

# A Statistically Significant Experimental Technique for Investigating Microsegregation in Cast Alloys

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A simple, statistically significant experimental technique was developed to investigate microsegregation in a model cast Al-4.5 wt pct Cu alloy. This technique involves systematic composition measurements of the primary alloy phase of polished samples by use of the electron microprobe. The microprobe data were processed to obtain the detailed composition vs fraction solid profile, which was an estimation of microsegregation of solute element in the sample. The number of data collected directly affected the statistical significance of the results. The results suggested that measurements of the order of 100 are adequate for obtaining statistically significant solute distribution profiles and, hence, for quantitatively determining the severity of microsegregation.

## I. INTRODUCTION

MICROSEGREGATION is a result of dendritic solidification. Microsegregation, that is, segregation of solute elements over distances on the order of dendrite arm spacings, has been an interest of many researchers, since it affects mechanical properties, corrosion properties, and workability of ingots and is carried over into wrought products, where it affects particularly transverse properties of wrought material.<sup>[1-5]</sup>

The extent of microsegregation in the alloy structures is determined experimentally by measuring one of the following: (a) amount of nonequilibrium eutectic, (b) amount of nonequilibrium second phase, (c) minimum solid composition, (d) ratio of minimum to maximum composition of the primary phase, or (e) composition vs fraction solid profiles, which will be discussed in this work.

The first theoretical treatment of microsegregation is given by the classical nonequilibrium solidification, or "Scheil," equation.<sup>[6,7,8]</sup> The Scheil equation predicts generally greater microsegregation than that found experimentally. The discrepancy between predicted and actual microsegregation measured experimentally arises from back diffusion in the solid and coarsening. The first quantitative analysis of microsegregation with the solid-state diffusion effect was made by Brody and Flemings.<sup>[9]</sup> Ever since, the subject of microsegregation has been addressed by many researchers, including analyses by Clyne and Kurz,<sup>[10]</sup> Solari and Biloni,<sup>[11]</sup> Basaran,<sup>[12]</sup> Kirkwood,<sup>[13]</sup> Roosz *et al.*,<sup>[14,15]</sup> Matsumiya *et al.*,<sup>[16]</sup> and Mortensen.<sup>[17]</sup>

Experimental techniques to investigate the severity of microsegregation include quantitative metallography (point count, areal, and lineal measurements), X-ray diffraction analysis, and microprobe measurements. Metallographic and X-ray techniques only provide an estimation of the volume fraction of second phase and are incapable of providing solute redistribution profiles.<sup>[1-3,5,18-21]</sup> Using

the electron microprobe, the composition minima and local solute redistribution profiles can be obtained from the polished sample surfaces.<sup>[14,17,19,20]</sup>

The aim of this work was to combine a metallographic technique with the electron microprobe technique to obtain detailed solute distribution profiles. These profiles not only would be statistically significant but would provide complete microsegregation information, including minimum composition and eutectic fraction.

## II. EXPERIMENTAL PROCEDURE

The material used was taken from many high-purity Al-4.5 wt pct Cu alloys produced by Reynolds Aluminum Company, Richmond, VA. The actual overall composition of copper in the alloy was 4.6 wt pct. The alloy was melted, degassed, and pressure cast into small molds (3.2 mm in diameter). The cast rods were then cut into small pieces (5 mm in length). Each sample was placed in a graphite container, heated above the liquidus temperature of the alloy (~920 K), and solidified at a controlled rate.

The samples were cross-sectioned and polished but were not etched. Microprobe analysis was carried out using a fully automated Cameca Camebax scanning electron microprobe. Composition measurements were made on horizontal, nontilted specimens with an X-ray takeoff angle of 40 deg. The operating voltage was 20 kV and the beam current was 20 nA. Al  $K_{\alpha}$ - and Cu  $K_{\alpha}$ -characteristic X-ray lines were used. Pure Al and Cu were used as standards.

A total of 300 measurements of the primary phase per sample was carried out using the coarse square-mesh systematic point count metallographic technique. Data obtained from the interdendritic region were disregarded. The microprobe step size (the distance between two consecutive measurements) was larger than the average secondary dendrite arm spacing of the cast sample. Several sections per sample were analyzed. The data from the microprobe measurements were processed in a manner described in the Appendix to obtain the solute redistribution profiles.

