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# Methodology to characterize microsegregation

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## ABSTRACT

Chemical microsegregation resulting from solidification of metallic alloys is most often characterised by EDS or WDS microanalysis using spot measurements located along a regular grid. Due to experimental limitations, the wave lengths of both dendrite arms and analysis grid are often of the same order of magnitude. Although this fact is generally eluded, it complicates the statistical analysis of the results, in particular when the objective is to validate a given solidification model or to prove the occurrence of solid state diffusion. This is first illustrated in the present work by means of experimental analysis performed on an Al alloy. The problem is then tackled using 2D simulations of more or less periodic solidification structures which are sub-sampled along periodic or random point distributions of different surface densities. Statistics tools are used to compare the resulting chemical distributions with the solidification model (Gulliver-Scheil model) injected in the simulation. This allows pointing out the limitations of classical statistical approach in that case, and finally to propose an optimum –at least less bad- procedure to characterise microsegregated structures.

## Introduction

Chemical heterogeneities that build up during casting and solidification of metallic alloys have been studied since long on both experimental and theoretical points of view. As shown in the recent work by Ganesan et al. <sup>1</sup> the experimental characterization of the so-called microsegregation, i.e. chemical heterogeneities built up at the scale of the solidification microstructure, is still a matter of debate. These authors presented an extensive review of the works done on this subject. They also proposed a methodology to decrease the intrinsic variability of the solute distribution curves estimated from microanalyses by sorting experimental distributions of multi-component alloys as a function of a weighted average variability of all the elements. In some way, this method is one step to the more elaborate method developed by Daly and Jeulin <sup>2</sup> who used a geostatistical approach to separate the physical noise from the microstructure effect in the case of X-ray maps obtained with a macroprobe. As a matter of fact, the statistical analysis of the confidence that can be put on such experimental composition distributions has been considered only by Gungor <sup>3</sup> who attempted to apply classical statistics to each

composition class, and by Yang et al. <sup>4</sup> who discussed their experimental results with regard to random sampling data recorded on highly regular simulated structures.

In the present work, we first illustrate the methodology of analysing solute distributions in the case of a multi-component aluminium alloy obtained by EDS measurements performed either along regular grids or by random sampling. We then compare the results obtained to analysis of “chemical” images simulated as described previously <sup>5</sup> and propose a methodology for experimental characterization of solute distributions. Finally, we shortly discuss the statistical validity of such approach.

## Experimental illustration

Series of EDS measurements were made on an Al-Cu-Mg-Si alloy with a nominal composition given as 10.5 Cu, 2.2 Mg and 2.2 Si (all in wt. %) and a microstructure illustrated with the micrographs in Fig. 1. The microstructure shows a dendritic array of (Al) fcc solid solution with a large amount of second phases and eutectic areas. The mean dendrite arm spacing (DAS) of the microstructure was evaluated at about 20  $\mu\text{m}$ . Among the second phases, that are best observed in Fig. 1-b, dark precipitates with Chinese-script like appearance are  $\text{Mg}_2\text{Si}$ , light and medium grey precipitates are two of the  $\text{Al}_2\text{Cu}$ ,  $\text{Al}_2\text{CuMg}$  and  $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$  phases as could be expected for such an alloy composition <sup>6</sup>. Finally, multi-phase eutectic areas are observed.

SEM observations were performed on a LEO VP100 equipped with a PGT system for EDS analyses. Standard conditions are a high voltage of 15 kV with a beam current regulated at 15 nA. In all cases, counting was carried out during 100 s and the apparent compositions were processed for standard corrections with the IMIX software. A particular area on the metallographic section was selected on which six series of 42 measurements were performed:

- three grids of 7x6 (42) points with a spacing of 0.7xDAS, 1.0xDAS and 1.3xDAS;
- three sets of 42 points located at random on the same area than for the previous grid at 1.3xDAS.

In addition, the average “global” composition of the selected zone was estimated by area scanning. Figure 2 presents a SEM micrograph on which the selected area and the locations for counting are apparent because of surface contamination.

