Chemical segregation of solute elements in ultrasonically gas atomized aluminium alloy powders

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Abstract. A new experimental approach to the evaluation of chemical segregation of solute elements in ultrasonically gas atomized aluminium-alloy powders using X-ray spectral data of scanning electron microprobe analyser is described. The experimentally obtained chemical segregation data is compared with the conventional method of quantitative analysis and with theoretical predictions as determined from Scheil's approach to the evaluation of elemental segregation during the solidification process. A comparison of experimental and theoretical predictions confirms the validity of the experimental approach in the estimation of solute segregation levels and also suggests that the solidification conditions considered for estimation of microchemical segregation can appropriately be applied to ultrasonically gas atomized powders.

Keywords. Segregation; solute elements; powders; microprobe.

1. Introduction

In recent years gas atomization of metals and alloys has emerged as an important technological process for the production of rapidly solidified powders in view of greater potential of alloying flexibility, microstructure and property control (Lavernia and Grant 1986; Wang *et al* 1987). Among the different gas atomization techniques used for production of metal alloy powders, ultrasonic gas atomization (USGA) has emerged as one of the major techniques for the production of fine powders with high solidification rates (10^4–10^5 K/s).

In any solidification process, when the starting liquid of uniform composition is solidified progressively, the composition of the solid is not uniform; the distribution of solute in the solid, when solidification is complete, is different from that in the liquid, although the total amount of solute remains unchanged (Chalmers 1964). There are several limiting cases for the solute redistribution in liquid and solid. These are discussed elsewhere (Chalmers 1964). Whatever may be the method of solidification process for the alloy, chemical segregation of alloying elements determines the ultimate properties of the alloy (Misra and Balasubramanian 1985; Misra *et al* 1987a, b).

Thus a study concerning the production of alloy using a rapid solidification processing route, in the present case, ultrasonic gas atomization, necessitates examination of chemical segregation of solute elements, particularly in view of their important role in consolidation and subsequent processing steps. The investigation of chemical segregants also allows monitoring of microstructural development during various stages of processing.

Our laboratory has recently undertaken a major programme in the production of rapidly solidified non-ferrous alloy powders, namely aluminium and copper alloys, by the ultrasonic gas atomization (USGA) technique. We report here the results

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concerning the chemical segregation of alloying elements in ultrasonically atomized aluminium-alloy powders using a scanning electron probe microanalyser (SEPMA). The new approach of utilising X-ray spectral data of SEPMA for evaluation of chemical segregation level is compared with the conventional method of quantitative analysis and theoretical segregation predictions as determined from Scheil's approach (Kurz and Fischer 1984) to the estimation of solute segregation.

2. Experimental

A series of aluminium-alloy powders of nominal composition: Al–5·45 Zn–1·30 Cu–2·07 Mg–0·16 Fe–0·11 Si–0·06 Mn (alloy-1) and Al–1·36 Li–0·92 Cu–0·66 Mg (alloy-2) (all in wt.%) were made by ultrasonic gas atomization (USGA) process. Details of ultrasonic gas atomization set-up and operating conditions are discussed elsewhere (Pandey *et al* 1987, 1988). The powders pertaining to each of the two aluminium-alloy powders were found to be essentially free of oxides. The microstructure and morphology of atomized powders were examined by optical and scanning electron microscopy (SEM) techniques and the extent of chemical segregation of alloying elements was studied with a scanning electron probe microanalyser (SEPMA).

The scanning electron microprobe has emerged as a powerful and ideally suited technique for the measurement of micro-chemical characterization in materials. The technique can be used in applications which require spatial resolution of the order of a micron or less depending on operating conditions. The scanning electron probe microanalyser (CAMEBAX-MICRO) used for the present work is an electron microprobe with an optical and secondary electron microscope for sample observation and imaging, equipped with a programmable microprocesser controlled wavelength dispersive type X-ray analyser system for chemical analysis, and a PDP 11/03 mini-computer for fast data acquisition and processing. In the present study, the three corrections, viz. atomic number (Z), absorption (A) and flourescence (F) were taken care of by the COR 2 ZAF programme run by the PDP computer with on-line facility.

Two different experimental approaches were used to study the extent of micro-chemical segregation of solute elements in the indigeneously produced aluminium alloy powders. In each of the two approaches, individual powder particles were selected for analyses and the electron probe focussed at the dendrite centre and dendrite edge regions respectively.

