

# THE INHOMOGENEITY VARIANCE OF COMPACT MATERIALS; THE DETERMINATION OF INHOMOGENEITY OF AN Al-Si ALLOY

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Methods are described in the paper of measurement by electron microprobe to obtain necessary information for the determination of principal components of the inhomogeneity variance. The results obtained on the studied material (an Al-Si alloy) are compared with those of another method using a part of the same material.

This paper deals with inhomogeneity of a compact Al-Si alloy with respect to Fe, Mn and Cu. The inhomogeneity variance,  $D_J^2(\omega)$ , of samples  $\omega$  is estimated from<sup>1</sup>

$$D_J^2(\omega) = D_f^2(\omega) + D_h^2(\omega) + D_r^2(\omega). \quad (1)$$

The intraphase variance,  $D_f^2(\omega)$ , is due to the concentration fluctuation about the mean in individual phases. The heterogeneity variance,  $D_h^2(\omega)$ , depends on the size and composition of grains of individual phases and on the non-uniformity of distribution of these grains within the material: The regression variance,  $D_r^2(\omega)$ , depends on the regression course of concentration.

Spatial distribution of the elements in the material was examined with the aid of an electron microprobe. The obtained data served to calculate the variance  $D_J^2(\omega)$  for samples  $\omega$  in the form of chips made from a part of the studied material. The inhomogeneity of the chips was measured by another method<sup>2</sup>.

## EXPERIMENTAL

*Material.* The studied material, an Al-Si alloy (for composition see Table 1), was shaped as a cylinder 4 cm in diameter. The distribution of elements was investigated on a longitudinal and lateral cut. Firstly, the material was found to contain two phases, designated formally as phases  $\alpha$  and  $\beta$ , of markedly different composition. Phase  $\alpha$  occupied most of the volume of the sample while phase  $\beta$  was scattered in isometric grains 10–50  $\mu\text{m}$  in diameter. The mean grain diameter on the surface of

a cut was  $\bar{d} = 21.9 \mu\text{m}$ . The mean cross sectional area occupied by a single grain of phase  $\beta$  was  $4.1 \cdot 10^{-4} \text{mm}^2$  and the mean number density of grains on the lateral cut was  $\bar{v} = 27.3 \text{mm}^{-2}$ . These data enable the mean surface concentration,  $\bar{p}_\beta$ , of phase  $\beta$  on the lateral cut to be calculated. In view of the stationary character of the number density of grains of phase  $\beta$  in the direction along the axis of the cylinder (see the following text) we thus obtain also the estimate of the mean volume concentration,  $\bar{v}_\beta$ , of phase  $\beta$ :  $\bar{v}_\beta - \bar{p}_\beta = 1.12 \cdot 10^{-2}$ .

The composition of phase  $\beta$  was analyzed by a JEOL-JXA 5 microanalyzer using the acceleration voltage of 25 kV. The analysis of several grains have revealed a relatively fixed composition of phase  $\beta$ , because the differences among individual grains did not exceed the statistical error of the instrument. Pure metals were used as standards. The recorded intensities were recalculated to give concentrations using the SONDA 03 program<sup>3</sup> in which corrections on absorption were made in accord with Philibert in Heinrich's modification. Correction on the atomic number was made according to Duncomb and on fluorescence by characteristic radiation according to Reed. The resulting mean weight concentrations  $\bar{c}_\beta$  are summarized in Table I.

Composition of phase  $\alpha$  was a great deal more variable. Mean concentrations of the elements in phase  $\alpha$ ,  $\bar{c}_\alpha$ , were calculated from the mean concentrations  $\bar{c}$  valid for the bulk of the material (analyzed by gravimetric methods) and from the values of  $\bar{c}_\beta$  using

$$\bar{c}\bar{s} = \bar{c}_\alpha\bar{s}_\alpha\bar{v}_\alpha + \bar{c}_\beta\bar{s}_\beta\bar{v}_\beta \quad (2)$$

$\bar{v}_\alpha$  is the volume concentration of phase  $\alpha$  determined from  $\bar{v}_\beta$ :  $\bar{v}_\alpha + \bar{v}_\beta = 1$  and  $\bar{s}$ ,  $\bar{s}_\alpha$ ,  $\bar{s}_\beta$  are mean specific weights. For the alloy we found  $\bar{s} = 2.737 \text{g cm}^{-3}$ . For  $\bar{s}_\beta$  we took the value resulting from the specific weights  $s_i$  of pure metals ( $i = 1, 2, \dots, 9$ ) and their concentrations  $\bar{c}_{\beta i}$  in phase  $\beta$  from the relation  $\bar{s}_\beta = 1 / \left( \sum_{i=1}^9 \bar{c}_{\beta i} / s_i \right)$ . (It is assumed tacitly that the volumes of atoms in the alloy are the same as those in pure

TABLE I

Mean Weight Concentrations of Elements in the Al-Si Alloy

Total concentration ( $\bar{c}$ ), in phase  $\alpha$  ( $\bar{c}_\alpha$ ), in phase  $\beta$  ( $\bar{c}_\beta$ ).

Concentration	Al	Si	Fe	Mn	Cu	Ni	Zn	Mg	Ti
$\bar{c} \cdot 10^2$	84.60	10.08	1.02	0.60	0.81	1.27	0.66	0.94	0.015
$\bar{c}_\alpha \cdot 10^2$	85.03	10.11	0.79	0.402	0.815	1.277	0.667	0.953	0.015
$\bar{c}_\beta \cdot 10^2$	58.75	8.36	17.48	14.81	0.50	0.75	0.18	0.05	0.020

metals. For several alloys of similar composition the specific weights obtained in this way differed from the tabulated values by at most 4%.) Thus we arrived at  $\bar{s}_\beta = 3.37 \text{ g cm}^{-3}$ . From  $\bar{s} = \bar{v}_\alpha \bar{s}_\alpha + \bar{v}_\beta \bar{s}_\beta$  we then obtained  $\bar{s}_\alpha = 2.729 \text{ g cm}^{-3}$ .