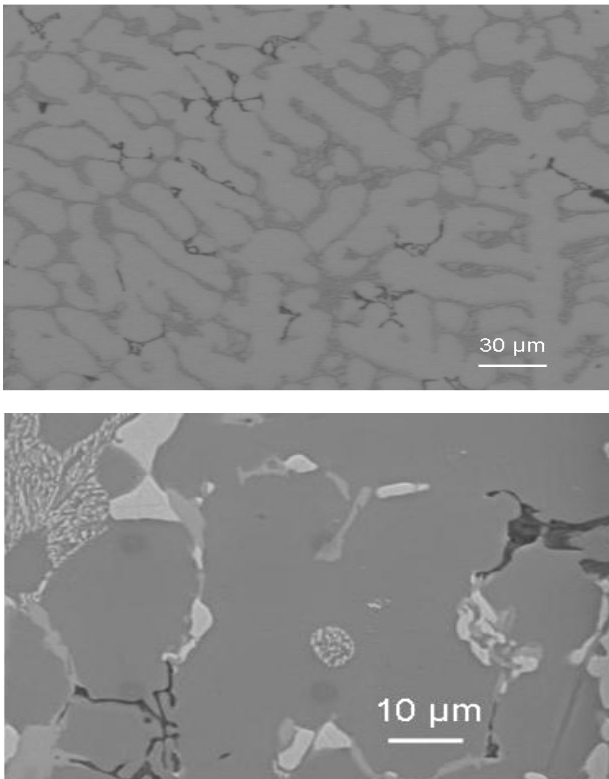


Fig. 1 : Optical and QBSD micrographs of the studied alloy.

Between each measurement series, the sample surface was cleaned by ion etching. Table 1 compares the global composition obtained (with the related standard deviation indicated between brackets) with the average values for each of the six series. The random series give values that may appear on the whole slightly less dispersed than the grid series.

(Cu,Mg) and (Si,Mg) correlations are shown in Figs. 3-a and 3-b respectively, where all the measurements from the six series have been reported, with solid symbols for those from random counting and empty symbols for those from grid analyses. In both cases, a dense cloud of points is observed near the (Al) corner, with clear tendency of other measurements to point to the compositions of  $Al_2Cu$  and

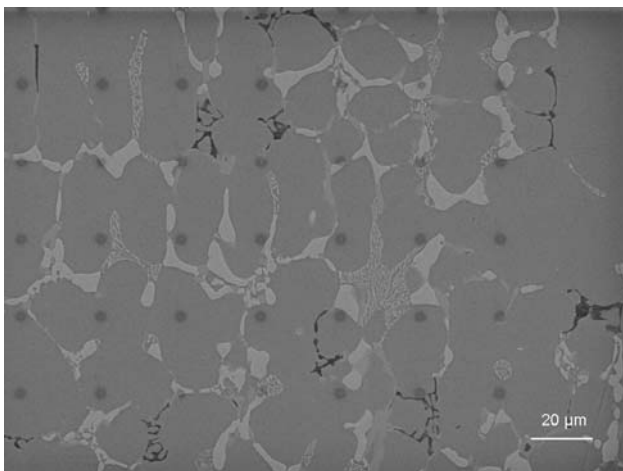


Fig. 2 : SEM micrograph of the area selected for analyses with dots showing the grid when the step spacing is 1.0x DAS.

**Table 1**

AVERAGE COMPOSITION (WT. %) OF THE ALLOY MEASURED FROM EDS ANALYSIS. "GLOBAL" ANALYSIS WAS PERFORMED BY AREA SCANNING OVER THE SELECTED AREA AT AN ENLARGEMENT OF 200; NUMBERS BETWEEN BRACKETS ARE THE STANDARD DEVIATIONS AS GIVEN BY THE IMIX PROGRAM, THEY ARE VALID ALSO FOR INDIVIDUAL MEASUREMENTS ON THE (Al) FCC MATRIX.

	Al	Cu	Mg	Si
global	86.1(0.8)	8.6(0.8)	1.8(0.2)	3.5(0.3)
0.7 DAS	91.1	4.2	2.2	2.5
1.0 DAS	86.7	8.3	2.1	2.9
1.3 DAS	83.8	11.4	1.9	2.9
random #1	89.1	7.1	1.7	2.2
random #2	84.3	10.0	2.8	2.9
random #3	87.8	8.2	1.6	2.4

$Al_5Cu_2Mg_8Si_6$  phases. Note however that measurements on  $Mg_2Si$  will be convoluted with data from the (Al) phase because of the thinness of these precipitates. Enlargement of the clouds of points at high Al content, thus related to the (Al) phase, are shown in Figs. 3-c and 3-d. The trends of these clouds may be explained if it is considered that  $Mg_2Si$  formed early during solidification, so that most of the transformation related in fact to a two-phase deposit of (Al) and  $Mg_2Si$ . Thus, although the partition coefficients between (Al) and the liquid are less than 1 for all the solutes Cu, Mg and Si<sup>6</sup>, the effective segregation of Mg is negative while the one for Cu is positive, and there is nearly no segregation of Si.

