typical simulated cooling curves for DTA experiments.
at the centre of the sample, where the thermocouple is normally inserted. The measured cooling curves from the experiments are also shown in Fig. 3 for each case. The typical calculated fraction of solids of the samples are shown in Fig. 4. The figure shows the fraction formed at different stages of solidification process for Cu–4%Sn. Two different cooling rates 0.018 and 0.17 K s$^{-1}$ are presented.

### 4.2 Fraction of solids

The microstructure of the samples formed during the solidification process consisted of dendrites. The total fraction of solid, formed before quenching, was determined by using a linear intercept analysis of a series of photographs for each sample. Ten random lines were drawn on each photomicrograph to determine the total fraction of solid. The local fraction of solid was also determined by including the dendrite crystals in a circle and performing point analysis. The results are plotted in Fig. 5. Here $t_{\text{quen}}$ and $t_{\text{solid}}$ denotes quenching and un-interrupted solidification times, respectively. Typical photographs from different stages of the solidification transformation for Cu–4%Sn are also shown in Fig. 5 at a magnification of 100 times. Two different cooling rates 0.018 and 0.17 K s$^{-1}$ are presented. The solidification temperature, $T_{\text{liq}}$, was 1065°C. The time from when the sample reached $T_{\text{liq}}$ until it was quenched was about 80 s and 202 s for the cooling rate of 0.17 K s$^{-1}$ and about 140 s and 343 s for the cooling rate of 0.018 K s$^{-1}$ respectively. The total solidification time for each alloy was determined from an experiment which was not interrupted by quenching. The structure consisted of primary solidified dendrites in a quenched matrix.

The fraction of primary solid in the matrix increases when increasing the quenching time. As expected, the solid fractions reach a maximum of 100% for each composition at the end of solidification. Consequently, in modelling the solidification, this variation of the fraction of solid should be taken into account.

Comparing the theoretical and measured results, presented here, shows that the measured solid fractions are much higher than the calculated ones. In order to illustrate this, the ratio of measured and calculated amount of fraction of solids, $\frac{f_s}{\text{meas.}} / f_s^{\text{calc.}}$, is plotted as a function of quenching time for different cooling rates and different alloys in Fig. 6. The figures show that the experimental values of $f_s$ are always higher than the calculated ones. The ratio is decreased when increasing the quenching time. The results show that the fraction of solid formed during the solidification coincides with the fraction of solid predicted theoretically for long solidification times. Therefore, it can be concluded that the solidified parts
of a sample, especially in the earlier stages of the solidification process are much higher than could be expected from the theoretical approach. The results will be discussed in next section, in connection with the formation of lattice defects.

4.3 Heat of fusion

Figure 7 shows the calculated fraction of latent heat from the measured cooling curves, divided by the tabulated equilibrium value \( \Delta H_{\text{calc}} / \Delta H_{\text{lab}} \), versus quenching time, \( t_{\text{quen}} / t_{\text{solid}} \) for the different alloys. The results show that the calculated values for heat of fusion are much lower than the tabulated ones. The figure also shows that an increase in quenching time will increase the value for \( \Delta H_{\text{calc}} \). It has been earlier\(^{18}\) been proposed that lattice faults, such as vacancies, formed during the solidification will change the thermodynamic properties and the phase diagram. Note that the cooling rate is very slow and therefore the latent heat of fusion is expected to be close to the tabulated ones. The figure, however, shows that the heat released from the sample during the solidification, especially at the beginning of the process, is much lower than the tabulated heat of fusion. This will be discussed in the next section.

Figure 8(a) shows the solidification undercooling, versus cooling rate in liquid obtained from DTA experiments together with the results presented earlier\(^{17,18}\) from mirror furnace equipment and levitation technique for higher cooling rates. The cooling rate was varied between 0.018 K s\(^{-1}\) in the DTA experiments, to a maximum of 110,000 K s\(^{-1}\), in the levitation experiments. It can be seen that the solidification temperature decreases, and consequently, the undercooling increases by increasing the cooling rate in the liquid. The undercooling normally reaches the highest value for each case at the highest cooling rate. The results will be discussed later in connection with the formation of lattice defects.

Finally, Fig. 8(b) shows calculated fraction of latent heat, \( \Delta H_{\text{calc}} / \Delta H_{\text{lab}} \), versus cooling rate produced in DTA experiments together with the results obtained earlier\(^{17,18}\) from mirror furnace equipment and levitation technique for higher cooling rates. The results show that the calculated values for heat of fusion are much lower than the tabulated ones. The figure also shows that an increase in cooling rate will decrease the values for \( \Delta H \). This relation can generally be described by:

\[
\Delta H = f \left( \frac{dT}{dt} \right).
\]
Fig. 6 Fraction of solids vs. quenching time for (a) $dT/dt = 0.17$ and (b) $dT/dt = 0.018$ Ks$^{-1}$.

5. Discussion

Figure 9 shows the calculated fraction of latent heat, $\Delta H_{\text{calc}}/\Delta H_{\text{tab}}$, versus fraction of solid measured from quenching experiments for the different alloys. The results show that the heat evolved from the samples is lower than the tabulated values. The figure also shows that an increase in the fraction of solid will increase the values of $\Delta H$. Note that the fraction of solid, found in the samples, is much larger than that expected from the theory (Figs. 5, 6). This can be explained by assuming that the solid formed has a higher free energy than expected from the thermodynamic laws of equilibrium and thus, the latent heat will be smaller.