Al-Si alloy was chosen for this study, among other reasons, for the possibility of comparing the measurements by microprobe with the values of the inhomogeneity variance published in ref.<sup>2</sup> for the elements Fe, Mn, Cu on chips made of the same material analyzed by gravimetric methods.

The chips were prepared by machine-cutting of a 0.1 mm thick layer off the lateral cut of the cylinder. Depending on their size the chips were divided into three categories, A, B, C, with the following mean dimensions in mm: A:  $0.1 \times 4.0 \times 4.56$ ; B:  $0.1 \times 4.0 \times 1.57$ ; C:  $0.1 \times 2.0 \times 0.5$ . The mean weight of a single chip was:  $G_A = 5.04 \cdot 10^{-3} \text{ g}$ ,  $G_B = 1.73 \cdot 10^{-3} \text{ g}$ ,  $G_C = 2.76 \cdot 10^{-4} \text{ g}$ . The average number of the chips of a given category in a 1 g sample was:  $k_A = 24$ ,  $k_B = 325$ ,  $k_C = 1138$ .

On calculating from the measurements by the microprobe the inhomogeneity variance  $D^2(A)$ , for a set of samples of the size and shape of the category A and similarly also  $D^2(B)$  and  $D^2(C)$ , one can calculate also the inhomogeneity variance for a set of 1 g samples of categories A, B, C in mixture (see Eq. (9) in ref.<sup>4</sup>)

$$D^2(1 \text{ g}) = G_A^2 k_A D^2(A) + G_B^2 k_B D^2(B) + G_C^2 k_C D^2(C). \quad (3)$$

*Regression variance.* The local mean (weight) concentration  $c(X)$  of an element  $X$  obtained by regression shall be designated by the symbol  $c_r(X)$ . The course of  $c_r(X)$  was examined both on the longitudinal and the lateral cut. The beam of electrons energized by 25 kV was expanded to 0.4 mm so that the samples were in shape of 0.4 mm in diameter cylinders about 3.5  $\mu\text{m}$  deep. The number of pulses was recorded in 100 s intervals for each examined spot. A stationary course of the concentration was found on the longitudinal cut in the direction along the axis of the cylinder. For each circle of radius  $\varrho$  we then calculated the average number of pulses per sample,  $N_r(\varrho)$ . The dependence of  $N_r(\varrho)$  on  $\varrho$  was approximated by a straight line. Average numbers of pulses for  $\varrho = 0$  and  $\varrho = 20 \text{ mm}$  (the surface of the cylinder) were 339 000 and 67000, 233 000 and 0, and 112 000 and 121000 for Fe, Mn and Cu respectively.

The distribution of grains of phase  $\beta$  displayed a similar course with 82 grains/ $\text{mm}^2$  at the axis ( $v_{\beta r}(0) = 3.36 \cdot 10^{-2}$ ) and a zero number density of grains at the surface ( $v_{\beta r}(20) = 0$ ). It was established that the composition of phase  $\beta$  at various positions is the same ( $c_{\beta r} = \bar{c}_s$ ). If we adopted the same for phase  $\alpha$  the course of  $c_r(\varrho)$  could be estimated from Eq. (2) leading to the values of grain distribution: for Fe  $c_r(0) = 1.471 \cdot 10^{-2}$ ,  $c_r(20) = 0.79 \cdot 10^{-2}$ , for Mn  $c_r(0) = 0.997 \cdot 10^{-2}$ ,  $c_r(20) = 0.402 \cdot 10^{-2}$  for Cu  $c_r(0) = 0.802 \cdot 10^{-2}$ ,  $c_r(20) = 0.815 \cdot 10^{-2}$ . The found concentration courses, however, are steeper just due to the dependence of  $c_{\alpha r}$  on  $\varrho$ .

The number of pulses  $N_r(\varrho)$  is proportional to the number of atoms of the analyzed

elements. However, it must be considered that the depth,  $h$ , of the sample is not the same in both phases ( $h_\alpha \neq h_\beta$ ). We thus may write

$$N_r(\varrho) = K_1 \{ p_{\alpha r}(\varrho) h_{\alpha r}(\varrho) s_{\alpha r}(\varrho) c_{\alpha r}(\varrho) + p_{\beta r}(\varrho) h_{\beta r}(\varrho) s_{\beta r}(\varrho) c_{\beta r}(\varrho) \}, \quad (4)$$

where  $K_1$  is the proportionality constant. The surface concentrations of phases  $p_{\alpha r}(\varrho)$  and  $p_{\beta r}(\varrho)$  are numerically equal to the volume concentrations  $v_{\alpha r}(\varrho)$  and  $v_{\beta r}(\varrho)$ . In view of the fixed composition of phase  $\beta$  ( $c_{\beta r}(\varrho) = \bar{c}_\beta$ ) we have  $h_{\beta r}(\varrho) = \bar{h}_\beta$ . In phase  $\alpha$  the dependence of  $h_{\alpha r}$  and  $s_{\alpha r}$  on  $\varrho$  is neglected and we put  $h_{\alpha r}(\varrho) = \bar{h}_\alpha$  and  $s_{\alpha r}(\varrho) = \bar{s}_\alpha$ . With the aid of Eq. (2), Eq. (4) can be rearranged to the form

$$N_r(\varrho) = K_2 \{ c_r(\varrho) - \Delta(\varrho) \}, \quad (5)$$

where  $\Delta(\varrho) = v_{\beta r}(\varrho) \bar{s}_\beta \bar{c}_\beta (\bar{h}_\alpha - \bar{h}_\beta) / \bar{h}_\alpha$  and  $K_2 = K_1 \bar{h}_\alpha$ .