In the first approach, absolute concentration of solute elements was determined using elemental standards for each of the two regions (dendrite centre and dendrite edge). The solute element segregation ratio, in this case, is defined as:

$$R_q = \frac{\% \text{ solute concentration (dendrite centre)}}{\% \text{ solute concentration (dendrite edge)}}. \tag{1}$$

In the second method of analysis, X-ray spectral data was printed graphically as a plot of crystal position in sin theta units against count rate and the extent of solute element segregation was evaluated in terms of a ratio, R_s defined by:

$$R_s = \frac{\text{peak area (dendrite centre)}}{\text{peak area (dendrite edge)}}. \tag{2}$$

X-ray spectral data for both dendrite centre and dendrite edge regions were obtained at identical operating conditions (i.e. same beam current, voltage etc). It is therefore possible to suitably utilise the spectra for evaluation of the extent of chemical segregation by comparing the elemental peak areas between the two spectra.

The chemical segregation data obtained experimentally by the aforementioned two approaches [(1) and (2)] using the scanning electron probe microanalyser was compared with the theoretical predictions as obtained from Scheil's approach to the evaluation of elemental segregation in the solidification process (Kurz and Fischer 1984, see below).

3. Results and discussion

A typical scanning electron micrograph of Al–Zn–Cu–Mg (alloy–1) powder is presented in figure 1. It may be noted from this figure that the particles are largely spherical in nature indicative of in-flight solidification of powder particles. However, a significant fraction of satellite population can also be seen. At high magnification, examination of the cross-section of the particle shows largely a dendritic structure, however, in some particles, a mixed structure comprising a columnar-equiaxed was observed. The equiaxed structure was characterized by the absence of directional growth in the polished section. A similar structure was observed for each of the two alloy powders.

Quantitative point analysis data pertaining to dendrite centre and dendrite edge for major solute elements are presented in table 1 for both the indigenously produced aluminium-alloy powders. Solute segregation ratios calculated from (1) is also presented in table 1. The ratios are indicative of a significant extent of segregation of alloying elements.

Typical X-ray spectral data obtained from a 40–50 μm Al–Zn–Cu–Mg (alloy–A) and Al–Li–Cu–Mg (alloy B) powder particles corresponding to the dendrite centre and dendrite edge are presented in figures 2 and 3 respectively. A comparison of elemental peak areas between the two spectra pertaining to the dendrite centre and dendrite edge clearly shows the presence of a significant amount of solute element enrichment at the dendrite edge. In a similar manner, analysis was carried out at different locations and for the other ultrasonically atomised aluminium-alloy powder particles. In each case powder particles of 40–50 μm size were selected for evaluation of microchemical segregation. The solute element segregation ratio, R_s [(2)] for both the aluminium-alloy powders is presented in table 1.

In an atomization process, heat transfer is a complex phenomenon, particularly, in view of its strong dependence on particle size and the comparatively weaker dependence on relative velocity between gas and particle and the atomizing gas (Clyne *et al* 1984). A knowledge of heat transfer coefficient allows evaluation of solidification time as described below.

The total heat to be removed in a superheated melt is given by (Clyne *et al* 1984)