One further observation can be made by comparing the measured and calculated values of both latent heat of fusion and solid fraction. Since the fractions of solid are known from the metallurgical examination, the following equation can be used:

$$f_s^{\text{calc}} \cdot \Delta H_{\text{tab}} = f_s^{\text{meas}} \cdot \Delta H_{\text{calc}}$$

(5)

The calculated fraction of latent heat, $\Delta H_{\text{calc}}/\Delta H_{\text{tab}}$, has been plotted in Fig. 10 as function of $f_s^{\text{meas}}/f_s^{\text{calc}}$. Again one can notice that the measured value of the latent heat is smaller than the tabulated value, especially in the beginning of the solidification process. It has been earlier stated$^{27}$ that vacancies exist in the liquid state and their fraction depends on the cooling conditions during solidification.

It can be assumed that vacancies are created at the liquid-solid interface at a concentration that corresponds to the liquid-solid density difference; the fraction of vacancies depends on this difference of densities. By rapid quenching from the melting temperature, higher vacancy concentration becomes quenched and trapped in, since there is insufficient time to reach an equilibrium concentration of vacancies.

The maximum vacancy concentration can be obtained from the density difference between solid and liquid:

$$\gamma_v = \frac{\Delta \rho}{\rho_s^\text{eq}} - \frac{\Delta \rho}{\rho_l^\text{eq}}$$

(6)

that $\Delta \rho \leq \rho_s^\text{eq} - \rho_l^\text{eq}$. Here, $\gamma_v$ is mole fraction of quenched vacancies, $\Delta \rho$ is the difference in equilibrium density of solid, $\rho_s^\text{eq}$, and liquid, $\rho_l^\text{eq}$.

However, at very high cooling rates, such as in the quenching experiments, when the fraction of vacancies exceeds the equilibrium value $\gamma_v \gg \gamma_v^\text{eq}$, an unordered solid state is expected to form with a large supersaturation of vacancies preserved at room temperature. This is due to the fact that there is insufficient time for the vacancies to diffuse and create clusters, to form dislocations or move to grain boundaries. Penetration of these vacancies in to the lattice, increases the free energy of the solid phase. Increasing $\Delta G$ results in a decrease
in the heat of fusion as well as a decrease in the melting point (Fig. 8(a)).

It was previously shown\(^{18}\) that the heat of fusion for pure Cu changes by the fraction of excess vacancies (those exceeding the equilibrium number) as follows:

$$\Delta H_{\text{calc}} = \Delta H_{\text{ab}} - (y_v - y_v^{\text{eq}}) \Delta H_v,$$  \hspace{1cm} (7)

where $\Delta H_v$ is enthalpy for formation of vacancies. The heat of fusion represents the energy required to melt a mass unit or a mole of substance; i.e. the total energy needed to break the bonds between the atoms in the crystal lattice. If vacancies are present, some bonds are missing, and thus, the total energy decreases with increasing vacancy concentration. The excess fraction of vacancies formed during a quenching experiment can be estimated by combining and rearranging eqs. (7) and (5). The result is shown in Fig. 11.

The fraction of vacancies are largest at the beginning of the solidification process. After that the fraction of vacancies decrease with the increase of the fraction of solid. This might be explained in the following way:

There is a tendency for vacancies to be attracted in to clusters and for some clusters to collapse in to dislocation loops which, can grow by absorbing more vacancies. The formation of such dislocation loops has been earlier\(^{27}\) reported. The vacancies can also be expected to move to the grain boundaries at lower cooling rates. This means that vacancies will be condensed gradually at dislocations and grain boundaries. The vacancies formed in the earliest part of the solidification process will thus condense during the later part of the solidification. During the condensation, heat will be released and thus, one gets closer to the equilibrium state and one will reach the tabulated value of the heat of fusion.

Finally, it is worthy to note that introducing such a large amount of vacancies to a lattice, not only causes a change in the total volume of the metal but also acts as a source for creating other types of lattice defects such as stacking faults.

**Concluding remarks**

The solidification behaviour of Cu–Sn alloys during a quenching experiment has been studied. The calculation of fraction of solid and latent heat of fusion were integrated to a FEM solidification program. The following main conclusion can be drawn:

a) The fraction of solid increases with increasing quenching time.

b) The heat of fusion decreases as a function of increasing cooling rate.

c) Calculated values for $\Delta H$ are much lower than tabulated ones.

d) Experimental values of the solid fractions are much higher than calculated ones. This can be explained by forma-
of vacancies.

e) The excess fraction of vacancies, penetrated in to the lattice decrease the heat of fusion.

f) The effect from formation of vacancies on the solidification behaviour should be reconsidered.

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Fig. 10 Heat of fusion vs. fraction of solid for (a) $dT/dr = 0.17$ and (b) $dT/dr = 0.018 \text{ K s}^{-1}$.

Fig. 11 Measured fraction of vacancies vs. fraction of solid for Cu–4%Sn.