The values of  $\bar{h}_\alpha$  and  $\bar{h}_\beta$  were estimated by linear interpolation using specific weight between the data published<sup>5</sup> for Al ( $h \approx 3.7 \mu\text{m}$ ) and Cu ( $h \approx 1.1 \mu\text{m}$ ) with the result  $\bar{h}_\alpha \approx 3.7 \mu\text{m}$  and  $\bar{h}_\beta \approx 3.4 \mu\text{m}$ .

The constant  $K_2$  can be obtained from Eq. (5) by substituting  $\varrho = (2/3)R = 13.3 \text{ mm}$  where  $R$  is the radius of the sample. With a linear dependence of  $c_r$  on  $\varrho$  ( $N_r(\varrho)$  and  $\Delta(\varrho)$  are linear) we find for the position two thirds of the radius away from the axis of the cylinder that  $c_r(13.3) = \bar{c}$ ,  $N_r(13.3)$  is known and  $\Delta(13.3)$  can be calculated ( $v_{\beta r}(13.3) = \bar{v}_\beta = 1.12 \cdot 10^{-2}$ ). Thus we can determine the course of the concentration from  $c_r(\varrho) = N_r(\varrho)/K_2 + \Delta(\varrho)$ . For Fe we obtain  $c_r(0) = 2.237 \cdot 10^{-2}$  and  $c_r(20) = 0.410 \cdot 10^{-2}$ , for Mn  $c_r(0) = 1.797 \cdot 10^{-2}$  and  $c_r(20) = 0$ , for Cu  $c_r(0) = 0.772 \cdot 10^{-2}$  and  $c_r(20) = 0.829 \cdot 10^{-2}$ .

As far as the dependence of  $c_{\alpha r}$  on  $\varrho$  is concerned the quantities  $c_{\alpha r}(0)$  and  $c_{\alpha r}(20)$  take the following values: for Fe  $1.568 \cdot 10^{-2}$  and  $0.411 \cdot 10^{-2}$ , for Mn  $1.23 \cdot 10^{-2}$  and 0, for Cu  $0.780 \cdot 10^{-2}$  and  $0.832 \cdot 10^{-2}$ .

For the calculation of the regression variance  $D_r^2(\omega)$  ref.<sup>1</sup> presents (Eq. (27) in ref.<sup>1</sup>) the formula  $[V(M)]^{-1} \int_{V(M)} (c_r - \bar{c})^2 dV$  where  $V(M)$  stands for the volume of the material,  $dV = dx \cdot dy \cdot dz$ ,  $c_r$  depends only on the coordinates  $x$ ,  $y$ ,  $z$ , and  $\bar{c}$  results from  $\bar{c} = [\bar{s} V(M)]^{-1} \int_{V(M)} c_r s_r dV$ . In our case it is more convenient to change from the cartesian coordinates to the cylindrical ones ( $\varrho, \varphi, z$ ) as the sample is a cylinder of radius  $R$ , height  $Z$  and  $c_r$  then depends only on the distance from the axis of the cylinder. Substituting  $V(M) = \pi R^2 Z$ ,  $dV = \varrho \cdot d\varrho \cdot d\varphi \cdot dz$  and using approximation  $s_r \approx \bar{s}$ , we obtain with a linear course of concentration ( $c_r(\varrho) = c_r(0) + [c_r(R) - c_r(0)]/R$ ), the following expression for the regression variance

$$D_r^2(\omega) = (2/R^2) \int_0^R [c_r(\varrho) - \bar{c}]^2 \varrho d\varrho = (1/18) [c_r(0) - c_r(R)]^2. \quad (6)$$

This expression yields the same value for one chip samples  $\omega = A$ ,  $\omega = B$ ,  $\omega = C$ .

For Fe we obtain  $D_r^2(A) = 1.854 \cdot 10^{-5}$ , for Mn  $D_r^2(A) = 1.792 \cdot 10^{-5}$  and for Cu  $D_r^2(A) = 1.87 \cdot 10^{-8}$ . Substituting  $D_r^2(A) = D_r^2(B) = D_r^2(C)$  into Eq. (3) the regression variance for a set of 1 g samples consisting of chips results as follows: for Fe  $D_r^2(1 \text{ g}) = 3.096 \cdot 10^{-8}$ , for Mn  $D_r^2(1 \text{ g}) = 2.99 \cdot 10^{-8}$  and for Cu  $D_r^2(1 \text{ g}) = 3.126 \cdot 10^{-11}$ .

*The intraphase variance.* The course of concentration for the calculation of the intraphase variance  $D_r^2$  was measured by a microprobe applying the accelerating voltage  $U_0 = 20 \text{ kV}$ ; the width of the electron beam was  $0.5 \mu\text{m}$ .

