Microsegregation and dendrite arm coarsening in tin bronze
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Specimens of the peritectic alloy Cu±10 wt-%Sn were subjected to various cooling rates typically observed in industrial casting processes. Some of the specimens were quenched immediately after the end of solidification to avoid further solute homogenisation of the dendrite structure during cooling to room temperature. Characterisation of specimens was carried out by measuring the distribution of secondary arm spacings and two microsegregation indices, namely the volume fraction of non-equilibrium phase and the segregation deviation parameter, calculated from a large number of microanalyses at random points. A tendency of increasing microsegregation with an increase in cooling rate was observed. The microsegregation results were compared with those of a comprehensive microsegregation model using different equations for coarsening of secondary dendrite arms. The comparison indicated that predictions are more accurate when an empirical equation for coarsening, based on the relationship between secondary arm spacing and cooling rate, is used.

Introduction

The effect of processing variables on microsegregation in metallic alloys has been under investigation since the pioneering work of Scheuer,1 concerning the effect of mould type on the amount of secondary phase in as cast aluminium and copper alloys. Only recently, however, has the mathematical modelling of microsegregation incorporated the important effects of coarsening2-5 and undercooling3,6 of dendrite tips and eutectic, by means of analytical and numerical techniques. The development of mathematical models for the microsegregation of peritectic alloys7-11 began even later, because of the complexity of handling two moving phase boundaries after occurrence of the peritectic reaction.

Coarsening of dendrite arms was incorporated in mathematical models of microsegregation by the gradual increase of a control volume placed between two adjacent secondary arms.2-4,12 The instantaneous control volume size \( L \) is governed by equations of the general form

\[
L = \frac{\lambda_2}{2} = K t^n
\]

where \( \lambda_2 \) is the instantaneous secondary arm spacing, \( t \) is the time elapsed after the beginning of solidification, \( K \) is a constant dependent on the alloy, and \( n \) is approximately 1/3 for most materials.2,13,14 In an empirical approach to model coarsening,13,14 these constants were obtained by experimental measurement, while in a semiempirical approach,2,3,11 which originated the dynamic coarsening models, isothermal coarsening equations were used.

Empirical coarsening models employ equations describing the secondary arm spacing as a function of elapsed time during solidification. Kattamis et al.16 showed that this equation could be approximated by the relationship between final secondary arm spacing and local solidification time, after substituting final secondary spacing by instantaneous spacing, and local solidification time by elapsed time. The dynamic coarsening equation given below was first used in microsegregation models by Roóisz et al.2

\[
\left[ \frac{\lambda_2(t)}{\lambda_2(0)} \right]^3 = \frac{BM}{\sigma D_L T_f} dt
\]

where \( \lambda_2(t) \) is the secondary arm spacing at time \( t \), \( B \) is a geometric parameter obtained experimentally by the authors,7 and \( M \) is given by

\[
M = -\frac{\sigma D_L T_f}{\Delta H_f m_t C_t (1-k)}
\]

where \( \sigma \) is the solid/liquid interfacial energy, \( D_L \) is the solute diffusion coefficient in the liquid, \( T_f \) is the melting point of pure solvent, \( \Delta H_f \) is the volumetric heat of fusion, \( m_t \) is the liquidus line slope, \( C_t \) is the average solute concentration in the liquid, and \( k \) is the solute partition coefficient. Battle and Pehlke3 compared experimental results of microsegregation in Al–Cu alloys with those of models that included empirical and dynamic coarsening equations. They noted that it was still not possible to conclude which approach gave more accurate results.

Results of comprehensive mathematical models of microsegregation for eutectic alloys were compared with experimental results from Al–Cu alloys.2-4 The agreement was good, but discrepancies of 100% were observed in some cases.2

Comparisons of model results and experiments for peritectic alloys were carried out mainly for multicomponent steels.7-9 Application of these models required estimates of thermodynamic parameters, such as solute partition coefficients for all alloying elements. Coarsening of secondary dendrite arms, however, was never included.