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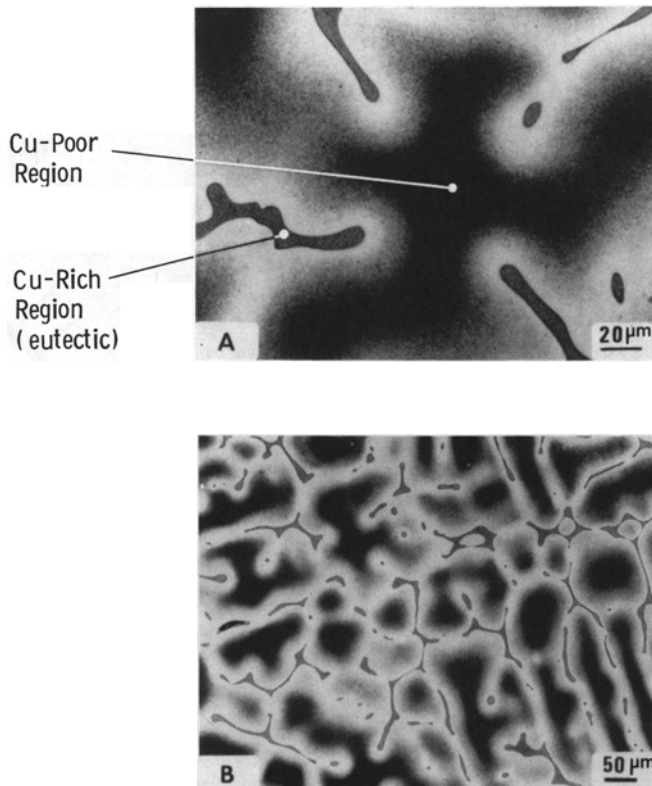


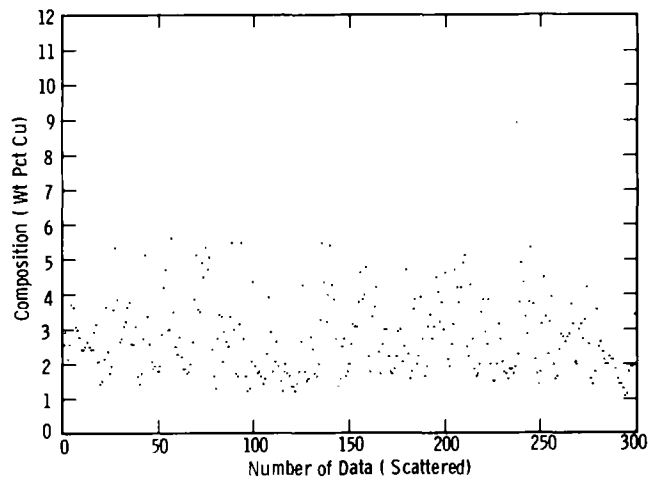
Fig. 1—Solidification microstructures of Al-4.5 wt pct Cu showing coring (Cu-poor, darker regions) and interdendritic eutectic (Cu-rich) both of which are results of microsegregation.

### III. RESULTS AND DISCUSSION

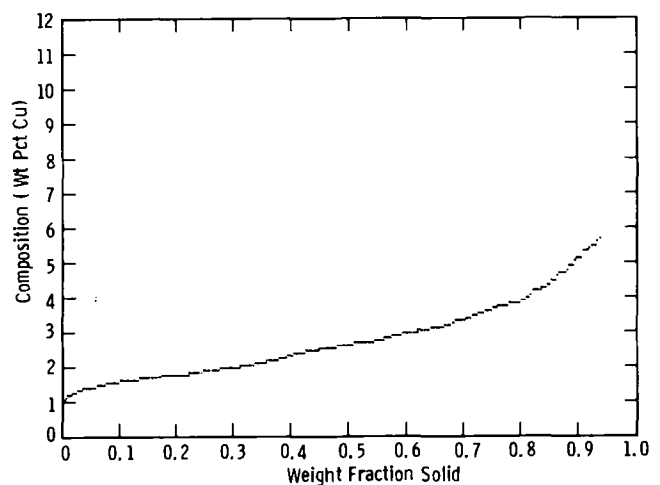
Typical dendritic microstructures of the Al-4.5 wt pct Cu alloy are shown in Figure 1. The features in the microstructure, as revealed by etching, are the primary phase dendrites and the interdendritic eutectic. Because of microsegregation, the isoconcentration contours (coring) are visible. In Figures 2(a) and (b), the end results of steps 1 and 5, respectively, explained in the Appendix, are plotted. Figure 2(b) is the final result and presents complete composition vs weight fraction solid solute distribution profile of an Al-4.5 wt pct Cu sample, whose local solidification time was 750 seconds. In this figure, there are 300 data points. Figure 2(b) was replotted in Figure 3 by using every fifth data point for simplified presentation. Data points in Figure 3 were connected by using second-order polynomial regression fit, which gave an empirical relation of  $C_s = af_s^2 + bf_s + c$ , where  $C_s$  is composition of the primary phase,  $f_s$  is the weight fraction of the primary phase, and  $a$ ,  $b$ , and  $c$ , are the constants. The constant  $c$  is equal to the minimum composition. In Table I, the results of two analyses are given.