Analysis of the solute distributions in the (Al) phase requires that every data not associated with this phase are first withdrawn. From Figs. 3-c and 3-d, measurements on (Al) are considered to correspond to values of Cu, Mg and Si respectively lower than 0.05, 0.01 and 0.02. By sorting successively the whole data sets according to each of these elements, all the measurements not related to (Al) could be eliminated. These data were finally sorted according to the Al content. In doing so, we acknowledge the fact that sorting with the major element (which was not always measured in previous works with WDS) is certainly the most efficient as the associated experimental variability is generally the lowest in agreement with the work by Ganesan et al.<sup>1</sup>. The cumulative distribution of Cu in (Al) is shown in Fig. 4 with solid symbols for data from random analyses and empty symbols for data from grid analyses. It is seen that the scattering of the distributions is much lower for random analysis than for grid analysis. A similar trend has been observed in the case of Mg and Si, though much less evident owing to the lower segregation tendency of these elements because of the concomitant deposition of (Al) and  $Mg_2Si$ . This result confirms that, in the case of a regular or nearly regular structure, microanalysis is certainly more accurate when performed with random localization of the counting points than with a regular grid. In other words, the larger differences observed between measurements performed on regular grids of different step sizes are an experimental illustration of the existence of measurement bias resulting

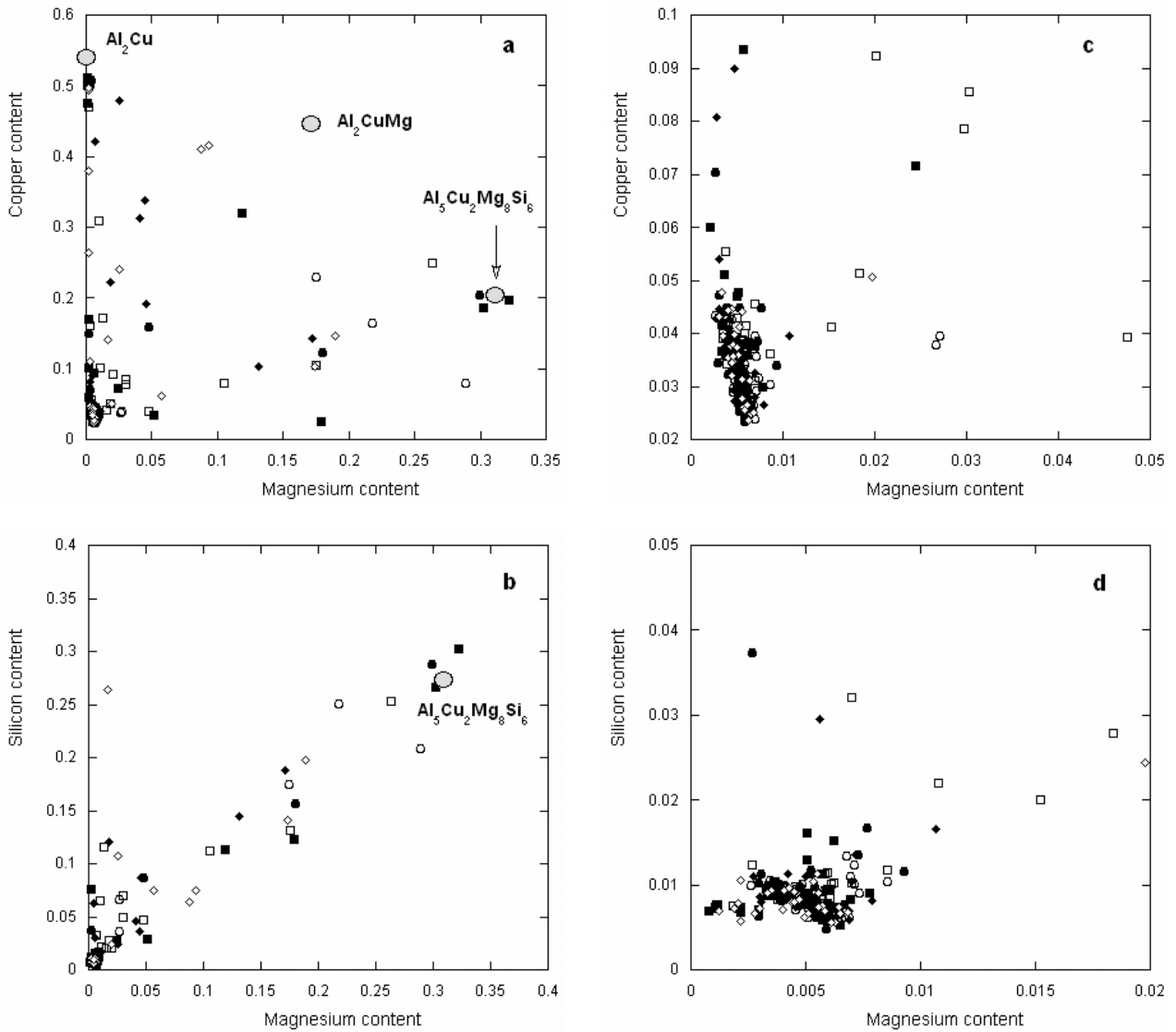


Fig. 3 : Correlations between solute contents: a) (Cu,Mg) and b) (Si,Mg). Graphs c and d are enlargement of the former ones. In a and b the compositions of the main intermetallics expected for this type of alloys have been indicated. Solid symbols relate to random analyses and empty symbols to grid analyses.

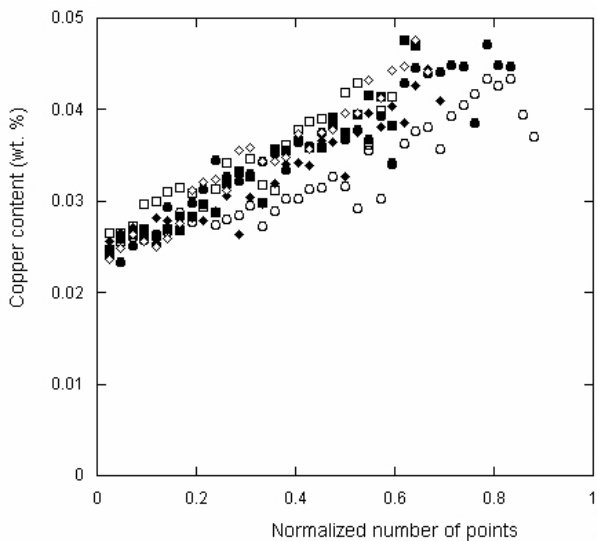


Fig. 4 : Cumulative distributions of copper in (Al) as obtained from random analyses (solid symbols) and grid analyses (empty symbols).

from the interference between analysis grid and solidification structure <sup>5</sup>.

### Suggested methodology for microsegregation analysis

The development of a methodology for microanalysis needs comparing data sets to a known distribution. In this line, the present work pursues a previous study <sup>5</sup> in which “chemical” images were created with an image analyser (APHELION from ADCIS, Caen, France) and then “analyzed” following rules similar to those described in the previous section. Typically, images 1200x1200 pixels in size with 12x12 grains were generated with seeds implemented with some restriction in order to have a more or less regular structure as described in this previous work. One seed is implemented in each of the box of size  $L=100$  pixels. These “solid” seeds are then dilated with a circle of increasing size and the new solid formed at each dilation is given a grey level proportional to the solute content as calculated with the Scheil’s model according to which the composition of the liquid,  $w^l$ , and that of the solid

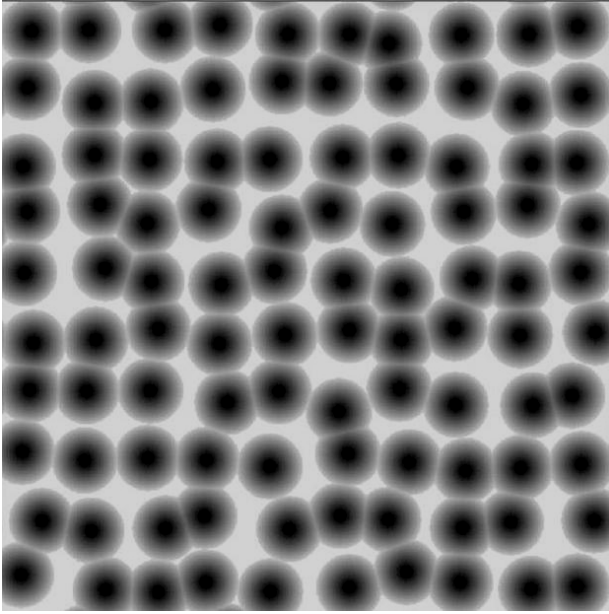


Fig. 5 : Example of simulated composition image.