Martorano and Capocchi17 compared experimental and model results for microsegregation in Cu–8 wt-%Sn peritectic alloys. (All compositions in this paper are given in wt-%.) Profiles given by their model, in which coarsening was incorporated, were compared with those constructed from a large number of microprobe analyses obtained at random points. Despite the good agreement, some discrepancy was observed at the low and high concentration regions of the profiles, and poor agreement existed for volume fractions of eutectoid, used as a microsegregation index.

The present work was aimed at studying the effect of cooling rate on microsegregation levels in Cu–10Sn alloy specimens consisting of only equiaxed dendrites. Experimental results have been compared with those from a validated mathematical model for peritectic alloys.11 In the model, two different coarsening modelling approaches are tested: empirical coarsening, using an empirical
equation obtained by the authors, and dynamic coarsening, employing the equations proposed by Kirkwood and Mortensen. The influence of secondary arm spacing distribution on the level of microsegregation calculated from the models has also been examined by constructing a concentration profile composed of simulations representing each spacing class in a specimen. Finally, the effect of cooling rate on the distribution of secondary dendrite arm spacing has been investigated.

Experiments and characterisation

Charges of nominal composition Cu–10Sn made from electrolytic copper and tin were melted in vitreous silica tubes, deoxidised by adding Cu–15P, and subjected to several cooling conditions. The average cooling rate between the liquidus (~1010 °C) and the peritectic temperature (~799 °C) is given in Table 1 for each experiment. In experiments CQ1, CQ3, and CQ4, the cooling conditions during solidification were similar to those in C1, C3, and C4, respectively. In the former, however, specimens were quenched in stirred water immediately below the peritectic temperature, whereas in the latter, the same cooling conditions were maintained until specimens reached room temperature. A comparison between results from the two sets of specimens would reveal the importance of solute homogenisation after solidification.

Slices cut from the specimens were ground and polished using conventional metallographic techniques. The average spacing between secondary dendrite arms was measured in 40 different fields of the same specimen using standard procedures. A distribution of secondary arm spacing was obtained in each specimen by measuring the distance between adjacent secondary arms chosen at random on the polished plane. In each specimen, ~200 spacings were measured and has in 10–12 classes to construct a relative frequency distribution. Since dendrite arms were chosen randomly, longer spacings were measured more frequently; therefore, the actual distribution was obtained only after a correction. This correction, however, had a negligible effect.

Both quenched and non-quenched specimens had secondary phase structures embedded in an α-Cu matrix containing tin. The structures, such as the α + δ eutectoid, were the result of several reactions and decompositions that would not have occurred for a Cu–10Sn alloy in the absence of microsegregation. Therefore, the volume fraction of secondary phase structures embedded in the α matrix was measured and used as a comparative index of microsegregation. To measure the volume fraction, a two-dimensional systematic point count technique was used.

Microanalyses were carried out by wavelength dispersive spectroscopy (WDS) in a microprobe operated under the following conditions:

- Accelerating voltage 20 kV
- Electron beam current 20-1 mA
- Approximate number of counts for tin 43 000
- X-ray take-off angle 40°
- Diffraction crystal for Cu Kα, LiF
- Diffraction crystal for Sn Lα, pentaerythritol

Approximately 100 microanalyses were carried out at random points in a region of ~1 cm² from each specimen. Using these results, a segregation deviation parameter $r_m$ was calculated according to

$$r_m = \frac{1}{nC_0} \sum_{i=1}^{n} |C_i - C_0|$$

where $n$ in this case is the total number of microanalyses carried out in the specimen, $C_i$ is the tin concentration of each microanalysis, and $C_0$ is the average tin concentration of all microanalyses in the specimen.