In Figure 3, the Scheil equation was also plotted for  $C_o = 4.6$  wt pct Cu and  $k = 0.17$ . (The Scheil curve represents the uppermost limit on microsegregation; any experimental measurements would deviate from its prediction.) Thus, the Scheil curve is used only for reference.

The parameters in considering the statistical uncertainties are the manner of sampling and sample size (number of measurements). The manner of sampling was



(a)



(b)

Fig. 2—(a) Composition vs scattered data and (b) composition vs fraction solid profile that were obtained from the microprobe analysis outlined in the Appendix. (a) and (b) correspond to step 1 and step 5, respectively. The profiles of intermediate steps are not shown.

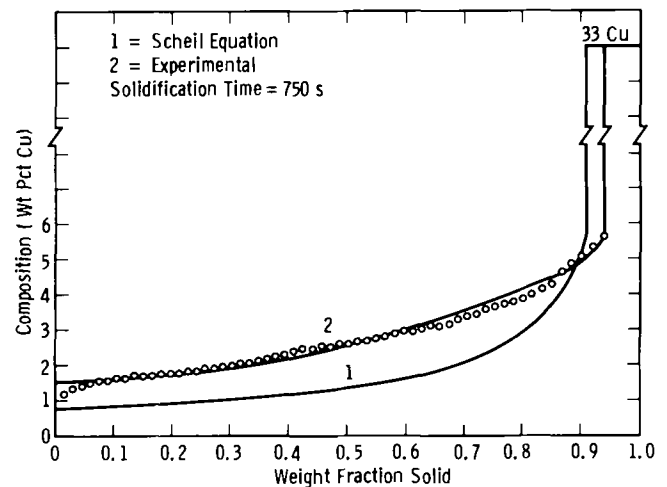


Fig. 3—Composition vs weight fraction solid curve as plotted using every fifth data point in Fig. 2(b). The Scheil equation was plotted for reference.

**Table I. Microprobe Analysis of Al-4.5 Weight Percent Cu**

Sample	Local Solidification Time (s)	Average Secondary Dendrite Arm Spacing ( $\mu\text{m}$ )	$a$	$b$	$c$	Eutectic (Wt Pct)
1	192	56	5.3	-0.7	1.2	7.0
2	750	112	3.7	0.4	1.5	6.3

$C_s = af_i^2 + bf_i + c$  (based on second-order polynomial regression fit of data, such as shown in Fig. 3);  $C_s$  = composition of the primary phase (wt pct Cu);  $f_i$  = weight fraction of the primary phase;  $a$ ,  $b$ , and  $c$  = constants ( $c$  is equal to the minimum composition, wt pct Cu); and eutectic (wt pct) = calculated from the materials balance (see step 5 in the Appendix).

a coarse square-mesh systematic point count measurement described by Hilliard and Cahn,<sup>[22]</sup> who evaluated all procedures available in quantitative metallography for volume fraction analysis. They proposed that the systematic point count techniques (one- or two-dimensional) were the most efficient and statistically the most accurate, provided that the grid spacing is coarse enough so that a given second phase does not occupy two grid points at the same time. They considered a two-phase microstructure consisting of the primary phase matrix and the second phase. Our microstructure also contains two features, the primary phase dendrites and the eutectic. However, in our analysis, we consider the primary phase to consist of a number of subprimary phases. Each subprimary phase is identified by its composition range.