which deposits,  $w^s$ , are related to the solid fraction,  $f^s$ , by:

$$w^s = k \cdot w^l = k \cdot w^0 \cdot (1 - f^s)^{k-1} \quad (1)$$

in case of single-phase precipitation, with  $w^0$  the nominal solute content of the alloy and  $k$  the solute partition coefficient between solid and liquid ( $k = w^s/w^l$ ), assumed to remain constant over the whole solidification range.

Figure 5 shows an image calculated with  $w^0 = 8.05$  wt. % and  $k = 0.17$ . The solute content was chosen in such a way that the eutectic fraction in the calculated images is about 20 %. In the present case, the position of the seeds was selected randomly in a square box with size  $L_C$  centred within each of the boxes of size  $L$ , with  $L_C/L = 0.4$ . To avoid edge effects, the composition image on which are carried out the analyses is obtained after withdrawing the outer band 100 pixels in size of the simulation image. More details on the algorithms used as well as on the different structures simulated can be found in <sup>5</sup>.

In our previous work <sup>5</sup> we proposed a methodology for microsegregation analysis, which can be summarised as follows:

- try to estimate the correlation lengths (also called '1-D range') representative of the solidification structure in both X and Y directions of the sample holder. This estimation can be obtained through automatic processing of back-scattered electron images, for instance using statistic tools such as grey level variogram. Using the same kind of tools, a procedure to determine the 2-D range has been detailed by Lantuejoul <sup>7</sup>.
- apply regular grid analysis if the X and Y step sizes can be chosen much larger (at least two or three times) than the estimated correlation lengths. In that case, spot measurements can be assumed to be independent and usual classical statistics tools can be used

- if not, i.e. correlation lengths not available or too large with respect to the analysable surface, prefer random sampling to avoid interference between grid and structure. However, it is worthwhile to note that random sampling does not ensure that the different point measurements are not correlated.

Following the conclusion drawn from Fig. 4 and in agreement with our previous work, only random countings were considered to analyse the simulated structure of Fig. 5. Figure 6 shows in dotted lines the solute distributions obtained from five successive analyses of 20 counting points, as compared to the actual distribution of the whole image drawn with a solid line. As we are interested in the solute distribution in the matrix, the scale of the y axis was limited to 10 wt. %. It is seen that, even with random analysis, the estimate of the true distribution may be hardly correct when only a limited number of measurements is used. It should be mentioned that, because of the use of a cumulative distribution, the apparent discrepancy from one distribution to another increases with solid fraction.

However, this does not apply to the estimate of the eutectic fraction, which is seen to change greatly from one curve to another. As a matter of fact, in case of independent measurement points, the variance of the eutectic fraction would be given as  $V_V \cdot (1 - V_V) / N$ , where  $V_V$  is the volume fraction of eutectic and  $N$  is the number of measurement points <sup>3</sup>. Taking  $V_V = 0.2$  gives a variance of 0.008 for 20 measurement points. This corresponds to a standard deviation of 9 %, which explains the change of the eutectic fraction from one series of measurements to another. Performing the calculation the other way, 1600 measurement points would be needed to estimate the eutectic fraction with a standard deviation of 1 %. In the case exemplified in this paper, where the randomly located points are however still correlated (i.e. the density of measurement points is larger than the density of solidification cells), this number would even be higher.

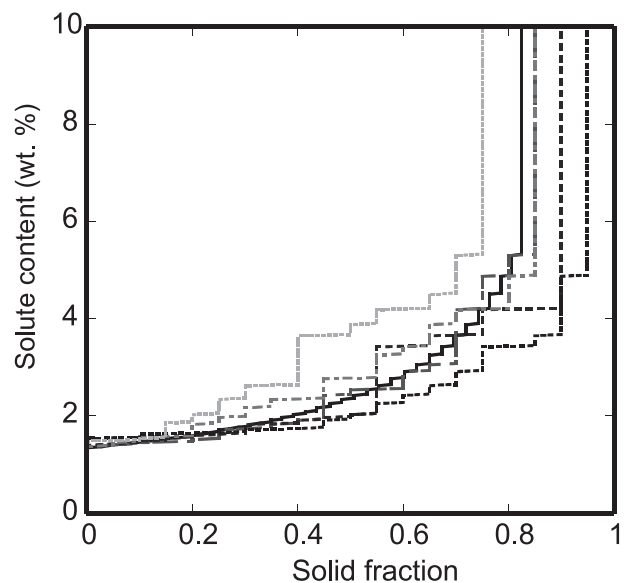


Fig. 6 : Solute distributions obtained from series of 20 counting points (dotted lines) as compared to the true distribution (solid line).