$$\Delta H = (\pi d^3/6)(C_L \Delta T_s + \Delta H_f), \tag{3}$$

where d is the particle diameter, C_L is the specific heat of liquid, ΔT_s is the superheat, ΔH_f is the latent heat of fusion. The time interval, t_f, required for removal of heat is given by (Clyne *et al* 1984)
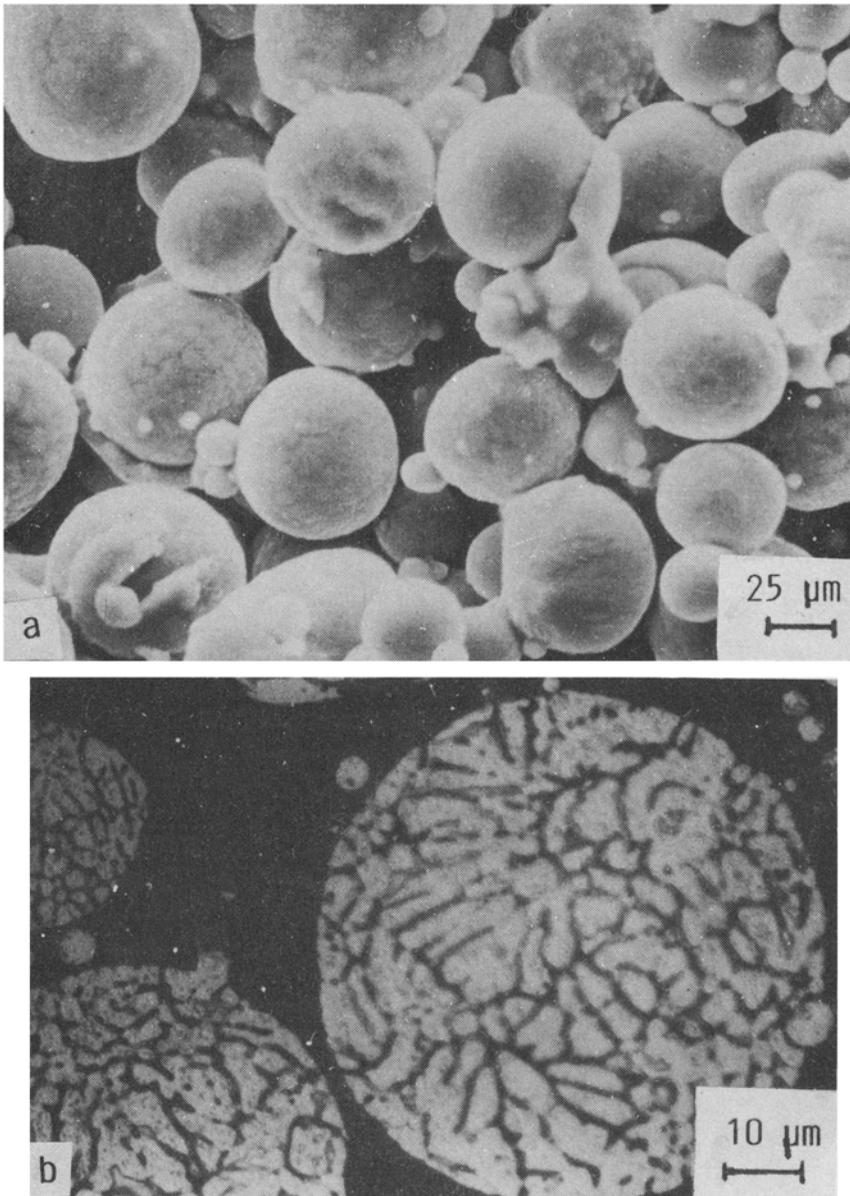
Figure 1. Typical scanning electron micrographs of Al–Zn–Cu–Mg alloy (alloy-A) powder produced by ultrasonic gas atomization technique, (a) low magnification micrograph showing spherical nature of particles, and (b) high magnification micrograph of the cross-section of the particle showing dendritic structure.

$$t_f \approx \Delta H/(h_i \Delta T_i \pi d^2) = d(C_L \Delta T_s + \Delta H_f)/(6h_i \cdot \Delta T_i),\tag{4}$$

where h_i is the interfacial heat transfer coefficient and ΔT_i is the temperature difference between isothermal droplet (assumed) and gas. The interfacial heat transfer coefficient, h_i, is given by (Clyne *et al* 1984):

Table 1. Composition of solute elements at the dendrite centre and dendrite edge as determined by quantitative microprobe analysis.

| Alloy systems | Solute elements | % Average composition | | Segregation ratio $R = \dfrac{\text{dendrite centre}}{\text{dendrite edge}}$ |
		Dendrite centre	Dendrite edge	
Al–5·45 Zn–1·30 Cu–2·07 Mg	Zn	2·23	6·52	0·342
–0·16 Fe–0·11 Si	Cu	0·06	1·52	0·039
	Mg	0·25	1·70	0·147
Al–1·36 Li–0·92 Cu–0·66 Mg	Cu	0·14	3·70	0·037
	Mg	0·25	1·61	0·155

$$h_i = (2\,K/d) + 0.6\,(u/d)^{1/2}\,(K^2 c)^{1/3}\,(\rho/\mu)^{1/6}, \tag{5}$$

where u is the convective flow velocity, K is the thermal conductivity, C is the specific heat, ρ is the density and μ is the viscosity.