We assume that there are  $R$  subprimary phases,  $\alpha_1, \alpha_2, \dots, \alpha_R$ . Thus, essentially, we are now dealing with a multiphase structure. The objective is then to estimate the volume fractions of these subphases,  $V_1, V_2, \dots, V_R$ . The measurements are the number of microprobe data points falling into each phase;  $K_1, K_2, \dots, K_R = N$  ( $N$  = total measurements). The estimate of volume fractions, the expected values, and the variances (or standard deviations) of the estimates were derived. It turned out that the results were identical to those of Hilliard and Cahn.<sup>[22]</sup> Therefore, the detailed derivations are not given here. The end results of the analysis are as follows: the maximum-likelihood estimate of volume fraction of subphase  $V_j$  is  $V_j^*$  and is given by

$$V_j^* = k_j/N \quad [1]$$

The expected value of  $V_j^*$  is  $E(V_j^*)$  and is given by

$$E(V_j^*) = V_j \quad [2]$$

The variance of  $V_j^*$  is  $\text{Var}(V_j^*)$  and is given by

$$\text{Var}(V_j^*) = V_j/N \quad [3]$$

and the standard deviation of  $V_j^*$  is  $\sigma(V_j^*)$  and is given by

$$\sigma(V_j^*) = (V_j/N)^{1/2} \quad [4]$$

Thus, as can be seen from Eqs. [3] and [4], statistical significance of our composition profiles depends on the total number of measurements ( $N$ ). As  $N \rightarrow \infty$ ,  $\text{Var}(V_j^*)$  and  $\sigma(V_j^*) \rightarrow 0$ , and the analysis will be consistent.

In our experiments, 300 data points per sample were collected. The statistical significance of this number is shown in Figure 4, in which a solute distribution histogram of the microprobe data sample 2 is plotted. In this histogram, there are six "subprimary phases" (the number six was arbitrarily chosen). Again, each phase was

identified by its composition range. For clarity, composition intervals of each subphase were taken to be equal ( $\Delta C = 0.8$  wt pct Cu). The volume fraction of each subphase was calculated using Eqs. [1] and [2]; *i.e.*, the number of data points falling into each phase divided by the total number of data points gives the volume fraction of that phase. The standard deviations were calculated using Eq. [4] and were marked on the histogram bars. The results show that the standard derivations are reasonably good and the analysis is statistically significant.

Since subphase size is arbitrarily defined, and the standard deviation (Eq. [4]) does not depend on subphase size, the experimental technique presented in this paper would have a minimal error, as long as the grid size chosen is larger than the size distribution range of the secondary dendrite arms. The average secondary dendrite arm spacing of the sample analyzed was  $56 \mu\text{m}$  and  $112 \mu\text{m}$  for the samples 1 and 2 of Table I, respectively, and the grid size used was  $250 \mu\text{m}$ . Our sample size was small, so we could not work more than a  $250\text{-}\mu\text{m}$  grid spacing. Ideally, grid size should even be larger than the size distribution range of the primary dendrite arm spacing and, perhaps, larger than the size distribution range of the grains. Such an arrangement would further minimize the effect of periodicity of composition distribution in the dendritic structure and crystallographic orientation of dendrites.

In summary, a simple, statistically significant experimental technique has been developed to investigate microsegregation in Al-4.5 wt pct Cu. This technique

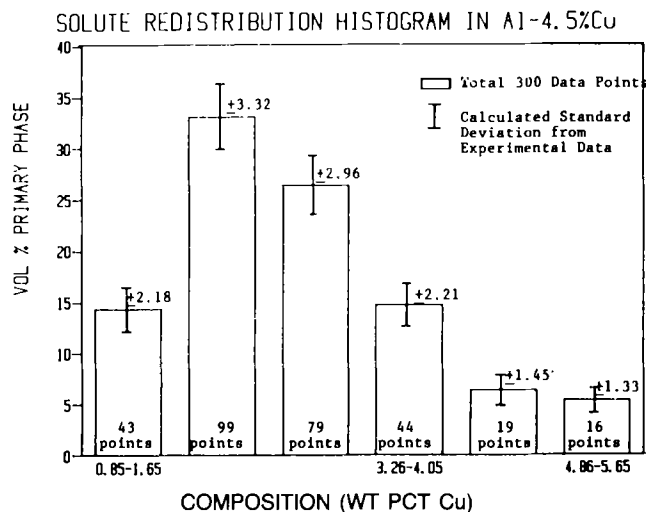


Fig. 4—Composition distribution histogram of an Al-4.5 wt pct Cu alloy whose local solidification time was 750 s.