Tin concentrations from the random microanalyses were used to construct profiles of tin content as a function of cumulative volume fraction of specimen. The range of tin contents obtained from all microanalyses in a specimen was divided into 10–12 classes. The fraction of the number of microanalyses in each class was used as the volume fraction of specimen with composition given by the lower and upper limits of that class. From each fraction, a cumulative volume fraction of specimen was calculated and used to construct the profile for that specimen. Consequently, the final profile would display the volume fraction of specimen with tin concentration equal to or lower than a given value. This profile could then be directly compared with those calculated using mathematical models. In models using a one-dimensional control volume, the cumulative volume fraction associated with a certain position along its length is simply the ratio between this position coordinate and the control volume length. Since each cumulative volume fraction was estimated from a fraction of points, some statistical uncertainty exists. Therefore, a 95% confidence interval (CI) was calculated for each fraction according to

$$CI = 1.96 \sqrt{\frac{(1-f_v) \cdot f_v}{n}}$$

where $f_v$ is the cumulative volume fraction of specimen.

Mathematical model

The mathematical model implemented by Martorano and Capocchi was used in the present investigation to simulate the microsegregation in the specimens under study. The model was based on numerical solution of Fick’s second law applied to all solid phases and liquid present in a one-dimensional control volume placed between two adjacent secondary dendrite arms.

Some important hypotheses of the model are:

(i) a one-dimensional platelike control volume is used, extending from the longitudinal axis of a secondary arm up to the middle point between it and the adjacent arm

(ii) the temperature of the control volume is assumed to be uniform and is obtained from the measured cooling curve of the corresponding specimen

(iii) the undercooling at dendrite tips is neglected

(iv) all phase boundaries within the control volume are planar

(v) there is thermodynamic equilibrium at every phase boundary.

Only new details about the model are described below, since other details and alloy properties used in the calculations are fully explained elsewhere. Coarsening of secondary dendrite arms is simulated by increasing the control volume size used in the mass transfer analysis after each time step of the numerical method. The new control volume size
is given by a coarsening equation similar to equation (1). In the present work, two types of equations were used, namely an empirical equation adapted from the measured relationship between final secondary arm spacing and local solidification time (empirical coarsening model), and an isothermal coarsening equation (dynamic coarsening model) based on first principles.

In dynamic coarsening, the following equation, derived from equation (2), was used to calculate the new control volume size \( L \) after each time step

\[
L = \frac{1}{2} \left( L + \Delta t \right) + B M \Delta t \}
\]

where \( L + \Delta t \) and \( L \) are the secondary arm spacing at time \( t + \Delta t \) and \( t \), respectively, \( \Delta t \) is the time step of the numerical method, \( M \) is given by equation (3), and \( B \) is a geometric parameter calculated by either Kirkwood’s 18 or Mortensen’s 19 model. In Kirkwood’s 18 model, it is assumed that the length of a cylindrical secondary arm decreases owing to its tip dissolution until it is totally consumed, as originally proposed by Kahlweit. 23 Mortensen’s 19 model, however, improves on that proposed by Kattamis et al. 16 who assumed that the diameter of a cylindrical secondary arm decreases until complete arm dissolution. The geometric parameters from the models are

\[
B = 128 \quad \text{(Kirkwood)} \quad (7)
\]

\[
B = \frac{27}{4} f_0 \left[ 1 - (f_0)^{1/2} \right] \quad \text{(Mortensen)} \quad (8)
\]

Note that \( m_s \), \( C_L \), and \( k \) in equation (3) for \( M \), and \( f_0 \) (control volume solid fraction) in the above equations for \( B \), are updated after each time step. The minimum value of \( f_0 \) used, however, was 0.1, because there is a singularity in Mortensen’s 19 model caused by some of the simplifying assumptions. To calculate \( M \) in equation (3), the following values were used: \( \sigma = 1.29 \text{ J m}^{-2} \), \( D_L = 3.23 \times 10^{-20} \text{ m}^2 \text{ s}^{-1} \), \( T_s = 1084^\circ \text{C} \), and \( \Delta H_s = 1703.5 \times 10^6 \text{ J m}^{-3} \). The liquidus slope \( m_L \) and the solute partition coefficient \( k \) were obtained from the Cu – Sn phase diagram 24 as a function of temperature.