For argon atomized particle of diameter $d = 50\ \mu$m, $K = 0.02\ \text{Wm}^{-1}\,K^{-1}$ (Clyne *et al* 1984), $\mu = 3 \times 10^{-5}\ \text{Pa s}$ (Clyne *et al* 1984), $c = 950\ \text{Jm}^{-3}\,K^{-1}$ (Clyne *et al* 1984), $\rho = 1.8\ \text{kgm}^{-3}$ (Clyne *et al* 1984) and $u = 307\ \text{ms}^{-1}$ (Wang *et al* 1987), (5) yields $h_i = 7.5 \times 10^3\ \text{Wm}^{-2}\,K^{-1}$. Now substituting $h_i = 7.5 \times 10^3\ \text{Wm}^{-2}\,K^{-1}$, $C_L = 2.4 \times 10^6$ $\text{Jm}^{-3}\,K^{-1}$ (Clyne *et al* 1987), $\Delta H_f = 9.4 \times 10^8\ \text{Jm}^{-3}$ (Clyne *et al* 1987), $\Delta T_i = 600\ K$ (assumed value) and our experimental values of $\Delta T_s = 150\ K$ gives $t_f = 2.5$ ms from (4).

An idea of solidification time allows the expected departure from the equilibrium conditions at the solidification interface to be known with a reasonably high degree of accuracy. It however does not permit a detailed analysis of the solidification process in view of the complex nature of transport equations which incorporate partitioning of solute at the interface, the dependence of growth velocities on interface temperature and composition etc. There, however, exists a method by which a simplified solidification analyses can be carried out. This involves application of Scheil equation (see below) (Kurz and Fischer 1984) to predict solute profiles arising from solidification for the limiting case of total equilibrium partitioning at the interface and with no backward diffusion in the solid. These solute profiles can then be utilised to estimate microchemical segregation levels. It has recently been shown that back diffusion is negligible for ultrasonically gas atomized aluminium–lithium alloy powders with cellular structure (Ricks *et al* 1986) and hence Scheil analysis can be used to predict solute composition profiles, for particle growth velocities of less than $1\ \text{ms}^{-1}$. The growth velocity of powder particles of diameter $50\ \mu$m, can be evaluated by dividing the dendritic arm spacing ($\sim 2\ \mu$m) by the solidification time ($t_f = 2.5$ ms). This gives a value of $u = 8 \times 10^{-4}$ ms^{-1}. Now having evaluated the particle growth velocity, it is now possible to estimate the solute enriched layer, β, given by