The size of the analyzed sample in phases  $\alpha$ ,  $\beta$  was estimated with the aid of a simplified model: The sample analyzed by the microprobe was assumed to be shaped as a rotational ellipsoid, the axis of rotation being identical with the axis of the electron beam. The ellipsoid touches the surface of the material at the point of impact of the primary electrons. The true, somewhat different shape of the sample, has been published elsewhere<sup>5</sup>. The dimensions of the ellipsoid in Al were assessed using recommendations published in ref.<sup>5-8</sup>:  $d = 4.4 \mu\text{m}$ , the depth  $h = 2.6 \mu\text{m}$ , the volume  $V = \pi d^2 h / 6 = 26.4 \mu\text{m}^3$ . The mean energy of the primary electrons decreases<sup>9</sup> with the distance,  $l$ , from the entrance point from the initial value  $E_0$  according to the formula:  $E(l) = (E_0^2 - bl)^{1/2}$  where  $b$  is a constant. It is assumed that at the limits of the analyzed region (ellipsoid)  $E(l_{A1})$  is just equal to the ionization energy of the line  $K_\alpha(\text{Al})$ , i.e.  $1.56 \text{ keV}$ .

For the purpose of determining the size of samples in phase  $\alpha$  it was assumed that scattering of electrons took place in the same way as in pure Al and that the region where we analyze for Cu (Fe, Mn) is delimited by the line on which the energy  $E(l_{\text{Cu}})$  equals the ionization energy of the line  $K_\alpha(\text{Cu})$ , i.e.  $8.98 \text{ keV}$ . The analyzed volume analyzed for Cu in phase  $\alpha$  was calculated by multiplying the quantity  $h$  and  $d$  by the ratio  $l_{\text{Cu}}/l_{\text{Al}} = 0.8$ . Thus resulted:  $d = 3.5 \mu\text{m}$ ,  $h = 2.1 \mu\text{m}$ ,  $V = 13.5 \mu\text{m}^3$ . For phase  $\beta$  the quantities  $d$  and  $h$  were multiplied by the ratio of the maximum depth of ionization<sup>5</sup>  $h_\beta/h_\alpha = 0.92$  where  $h \approx h_{\text{Al}} = 1.9 \mu\text{m}$ ;  $h = 1.75 \mu\text{m}$  was evaluated by linear interpolation according to the specific weight between the values  $h_{\text{Al}}$  and  $h_{\text{Cu}} = 0.5 \mu\text{m}$ . For the analysis of Cu in phase  $\beta$  we obtained:  $d = 3.2 \mu\text{m}$ ,  $h = 1.9 \mu\text{m}$ ,  $V = 10.5 \mu\text{m}^3$ . (For Fe and Mn analogously.)

The analysis of Cu was carried out by the microprobe on the surface of the lateral cut along the segment of a straight line  $3 \text{ mm}$  long whose center was  $6 \text{ mm}$  from the axis of the sample cylinder. The concentrations were read off at  $300$  points along this segment,  $c(j)$ ,  $j = 1, 2, \dots, 300$ . These results were processed to give the deviations  $\delta c_r(j)$  of the concentrations  $c(j)$  from the mean phase concentrations in a given point (regression concentrations):  $\delta c_r(j) = c(j) - c_{\alpha r}$ , or  $\delta c_r(j) = c(j) - c_{\beta r}$ . These deviations were in turn used to calculate the intraphase variances:  $D_{\text{ra}}^2(a_\alpha^3) = 3.82 \cdot 10^{-6}$  and  $D_{\text{r}\beta}^2(a_\beta^3) = 1.18 \cdot 10^{-7}$ .

In phase  $\alpha$ , where  $d/h = 1.7$ , the corresponding<sup>1</sup> correction coefficient on non-cubic shape is  $\varepsilon_\alpha = 1.1$ . Hence the analyzed volume  $V = 13,5 \mu\text{m}^3$  has the corresponding correlation-equivalent cubes have the volume  $a_\alpha^3 = \varepsilon_\alpha V = 14.9 \mu\text{m}^3$ . For phase  $\beta$   $d/h$  equals also 1.7 and thus  $a_\beta^3 = 11.6 \mu\text{m}^3$ . For the estimated range of the correlation in phase  $\beta$ , i.e. about 20–50  $\mu\text{m}$ , and for an increased volume of the sample in phase  $\beta$  from  $a_\beta^3$  to  $a_\alpha^3$  the variance  $D_f^2$  remains practically unchanged ( $D_{f\beta}^2(a_\alpha^3) \approx D_{f\beta}^2(a_\beta^3)$ ) (see<sup>1</sup> Fig. 2). The field of the deviations  $\delta_{1c_f}$  corresponding to the standardized volume of the sample ( $a_\alpha^3$ ) is identical with the field of measured deviations  $\delta_{c_f}$ . The next arrangement<sup>1</sup> is multiplication of the deviations  $\delta_{1c_f}$  in phase  $\alpha$  by the coefficient  $\bar{s}_\alpha/\bar{s} = 0.997$  and in phase  $\beta$  by the coefficient  $\bar{s}_\beta/\bar{s} = 1.234$ . Thus obtained deviations  $\delta'_{1c_f}$  have corresponding phase variances  $3.79 \cdot 10^{-6}$  and  $1.80 \cdot 10^{-7}$ . The normalized deviations  $\delta'_{1c_f} = \delta'_{1c_f}/D'_{f\alpha}(a_\alpha^3)$ , or  $\delta'_{1c_f}/D'_{f\beta}(a_\alpha^3)$  were further recalculated to yield the normalized correlation function  $\rho^*(x)$  shown in Fig. 1. Its non-periodic part,  $\rho_n^*(x)$ , is shown in Fig. 2. The periodic part is given by  $\rho_p^*(x) = 0.1 \cdot \cos(2\pi x/2\lambda)$  where  $\lambda = 77 \mu\text{m}$ .