The effect of secondary arm spacing distribution on the microsegregation of a specimen was analysed by constructing a combined concentration profile. The combined profile was constructed by calculating the microsegregation profile for the representative arm spacing of each class in the distribution. As a result of the numerical microsegregation model, the calculated profile associated with a spacing class is actually a table of concentration values, one for each node of the numerical mesh. In all tables associated with each class of the spacing distribution for one specimen, the concentration values were considered to belong to a set of random point microanalyses. All values for the specimen were mixed and sorted in increasing order of tin concentration, and each value was assumed to represent a volume fraction of specimen equal to \( 1/n \), where \( n \) is the total number of concentration values calculated for a sample. In the mixing process, before sorting, each table associated with a spacing class was added to the general profile as many times as the number of spacings in the class. Therefore, the microsegregation associated with a spacing class that had a greater relative frequency in the distribution should have a more important contribution to the general microsegregation in the specimen. The calculated combined profile was finally compared with those obtained experimentally from the random microanalyses.

### Results and discussion

#### DENDRITE STRUCTURE

A typical dendritic structure observed in all specimens studied is shown in Fig. 1. It is possible to see equiaxed dendrites displaying primary, secondary, and tertiary arms, with interdendritic porosity. Tertiary arms have possibly undergone some coalescence, forming plates. The effect of coalescence between primary arms and secondary ramifications is also observed.

The atomic number contrast in the backscattered electron image shows tin rich regions between dendrite arms, with tin rich phases in between. In all specimens not quenched after solidification, these regions consisted of the \( \alpha + \delta \) eutectoid. In quenched specimens, on the other hand, the eutectoid decomposition did not occur, resulting in a different type of secondary phase present between arms. Microanalyses of this phase indicated an average tin content of \( \approx 25-70 \% \), which is in the range of tin contents of \( \beta \) and \( \gamma \) phases, or some metastable phase originated from them. In the present work, the total volume fraction of the secondary phase structure, such as the \( \alpha + \delta \) eutectoid found in non-quenched specimens, was used as a comparative index of microsegregation severity.

#### SECONDARY DENDRITE ARM SPACING

Results for average secondary arm spacing as a function of cooling rate are shown in Fig. 2, compared with results from empirical equations given by Mortarano and Capocchi 25 and Sugiyama et al. 26 The experimental results of Bower...
The standard deviation of the normalised distribution of secondary arm spacing decreased as a function of the local solidification time. Regression equations for the results of the present work are given by

\[ \lambda_2 = 114.5 R^{-0.31} \]  
\[ \lambda_2 = 6.07 R^{0.31} \]

where \( \lambda_2 \) is the final secondary arm spacing (\( \text{m} \)), \( R \) is the average cooling rate (K min\(^{-1} \)) during solidification, and \( t_L \) is the local solidification time (s).

It is possible to calculate the secondary arm spacing as a function of elapsed time using equation (2), where \( M \) is defined by equation (3) and \( B \) is given either by equation (7), for Kirkwood’s model, or by equation (8), for Mortensen’s model. Equation (2) was integrated by Kirkwood for a constant cooling rate and by Mortensen, who assumed a linear increase of solid fraction with time, and considered that the liquid concentration followed Scheil’s model. The spacing calculated from these two models, shown in Fig. 2, is always greater than the experimental measurements, although Mortensen’s model results are in better agreement. The discrepancy might be attributed to the large number of simplifications made in both models, particularly that coarsening continues until the end of the solidification period, increasing the calculated final arm spacing. Actually, for a large solid fraction, coalescence mechanisms will be more important than the coarsening mechanisms assumed by the models.

Using the average secondary arm spacing \( \lambda_{2av} \), distributions of normalised spacing \( \lambda_2/\lambda_{2av} \) were constructed for all specimens. In Fig. 3, results show that no dendrite arm spacing is larger than \( \approx 1.5 \lambda_{2av} \). This reinforces the similarity between dendrite arm coarsening theories and spherical particle coarsening theories, since the latter indicate that the maximum radius of particles in a coarsened structure would be about twice the average value.