$$\beta = D_L/u, \tag{6}$$

where D_L is the diffusivity of the solute in the liquid alloy. For $D_L = 10^{-8}\ \text{m}^2\ \text{s}^{-1}$, and $u = 8 \times 10^{-4}\ \text{ms}^{-1}$ (see above), the extent of solute enriched layer β is $12\ \mu$m. A comparison of this value with the dendrite arm spacing of $2\ \mu$m, implies that the liquid will be homogeneous during the lateral growth process—a condition
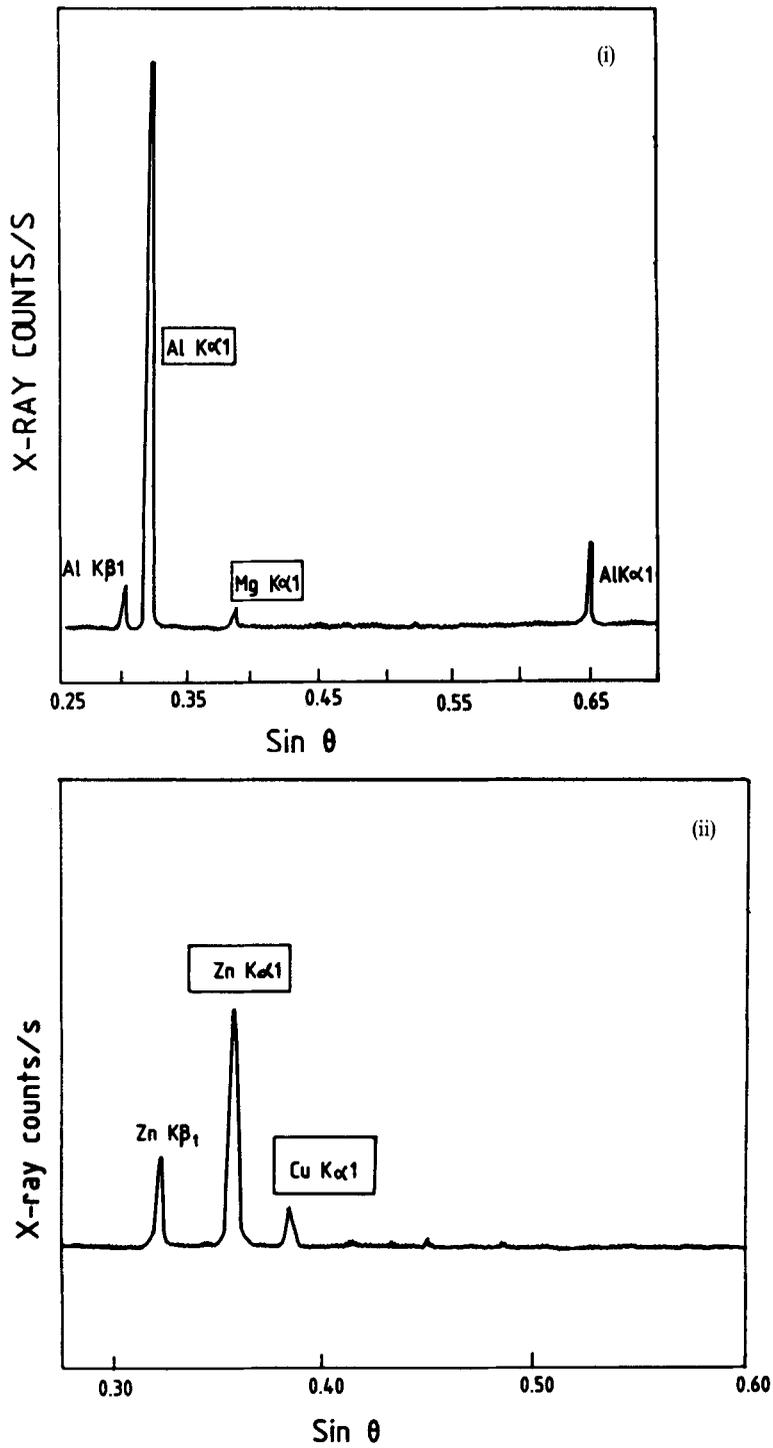
Figure 2. X-ray spectral data obtained from the (a) dendrite centre and (b) dendrite edge in an Al–Zn–Cu–Mg alloy powder of 40 μm diameter (alloy-A). (i) and (ii) are spectral data obtained from two different spectrometers in order to cover all the alloying elements of interest. (Elemental peaks that are enclosed in boxes are the ones that have been considered for calculation of segregation ratio.)
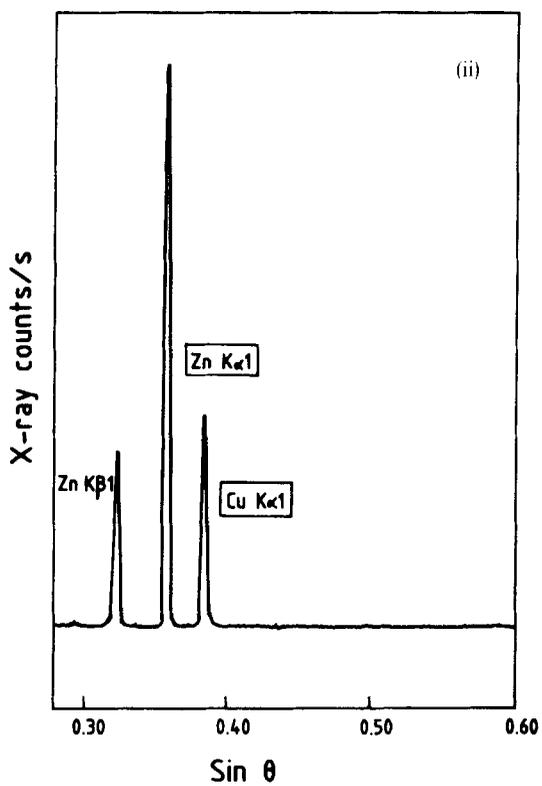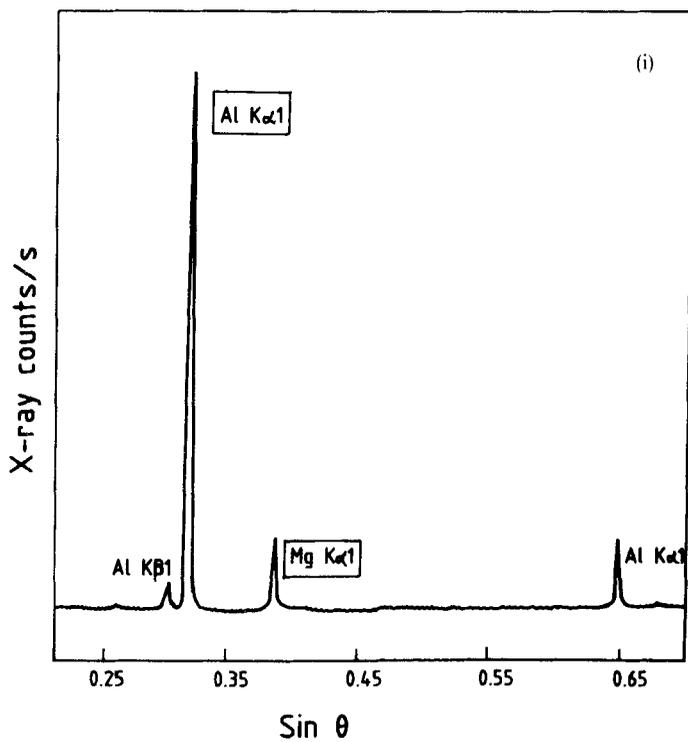
Figure 2b. (i) **and** (ii).