Analogous measurements on the longitudinal cut have shown that in the direction along the axis of the cylinder the range of the correlation as well as its period are approximately twice that found on the lateral cut. This correlation anisotropy was compensated by taking only half of the dimension of the chips A, B, C in the direction of the axis of the cylinder (taking 50  $\mu\text{m}$  instead of 100  $\mu\text{m}$ ) and assuming that the correlation function  $\rho^*(x)$ , computed from measurements on the lateral cut, is valid for all directions

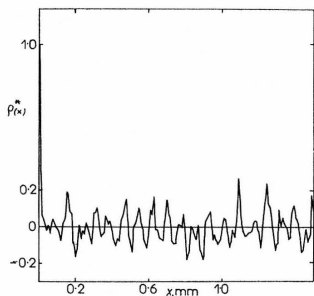


FIG. 1

Correlation Function of Normalized Concentration Deviations from Intrapphase Means for Cu

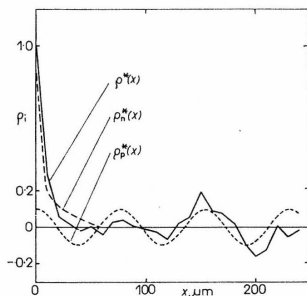


FIG. 2

Correlation Function, Its Non-Periodic and Periodic Parts

For the chips A, B, C the non-periodic part of the variance was found from (ref.<sup>1</sup>, Eq. (9))

$$d_n^{*2}(ka_a^3) = k^{-2} \sum_{i=1}^k \sum_{j=1}^k \varrho_n^*\{x_{ij}\} =$$

$$= k^{-2} \sum_{x=1}^{k_1} \sum_{y=1}^{k_2} \sum_{z=1}^{k_3} \sum_{x'=1}^{k_1} \sum_{y'=1}^{k_2} \sum_{z'=1}^{k_3} \varrho_n^*\{a_a[(x-x')^2 + (y-y')^2 + (z-z')^2]^{1/2}\}, \quad (7)$$

where  $k = k_1 k_2 k_3$  is the number of the cubes  $a_a^3$  in a chip – the parallelepiped of the dimensions  $k_1 a_a$ ,  $k_2 a_a$ ,  $k_3 a_a$ . Thus  $d_n^{*2}(A) = 2.9 \cdot 10^{-5}$ ,  $d_n^{*2}(B) = 8.5 \cdot 10^{-5}$ ,  $d_p^{*2}(C) = 5.0 \cdot 10^{-4}$ .

The periodic part of the variance was computed from (see ref.<sup>1</sup> Eq. (5))

$$d_n^{*2}(b_1 b_2 b_3) = 1/4 \varrho_p^*(0) (\lambda/\pi b_1)^2 \sin^2(\pi b_1/\lambda) (\lambda/\pi b_2)^2 \sin^2(\pi b_2/\lambda) \cdot$$

$$\cdot (\lambda/\pi b_3)^3 \sin^2(\pi b_3/\lambda) \quad (8)$$

where  $b_1, b_2, b_3$  are dimensions of the parallelepiped – the chip and  $\lambda = 77 \mu\text{m}$  is the period of the function  $\varrho_p^*(x)$ . Then:  $d_p^{*2}(A) = 6 \cdot 10^{-12}$ ,  $d_p^{*2}(B) = 5 \cdot 10^{-11}$  and  $d_p^{*2}(C) = 2 \cdot 10^{-9}$ .

According to Eq. (20) of the previous paper the intraphase variance for the chips can be estimated from

$$D_{r_0}^2(A) = d^{*2}(A) [\bar{v}_\alpha D_{r_\alpha}^2(a_\alpha^3) + \bar{v}_\beta D_{r_\beta}^2(a_\beta^3)], \quad (9)$$

where  $d^{*2}(A) = d_n^{*2}(A) + d_p^{*2}(A)$ . For the chips B, C analogously. Thus:  $D_{r_0}^2(A) = 1.1 \cdot 10^{-10}$ ,  $D_{r_0}^2(B) = 3.1 \cdot 10^{-10}$ ,  $D_{r_0}^2(C) = 1.9 \cdot 10^{-9}$ . From here one can estimate the intraphase variance for 1 g samples of the chips using Eq. (3) with the result:  $D_{r_0}(1 \text{ g}) = 8.2 \cdot 10^{-13}$ .

Judging from the course of  $c_f$  for Fe and Mn the intraphase variances for these elements do not exceed the values calculated for Cu.

*The heterogeneity variance.* The heterogeneity variance  $D_n^2$ , caused by the fluctuation of the volume concentration of phase about its regression mean,  $v_{pr}$ , was found by the method of parallelepipeds<sup>1</sup>. The length of the parallelepiped was chosen to be 4 mm (these parallelepipeds compose the chips A and B) or 2 mm (for the chips C). The remaining dimensions of the parallelepiped are equal to the depth,  $h$ , of the analyzed layer.

On a cut perpendicular to the axis of the cylinder we photographed a  $4 \times 4$  mm surface (magnification 27.5) whose center was 3 mm from the axis of the cylinder. This photographed surface was covered by a set of 220 parallel lines 0.5 mm apart

representing the parallelepipeds. Next, we counted how many times each line intersects with a grain of phase  $\beta$ . With the average length of the intersecting segment being  $17.21 \mu\text{m}$  we could compute the volume concentrations,  $v_{\beta}(\omega_1)$ , of phase  $\beta$  in the samples  $\omega_1$  — the parallelepipeds.