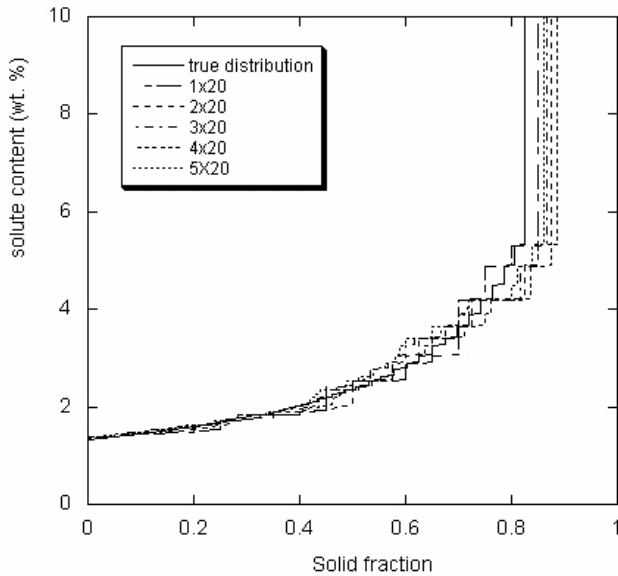


Fig. 7 : Average solute distributions obtained from series of counting points (dotted lines) as compared to the true distribution (solid line). The first series is the same than in Fig. 6, the second is the average of the first two in Fig. 6, and so on.

This figure suggests the following procedure to optimise random sampling:

- perform  $n$  successive random analyses with a limited but constant number of counting points, say  $p$ , such as those plotted in Fig. 6;
- compare the average distribution obtained after  $n$  analyses with the average one obtained after  $(n-1)$ , as shown in Fig. 7 where it is seen that the successive distributions presently done converge rapidly. Note however that the rate at which this convergence proceeds depends on the order the series are added to the average.
- Evaluate this convergence by quantifying the difference between distributions at steps  $n$  and  $(n-1)$ . Such an evaluation may be made by means of various functions of the chemical distributions. An evident one is the function  $\Sigma^2 = \sum_i (f_n^i - f_{n-1}^i)^2$ , where  $i$  scans the whole set of classes for solute content, and  $f_n^i$  and  $f_{n-1}^i$  are the solid fraction at steps  $n$  and  $n-1$  associated to the solute content in class  $i$ .

In the present case, it was found, in agreement with the analysis of Fig. 7, that  $\Sigma^2$  strongly decreases between the first and second steps, then increases again before to tend

slowly to zero. This behaviour just illustrates the unsteadiness of class distributions when estimated with a too low number of measurements. Some other parameters not based on differences between class numbers could likely result in a continuous convergence. Note that two rules are also possible for setting up the successive series of  $p$  measurement points: either all sets of points can be located on the same but –if possible– large surface area or each successive set can be set up on a different region. In this latter case, a second test has also to be performed to ensure the stability of the mean chemical compositions, i.e. the so-called ergodicity of the structure.

## Conclusion

The present paper just stated elementary common sense rules for efficiently collecting composition data relative to solidification microsegregation. Then, different ways of analysing and representing such data can be found in the recent paper by Ganesan et al. <sup>1</sup>. Finally, classical statistical approaches are available in Gungor's article <sup>3</sup> to estimate the confidence interval for each class of a composition distribution. Unfortunately, they only apply when measurement points can be considered to be independent. As discussed in this paper and in a previous one <sup>5</sup>, this situation is actually very rare in practice, leading to confidence intervals significantly larger than those generally assumed. As far as we know, no work can be found in the literature where this problem would have been successfully treated. The techniques of confidence range estimation based on sub-samplings of experimental data are a possible track to resolve this question. The use of simulated microsegregation structures would probably help to test the efficiency of these techniques - which have been developed for large data sets - in the case of relatively few composition measurements.

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