necessary for application of Scheil's equation. It is known (Ricks *et al* 1986) that for the aforementioned solidification conditions, back diffusion will be negligible and hence Scheil's equation can be used to theoretically predict solute composition profiles. The Scheil equation may be written as (Kurz and Fischer 1984; Ricks *et al* 1986):

$$C_s^i = kC_0 (1 - f_s)^{(k-1)}, \tag{7}$$

where C_s^i is the interfacial solid composition, C_0 is the average alloy composition, f_s is the fraction of solid and k is the partition coefficient. The theoretical solute profiles across a dendrite with the dendrite boundary being defined at the (solid) copper concentration are presented in figures 4 and 5 for both the alloy powders. The values of the partition coefficient used to construct the profile are: $k_{Cu} = 0.13$, $k_{Mg} = 0.49$ and $k_{Zn} = 0.72$ (Ricks *et al* 1986).
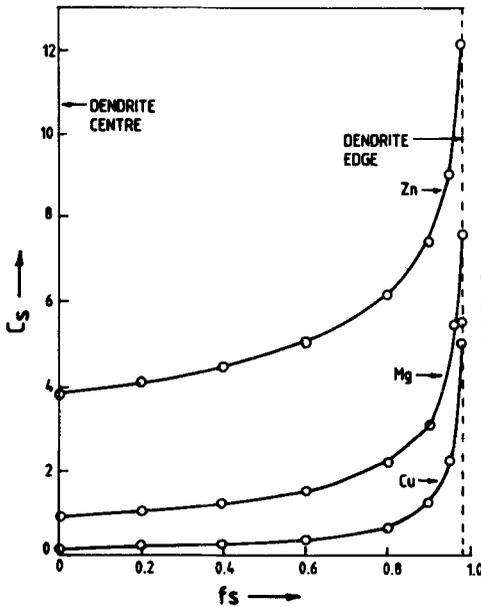

Figure 3. Solute composition profiles for Al–Zn–Cu–Mg alloy (alloy-A) across the dendritic solidification structure as calculated from Scheil's analysis, (7).
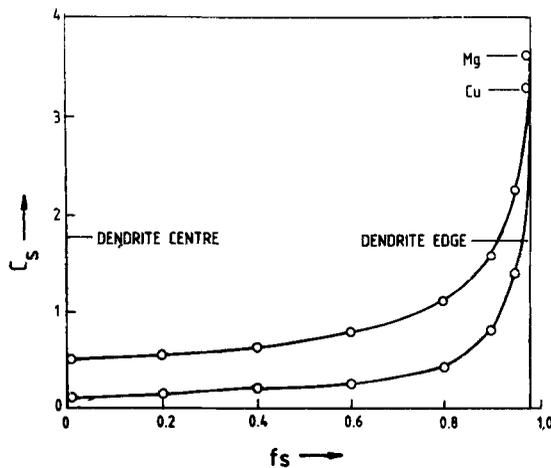