The heterogeneous component of the concentration fluctuation  $\delta c_h$  can be expressed<sup>1</sup> by the relation:  $\delta c_h = c_{hr}(\omega_1) - c_r = \sum_{i=1}^m c_{ir} \{v_i(\omega_1) s_{ir} / \sum_{j=1}^m v_j(\omega_1) s_{jr} - v_{ir} s_{ir} / s_r\}$ . In our case we may neglect the differences between the specific weights of individual samples  $\omega_1$  — the parallelepipeds, i.e.  $\sum_{j=1}^m v_j(\omega_1) s_{jr} = s_r$ . Then  $\delta c_h = \sum_{i=1}^m [v_i(\omega_1) - v_{ir}] s_{ir} / s_r = \sum_{i=1}^m \delta v_i s_{ir} / s_r$ . On replacing the phase index  $i$  by the indices  $\alpha$  and  $\beta$  and on using the relation valid for two-phase materials:  $\delta v_{\alpha} = -\delta v_{\beta}$  we obtain

$$\delta c_h = [c_{\beta r} s_{\beta r} / s_r - c_{\alpha r} s_{\alpha r} / s_r] \delta v_{\beta} \quad (10)$$

( $s_r, s_{\alpha r}, s_{\beta r}, c_{\alpha r}, c_{\beta r}$  designate regression values of the corresponding quantities at the particular photographed spot).

From the deviations  $\delta v_{\beta}$  we can thus calculate the variances  $\Delta_h^2$  of the volume concentrations of phase  $\beta$  in the chips A, B, C. Multiplying these variances by the factor  $(\delta c_h / \delta v_{\beta})^2 = [(s_{\beta r} / s_r) c_{\beta r} - (s_{\alpha r} / s_r) c_{\alpha r}]^2$  the heterogeneity variances,  $D_h^2$ , corresponding to the deviations  $\delta c_h$  for individual elements result.

The correlation function  $R_2(l)$  of the deviations  $\delta v_{\beta}$  for the 2 mm parallelepipeds and  $R_4(l)$  for 4 mm long parallelepipeds are shown in Fig. 3. Their non-periodic parts,  $R_{2n}(l)$  and  $R_{4n}(l)$ , are also shown in that figure. For their periodic parts we found the following expressions (1 in  $\mu\text{m}$ )

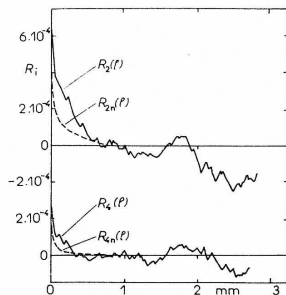


FIG. 3

Correlation Functions of Volume Concentration Fluctuations of Phase  $\beta$  in  $2 \times 4$  mm Parallelepipeds

$R_{2n}(l)$  and  $R_{4n}(l)$  are the non-periodic parts of the functions  $R_2(l)$  and  $R_4(l)$ .



$$R_{2p}(l) = 10^{-5} \{2.22 \cos(2\pi l/107) + 7.41 \cos(2\pi l/963) + 7.41 \cos(2\pi l/1635) + 7.41 \cos(2\pi l/4360)\},$$

$$R_{4p}(l) = 10^{-5} \{1.48 \cos(2\pi l/107) + 4.62 \cos(2\pi l/963) + 2.77 \cos(2\pi l/1635) + 1.00 \cos(2\pi l/4360)\}. \quad (11)$$

The non-periodic part  $\Delta_{\text{hn}}^2(\mathbf{A})$  of the variance  $\Delta_n^2(\mathbf{A})$  of the volume concentrations of phase  $\beta$  in the chips A is given by  $k^{-2} \sum_{i=1}^k \sum_{j=1}^k R_{4n}(l_{ij})$  (see ref.<sup>1</sup> Eq. (9)) where  $k$  designates the number of parallelepipeds forming the chip A. The length of the parallelepipeds (4000  $\mu\text{m}$ ) is identical with the length of the chip. In the direction of the width of the chip (4560  $\mu\text{m}$ ) individual parallelepipeds shall be distinguished by the subscript  $x$  ( $x = 1, 2, \dots, k_1$ ;  $k_1 = 4560/h$ ); in the direction of the thickness of the chip (100  $\mu\text{m}$ ) by the subscript  $y$  ( $y = 1, 2, \dots, k_2$ ;  $k_2 = 100/h$ ). The number of the parallelepipeds is thus  $k = k_1 k_2$ . Position of a parallelepiped is fixed by a pair of numbers  $x, y$ , and the distance of a parallelepiped  $(x, y)$  from  $(x', y')$  is given by  $h \cdot \sqrt{(x - x')^2 + (y - y')^2}$ . Thus we use the expression

$$\Delta_{\text{hn}}^2(\mathbf{A}) = (k_1 k_2)^{-2} \sum_{x=1}^{k_1} \sum_{y=1}^{k_2} \sum_{x'=1}^{k_1} \sum_{y'=1}^{k_2} R_{4n}(h \sqrt{(x - x')^2 + (y - y')^2}). \quad (12)$$

For the chips B analogously. For C we use the function  $R_{2n}$  to obtain  $\Delta_{\text{hn}}^2(\mathbf{A}) = 0.49 \cdot 10^{-5}$ ,  $\Delta_{\text{hn}}^2(\mathbf{B}) = 1.33 \cdot 10^{-5}$ ,  $\Delta_{\text{hn}}^2(\mathbf{C}) = 12.88 \cdot 10^{-5}$ .