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only by several orders of magnitude variation in the cooling rate.

All measured microsegregation indices are lower than those obtained by the model using dynamic coarsening, i.e. those that employed either Kirkwood’s or Mortensen’s coarsening equations. As shown in Fig. 2, these coarsening equations result in greater final secondary arm spacing, causing less homogenisation of the solid and, consequently, more segregation. Results of microsegregation from the model using the empirical coarsening equation lead to the best agreement with experimental results, especially at greater cooling rates. In contrast with the dynamic coarsening equations, the empirical coarsening equation gives secondary arm spacings very close to those measured. Therefore, it is clear that the secondary spacing is a critical parameter whose calculation and measurement accuracy must be improved for better microsegregation model results.

Results from the combined profile model do not present a better agreement with measurements than those from the model using the empirical coarsening equation. Some oscillation is observed in \( \sigma_n \) and \( V_v \), shown in Fig. 5. This is a result of the natural variation of measured average secondary spacing from specimen to specimen, as indicated by Fig. 2. The empirical coarsening model does not show this oscillation, because it is based on a regression equation fitted to experimental results, rather than the average spacing of the specimen itself.

The combined profiles of tin content as a function of cumulative volume fraction, constructed as described above in ‘Experimental and characterisation’, profiles calculated using the empirical coarsening equation, and the measured profiles are shown in Fig. 6. Results of the worst and best agreement between calculations and measurements are plotted. Similar to the microsegregation indices, the best agreement was obtained for specimens subjected to greater cooling rates, such as specimen C5 (Fig. 6b).

Profiles from the model using empirical coarsening are similar to those from the combined profile model. Nevertheless, as shown in Fig. 6, some difference exists at regions of both high and low tin contents. The combined profiles have a negative curvature at low contents, not observed in the results from the empirical model, which is based on the average arm spacing. The negative curvature is not seen in profiles calculated by other authors, who also used the average secondary arm spacing. Note that the experimental profiles are based on microanalyses carried out throughout the specimen, and not only on measurements across a particular dendrite arm spacing. Therefore, they should be affected by the microsegregation present between all types of dendrite arms in the specimen, which is the idea behind the combined profile. As observed by Roosz et al. and Singh et al., mathematical models of solute homogenisation based on average spacing fail to predict the microsegregation decrease beyond a certain time. After this time, the microsegregation between greater secondary arm spacings or even primary spacings prevails in the structure as a result of the long distances for deformation during homogenisation.

**Conclusions**

1. For Cu–10 wt-%Sn alloys, secondary dendrite arm spacing \( \lambda_2 \) decreases with increasing cooling rate \( R \)
or decreasing local solidification time $t_L$ according to

$$\lambda_2 = 114.5 R^{-0.31}$$

$$\lambda_2 = 6.07 R^{0.31}$$

where $\lambda_2$ is given in $\mu$m, $R$ in K min$^{-1}$, and $t_L$ in s.

2. A comparison between results of the present work and those of Martorano and Capocchi\(^{25}\) shows that greater tin contents in the alloy cause a decrease in secondary dendrite arm spacing in specimens subjected to similar cooling rates.

3. The secondary dendrite arm spacing calculated by Kirkwood’s\(^{173}\) model is eight times as great as the experimental value for some specimens of Cu–10Sn alloy, whereas that derived from Mortensen’s\(^{15}\) model is only twice as great.

4. Any individual spacing between two secondary arms is usually shorter than $\sim 1.5$ times the average spacing in the specimen.

5. The standard deviation of the normalised distribution of secondary arm spacing decreases with an increase in local solidification time.

6. The majority of specimens quenched in water immediately after solidification present microsegregation indices greater than those measured in non-quenched specimens subjected to the same solidification cooling rate.

7. In non-quenched specimens of Cu–10 wt.%Sn alloys there is a tendency of increasing microsegregation degree with an increase in the solidification cooling rate.

8. In the lower tin region, combined profiles present a negative curvature not observed in results from microsegregation models based on average secondary arm spacing.

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