Figure 4. Solute composition profiles for Al–Li–Cu–Mg alloy (alloy-B) across the dendritic solidification structure as calculated from Scheils analysis, (7).

Table 2. Degree of segregation in ultrasonically gas atomized aluminium-alloy powders.

Alloy systems	Solute elements	Degree of segregation		
		Theoretical ratio	Experimental ratio	
			From X-ray spectral data	From quantitative point analysis
Al–5·45 Zn–1·30 Cu–2·07 Mg–0·16 Fe–0·11 Si	Zn	0·32	0·290	0·342
(Alloy A)	Cu	0·030	0·036	0·039
	Mg	0·128	0·112	0·147
Al–1·36 Li–0·92 Cu–0·66 Mg	Li	–	–	–
(Alloy B)	Cu	0·033	0·036	0·037
	Mg	0·136	0·129	0·155

The theoretical values of segregation level calculated from solute composition profiles [figures 5 and 6; Scheil equation (7)] are listed in table 2. A comparison of the predicted values obtained from Scheil analysis and the experimentally determined values from electron microprobe analysis [quantitative point analysis, (1), and X-ray spectral data, (2)] shows that there exists a favourable correlation between the two sets of data. The favourable agreement confirms that the conditions of solidification assumed for microchemical segregation studies can be appropriately applied to ultrasonically gas atomized aluminium-alloy powder particles of diameter less than 50 μm. It also clearly demonstrates the validity of the experimental approach in the estimation of the extent of microchemical segregation.

4. Conclusions

(i) Microchemical examination of ultrasonically gas atomized aluminium-alloy powders has indicated the presence of equilibrium segregation of all the major alloying elements in the particles of 40–50 μm diameter to a considerable extent.
(ii) There is fair agreement between experimentally and theoretically determined values of chemical segregation level, which confirms the validity of the experimental approach.
(iii) The solidification conditions assumed to predict solute composition profile are applicable to atomized powders produced by ultrasonic gas atomization.
(iv) The study highlights the relevance of microchemical characterization of atomized powders which is of importance in subsequent stages of powder processing.

Acknowledgements

References

Chalmers B 1964 *Principles of solidification* (New York: Wiley)
Clyne T W, Ricks R A and Goodhew P J 1984 *Int. J. Rapid Solidification* **1** 59

Clyne T W, Ricks R A and Goodhew P J 1987 *Proc. 5th Int. Conf. on Rapidly Solidified Metals* (eds) S Steels and H Worlimont Wurzburg, p. 903

Kurz W and Fischer D J 1984 *Fundamentals of solidification* (Switzerland: Trans Tech Publications) p. 129

Lavernia E J and Grant N J 1986 *Met. Powder Rep.* 255

Misra R D K and Balasubramanian T V 1985 *Scr. Metall.* **19** 1177

Misra R D K, Balasubramanian T V and Rama Rao P 1987a *Mater. Sci. Lett.* **6** 125

Misra R D K, Balasubramanian T V and Rama Rao P 1987b *Acta Metall.* **35** 2995

Misra R D K, Prasad C Y, Balasubramanian T V and Rama Rao P 1987c *Scr. Metall.* **21** 1067

Pandey A B, Sood R K and Kumar M 1987 *Trans. Indian Inst. Met.* (in press)

Pandey A B, Misra R D K and Kumar M 1988 *Int. J. Rapid Solidification* (to be submitted)

Ricks R A, Budd P M, Goodhew P J, Kohler V L and Clyne T W 1986 *Proc. 3rd Int. Conf. on Aluminium-Lithium Alloys* (eds) C Baker, P J Gregson, S J Harris and C J Peel (London: Institute of Metals) p. 97

Wang W, Liu D and Grant N J 1987 *Scr. Metall.* **21** 1279