The periodic parts were computed from the equations (see ref.<sup>1</sup> Eqs (6), (4))

$$\Delta_{\text{hp}}^2(\mathbf{A}) = \sum_{j=1}^4 \Delta_{\text{hpj}}^2(\mathbf{A}), \quad (13)$$

$\Delta_{\text{hpj}}^2(\mathbf{A}) = 1/2 R_{4pj}(\alpha_j/4560\pi)^2 \sin^2(4560\pi/\alpha_j) (\alpha_j/100\pi)^2 \sin^2(100\pi/\alpha_j)$ , where we substitute from Eq. (11) the amplitudes  $R_{4pj}$  ( $R_{4p1} = 1.48 \cdot 10^{-5}$ ,  $R_{4p2} = 4.62 \cdot 10^{-5}$ ,  $R_{4p3} = 2.77 \cdot 10^{-5}$ ,  $R_{4p4} = 1.00 \cdot 10^{-5}$ ) and the periods  $\alpha_j$  ( $\alpha_1 = 107 \mu\text{m}$ ,  $\alpha_2 = 963 \mu\text{m}$ ,  $\alpha_3 = 1635 \mu\text{m}$ ,  $\alpha_4 = 4360 \mu\text{m}$ ). The dimensions of the chip A are 4560  $\mu\text{m}$  and 100  $\mu\text{m}$ . For the chips B, C analogously. We obtain:  $\Delta_{\text{hp}}^2(\mathbf{A}) = 1.3 \cdot 10^{-7}$ ,  $\Delta_{\text{hp}}^2(\mathbf{B}) = 4.0 \cdot 10^{-6}$ ,  $\Delta_{\text{hp}}^2(\mathbf{C}) = 6.2 \cdot 10^{-5}$ .

In the calculation it was assumed that the correlation functions  $R_2(l)$  and  $R_4(l)$  remained valid also in the plane of the longitudinal cut. Strictly speaking though, this assumption is not justified because random aggregates of the grains were of circular shape on the lateral cut while on the longitudinal cut they were markedly prolonged in the direction of the axis of the cylinder. A test calculation for samples of area

identical with that of the chips A, B, C but consisting only of a single layer of parallelipeds ( $k_2 = 1$ ) revealed that the appropriate variances  $A_{\text{hn}}'^2$  are only slightly larger than  $A_{\text{hn}}^2$  computed above ( $A_{\text{hn}}'^2(\text{A}) = 1.3 \cdot 10^{-7}$ ,  $A_{\text{hn}}'^2(\text{B}) = 4.1 \cdot 10^{-6}$ ,  $A_{\text{hn}}'^2(\text{C}) = 6.2 \cdot 10^{-5}$ ) and that  $A_{\text{hp}}'^2 = A_{\text{hp}}^2$ . With increasing range of correlation in the direction of the axis of the cylinder the variances  $A_{\text{hn}}^2$  reach  $A_{\text{hn}}'^2$  at most. This difference is regarded as insubstantial and, accordingly, the correlation anisotropy was disregarded.

The appropriate variances  $A_{\text{h}}'^2 = A_{\text{hn}}'^2 + A_{\text{hp}}'^2$  were also determined on seven spots on the lateral cut directly by measuring the surface concentration of grains of phase  $\beta$  on the surfaces equaling in size to the extent of the chips A, B, C. It turned out that the variance  $A_{\text{h}}'^2$  decreases with the distance from the axis of the cylinder. At the photographed point, where the correlation functions  $R_2(l)$  and  $R_4(l)$  had been determined, the surface variance  $A_{\text{h}}'^2$  was four times greater than the mean for the whole sample. For this reason the heterogeneity variances were computed from

$$D_{\text{h}}^2 = (1/4) (\delta c_{\text{h}} / \delta v_{\text{h}})^2 A_{\text{h}}^2 \quad (14)$$

with the results: for Fe  $D_{\text{h}}^2(\text{A}) = 0.55 \cdot 10^{-7}$ ,  $D_{\text{h}}^2(\text{B}) = 1.81 \cdot 10^{-7}$ ,  $D_{\text{h}}^2(\text{C}) = 20.7 \cdot 10^{-7}$ , for Mn  $D_{\text{h}}^2(\text{A}) = 0.42 \cdot 10^{-7}$ ,  $D_{\text{h}}^2(\text{B}) = 1.38 \cdot 10^{-7}$ ,  $D_{\text{h}}^2(\text{C}) = 15.8 \cdot 10^{-7}$ , for Cu  $D_{\text{h}}^2(\text{A}) = 0.41 \cdot 10^{-11}$ ,  $D_{\text{h}}^2(\text{B}) = 1.29 \cdot 10^{-11}$ ,  $D_{\text{h}}^2(\text{C}) = 14.8 \cdot 10^{-11}$ . The inhomogeneity variances for 1 g samples  $D_{\text{h}}^2(1 \text{ g})$  computed from the previous data using Eq. (3) are summarized in Table II.

## DISCUSSION

The computed values of the regression variance  $D_{\text{r}}^2$ , the intraphase variance  $D_{\text{f}}^2$ , the heterogeneity variance  $D_{\text{h}}^2$ , and their sum the inhomogeneity variance  $D_{\text{j}}^2$  related to a 1 g sample are summarized in Table II.

For comparison Table II shows also the inhomogeneity variances determined<sup>2</sup> for the chips of the same material from analyses by gravimetric methods (designated by  $\sigma_{\text{h}}^2(1 \text{ g})$ ). For Fe and Mn the computed variance  $D_{\text{j}}^2$  approximately corresponds to the measured variance  $\sigma_{\text{h}}^2$ . In case of Cu a serious discrepancy exists between the two values. A probabilistic interpretation of results<sup>2</sup> admits as an alternative the agreement between  $\sigma_{\text{h}}^2$  and  $D_{\text{j}}^2$  only with a 1% probability. The disagreement between  $\sigma_{\text{h}}^2$  and  $D_{\text{j}}^2$  can be attributed to the following causes: Failure to satisfy the condition of independence of the variance of the measuring method  $\sigma_{\text{m}}^2$  on the amount of the sample (losses during dissolution, etc.), different distribution of Cu in the part used to make the chip, the error of the method<sup>1</sup> used to process the measurements by the microprobe. The last possibility was tested experimentally: The examined material was analyzed on the lateral cut by the microprobe using a wider beam of rays. The analyzed samples were in the shape of discs 400  $\mu\text{m}$  in diameter. A set of 24 measure-

ments yielded the inhomogeneity variance  $D_{\text{exp}}^2 = 1.8 \cdot 10^{-8}$  due to the fluctuation of Cu concentration about  $c_r$ . Corresponding variance<sup>1</sup> is  $D_r^2 + D_h^2$ . (The method<sup>1</sup> of calculation of  $D_r^2$  is supported by the results for Fe and Mn given in Table II).