involves systematic microprobe measurements from polished sample surfaces. Although the solidification process is such a complex phenomenon, and local solidification times may vary from location to location (hence, secondary dendrite arm spacing and micro-segregation), this technique gives an average composition profile within a specimen and, at the same time, predicts an average eutectic fraction, both of which were not attainable simultaneously before with the other existing experimental techniques. Statistical analysis indicates that the required number of microprobe measurements depends on a required standard deviation. From a practical point of view, measurements on the order of 100 may be required in order for the results to be statistically significant. This technique is perhaps best applicable to randomly oriented dendritic microstructures and should be avoided for unidirectionally solidified microstructures. Microprobe measurements described in this paper cannot be applicable to rapidly solidified alloy microstructures because they may display finer secondary dendrite arm spacings than effective electron beam size of the microprobe. Therefore, if this technique is intended to be applied for such microstructures, other means of composition measurement techniques must be considered (e.g., scanning transmission electron microscope analysis).

## APPENDIX

The data from the microprobe analyses were processed to obtain detailed solute redistribution profiles. The procedure of the data processing will be outlined here as follows:

*Step 1.* The scattered data (as measured compositions) were entered into a computer, and composition vs scattered data were plotted.

*Step 2.* The scattered data were put in ascending order, and composition vs ordered data were plotted.

*Step 3.* Ordered data axis ( $x$ -axis) was converted to volume fraction by dividing each data number by total data number. The composition vs volume fraction solid (primary phase) was then plotted.

*Step 4.* Volume fraction solid axis was converted into weight fraction solid using the following equations:

$$f_{si} = \rho_i V_{si} / \bar{\rho} \quad [A1]$$

$$\rho_i = 2.3C_i + 2.7 \quad [A2]$$

where  $f_{si}$  and  $V_{si}$  are the weight and volume fractions of datum  $i$ , respectively,  $\rho_i$  is the density (g/cc) of datum  $i$ ,  $\bar{\rho}$  is the average density (g/cc) of all data, and  $C_i$  is the composition (wt pct Cu) of datum  $i$ . After conversion, composition vs weight fraction solid (primary phase) was plotted.

*Step 5.* Eutectic fraction was incorporated into composition vs weight fraction solid profile by multiplying the data of the  $x$ -axis of step 4 by  $(1 - f_e)$  where  $f_e$  is weight fraction of the eutectic. Using the material balance consideration,  $f_e$  is readily calculated as follows:

$$C_s f_s + C_e f_e = C_o \quad [A3]$$

$$f_s + f_e = 1 \quad [A4]$$

where  $C_s$  = average composition of the primary phase (wt pct Cu) obtained from all data points;

$C_e$  = eutectic composition (33.2 wt pct Cu);

$C_o$  = overall average composition of the alloy (4.61 wt pct Cu);

$f_s$  = weight fraction of the primary phase; and

$f_e$  = weight fraction of the eutectic.

The results of step 5 were plotted as in Figure 2(b). Steps 1 through 5 were documented in a table similar to Table II.

*Notes:*

(1) The average density term,  $\bar{\rho}$  in Eq. [A1], should be replaced by

$$\sum_{i=1}^N \rho_i V_{si}$$

for more accurate calculations ( $N$  = total number of data). Using  $\bar{\rho}$  instead is easier and makes an insignificant difference. However, it requires the  $x$ -axis data to be normalized after step 4.

(2) Equation [A2] was generated from the calculated data from Reference 18 and the measured density values in this work.

Table II. Al-4.5 Weight Percent Cu Microprobe Data Analysis

Data Number	Wt Pct Cu Scattered Data	Wt Pct Ordered Data	Vol Pct Primary Phase	Density (g/cc)	Wt Pct Primary Phase	Normalized Wt Pct Primary Phase	Wt Pct Solid Including Eutectic
1	2.57	1.06	0.33	2.73	0.33	0.32	0.30
2	2.87	1.15	0.67	2.73	0.66	0.64	0.60
3	2.14	1.17	1.00	2.73	0.99	0.96	0.90
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
298	1.88	5.46	99.23	2.83	101.51	99.08	92.85
299	3.40	5.61	99.57	2.84	101.98	99.53	93.27
300	5.65	5.65	100.00	2.84	102.46	100.00	93.70
						Wt Pct Eutectic:	6.30

Local solidification time of this sample was 750 s (sample 2 of Table I).

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