The intraphase variance  $D_r^2 = D_{r_n}^2 + D_{r_p}^2$  was computed for the discs by the above outlined method:  $D_{r_n}^2 = 2.1 \cdot 10^{-8}$ ,  $D_{r_p}^2 = 6 \cdot 10^{-10}$ .

The heterogeneity variance for the discs,  $D_h^2$ , was determined by interpolation. On part of greater samples the variances of samples equalling in extent to the area of the chips A, B, C are known as well as the thickness given by the depth of the analyzed layer. For samples smaller than the grain of phase  $\beta$  the heterogeneity variance was computed from (Eq. (23) in ref.<sup>1</sup>)

$$D_h^2(\omega) = v_{\alpha r}(c_{\alpha r} - c_r)^2 + v_{\beta r}(c_{\beta r} - c_r)^2 - r_\omega \frac{1}{\bar{v}} S_{\alpha\beta}(c_{\alpha r} - c_{\beta r})^2 = \\ = (11.0 - 0.31r_\omega) 10^{-8}. \quad (15)$$

$r_\omega$  (in  $\mu\text{m}$ ) is the radius of the cylinder  $\omega$ ,  $S_{\alpha\beta} = \bar{v}\pi\bar{d}$  is the area of interface between phases  $\alpha$  and  $\beta$  in a unit volume,  $\bar{v} = 27.3 \text{ mm}^{-2}$  is the mean number of grains on a unit area of lateral cut and  $\bar{d} = 21.9 \mu\text{m}$  is the mean diameter of grains on the cut. Graphical interpolations for the disc of radius  $400 \mu\text{m}$  yielded the value  $D_h^2 = (3 \pm 2) \cdot 10^{-9}$  and  $D_r^2 + D_h^2 \approx 2.4 \cdot 10^{-8}$ . This value, according to our opinion, is in a satisfactory agreement with the experimental value  $D_{\text{exp}}^2 = 1.8 \cdot 10^{-8}$ .

From our supplementary experiment it thus follows that the disagreement between the inhomogeneity variance found for Cu in this and the previous work rests in the erroneous value in the earlier work<sup>2</sup>. The cause of this error was probably an accidental loss of material on dissolution of some of the samples. With a relatively small number of analyses this could significantly impair the result.

Table II

Inhomogeneity Variance and Its Components for Fe, Mn, and Cu in the Al-Si Alloy

Variance	Fe	Mn	Cu
$D_r^2$ (1 g)	$3.10 \cdot 10^{-8}$	$2.99 \cdot 10^{-8}$	$3.13 \cdot 10^{-11}$
$D_f^2$ (1 g)	$< 10^{-12}$	$< 10^{-12}$	$8.2 \cdot 10^{-13}$
$D_h^2$ (1 g)	$3.9 \cdot 10^{-10}$	$3.0 \cdot 10^{-10}$	$2.8 \cdot 10^{-14}$
$D_f^2$ (1 g)	$3.14 \cdot 10^{-8}$	$3.02 \cdot 10^{-8}$	$3.21 \cdot 10^{-11}$
$\sigma_h^2$ (1 g)	$1.29 \cdot 10^{-8}$	$3.52 \cdot 10^{-8}$	$2.67 \cdot 10^{-8}$

In comparison with the previous paper the method used in this work yields more reliable results. In addition, one can make use of the obtained information about the structure of the inhomogeneity variance to optimize the size and/or shape of the chips: The dominant role of the regression variance  $D_j^2$  for the examined material suggests that for samples of the size of a single chip the inhomogeneity variances are virtually the same:  $D_j^2(A) = D_j^2(B) = D_j^2(C)$ . From this we may conclude that the homogeneity of the chips can be achieved by diminishing their size: 1 g of chips A consists of 198 chips and their inhomogeneity variance for a sample of this weight is at good mixing  $D_j^2(A)/198$ , while 1 g of the chips C contains 3622 chips and the corresponding variance is  $D_j^2(C)/3622$ . Granular material consisting of the chips C thus displays homogeneity by an order of magnitude better than the material consisting of the chips A.

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#### REFERENCES

1. Boháček P.: This Journal, in press.
2. Boháček P., Novák J., Ryšavá N.: This Journal 37, 1227 (1972).
3. Škvára F., Hulínský V.: Exp. Tech. Physik 19, 6 (1971).
4. Boháček P.: This Journal, in press.
5. Shinoda G.: Presented at the Vth Int. Congr. X-Ray Optics and Microanalysis, Tübingen 1968.
6. Read S. J. B.: Presented at Conf. on X-Ray Optics and Microanalysis, University of Paris, Paris 1966.
7. Shinoda G., Murata K., Shimizu R.: Special Publ. NBS 298, Washington D.C. 1968.
8. Andersen C. A.: Brit. J. Appl. Phys. 18, 1033 (1967).
9. Cosslet V. E., Thomas R. N.: Presented at Conf. on X-Ray Optics and Microanalysis, University of Paris, Paris 1966.

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