JOURNAL OF MATERIALS SCIENCE 14 (1979) 423–430

Grain-to-grain variations in NbC particle size distributions in an austenitic stainless steel

C. Y. BARLOW, B. RALPH, B. SILVERMAN*, A. R. JONES
Department of Metallurgy and Materials Science, University of Cambridge, UK

Quantitative information has been obtained concerning the size distributions of NbC precipitate particles in different grains in a deformed and aged austenitic stainless steel specimen. The precipitate size distributions obtained differ from one grain to another. The average disparity measured between the mean precipitate sizes was a function of the distance betwen the grains compared. The results obtained are considered in terms of differences in precipitation behaviour due to variations in the levels of plastic strain in constituent grains of the deformed specimen.

1. Introduction

The precipitation of NbC in an austenitic stainless steel occurs by a process of heterogeneous nucleation followed by growth and coarsening. Particles are nucleated on lattice imperfections in the matrix [1, 2], at grain boundaries [3], and also on coherent twin interfaces containing dislocation structures [4]. Specimen material is usually lightly cold-worked prior to ageing to generate dislocations which will act as sites for the nucleation of NbC particles. Cold-working and ageing specimens in this manner results in a fairly uniform spatial distribution of precipitates. However, the nucleation density and growth/coarsening kinetics of particles will be affected by the detailed arrangement of local dislocation substructures [5], since individual dislocations act not only as precipitate nucleation sites but also as short circuit diffusion paths during growth/coarsening. This implies that changes in the density and interlinking of dislocation substructures will modify the characteristics of the resulting particle size distributions. Experimental work has shown that during the deformation of a polycrystalline specimen, individual grains undergo different plastic strains [6]. The following sections present the results of an investigation which was initiated to establish and compare the characteristics of NbC particle size distributions in different grains in a deformed and aged austenitic stainless steel.

2. Experimental details

The alloy studied was a niobium stabilized austenitic stainless steel of composition 20 wt% chromium, 25 wt% nickel, 0.5 wt% niobium, 0.05 wt% (carbon plus nitrogen), balance iron.

A strip specimen of the above alloy was solution-treated for 1 h at 1300° C. The specimen was then cold-rolled to a 50% deformation and recrystallized at 1300° C. This recrystallization anneal was performed to reduce the relatively large grain size resulting from the solution treatment anneal. The final grain size of the strip specimen, measured as a mean linear intercept, was $\sim 15\,\mu m$. The specimen was then deformed by a further 5% prior to ageing for 1 h at 930° C. A 10 mm length section was spark-machined from the middle of the deformed and aged strip. This region of specimen was used to provide carbon extraction replicas (using standard techniques [7]) for examination in the electron microscope. Following the preparation and examination of extraction replicas, 3 mm diameter discs were cut from the same specimen area. These discs were jet-polished

*Formerly Department of Pure Mathematics and Mathematical Statistics, University of Cambridge. Present address: School of Mathematics, University of Bath.

to perforation prior to examination in the electron microscope.

Micrographs were taken of the NbC particle distributions extracted on the replica specimens. These micrographs were photographically enlarged and printed to provide the "raw" data for quantitative assessment. All quantitative data were analysed using a Quantimet 720 image analysing computer equipped with full pattern recognition facilities and a calculator interface. Full details of the procedures involved in preparing and analysing the data may be found elsewhere [7].

The magnification of the printed and enlarged micrographs was determined using a standard diffraction grating. However, the true particle sizes were inconsequential to the statistical interpretation of the results, since the important conclusions of the present investigation are comparative and not absolute in character.

3. Experimental results

3.1. Thin foil observations

Figs. 1 and 2 show typical thin foil observations of the NbC precipitates and dislocations in the specimens examined. Both figures illustrate that the spatial distribution of NbC particles is relatively uniform over distances which are large compared to the interparticle spacing. However, in neither figure are the particles distributed randomly, since the positions of precipitate particles reflect the arrangement of the dislocation substructures on which nucleation occurred. This also accounts for the general tendency for particles to be arranged in rows (arrowed in both figures). The complex contrast seen in Figs. 1 and 2 indicates why useful quantitative data could not be acquired by ordinary bright-field transmission electron microscope techniques: the contrast from individual particles was often obscured by contrast from the dislocation substructures. An alternative method of obtaining particle size distribution data from thin foils, that of using precipitate-centred dark-field images, also proved to be inadequate. Using this technique, some particles observed in the bright-field image gave only weak contrast or no contrast in the centred dark-field image, while others showed contrast implying an incorrect shape or size. These problems were avoided by using carbon-extraction replicas as the source of data. The large areas of replica available for examination also facilitated the procedure.

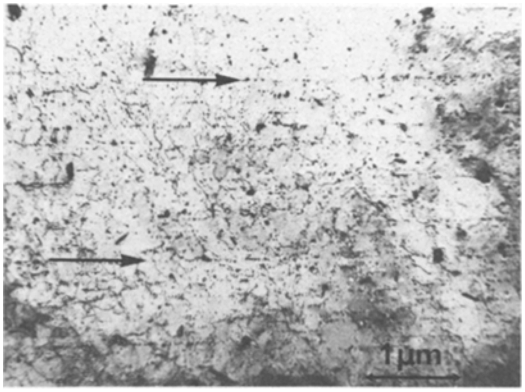

Figure 1 A bright-field micrograph showing NbC precipitates in association with dislocations. A tendency for alignment of precipitates is arrowed.

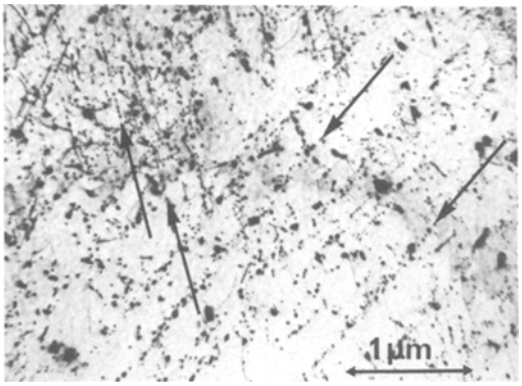

Figure 2 NbC precipitates in a thin foil specimen. Precipitates are aligned along the directions arrowed.

3.2. Carbon-extraction replica data

Particle-size distribution data from a total of thirteen grains were collected and analysed. The spatial arrangement of these thirteen grains is illustrated schematically in Fig. 3. Two different replica specimens were examined and data obtained from individual grains on each replica. Sampling was restricted to regions near to the centre of each of the grains analysed, to avoid the effects of inhomogeneous dislocation distributions near to grain and twin boundaries [3]. Clusters of grains which are termed "adjacent" were separated by no more than four or five grain diameters on the replicas. The number of particles sampled in each grain varied from a minimum of 752 to a maximum of 1759. Particle sizes were determined using the "equivalent circle diameter" method, which is described in detail elsewhere [8]. The particle size data for each grain were tabled

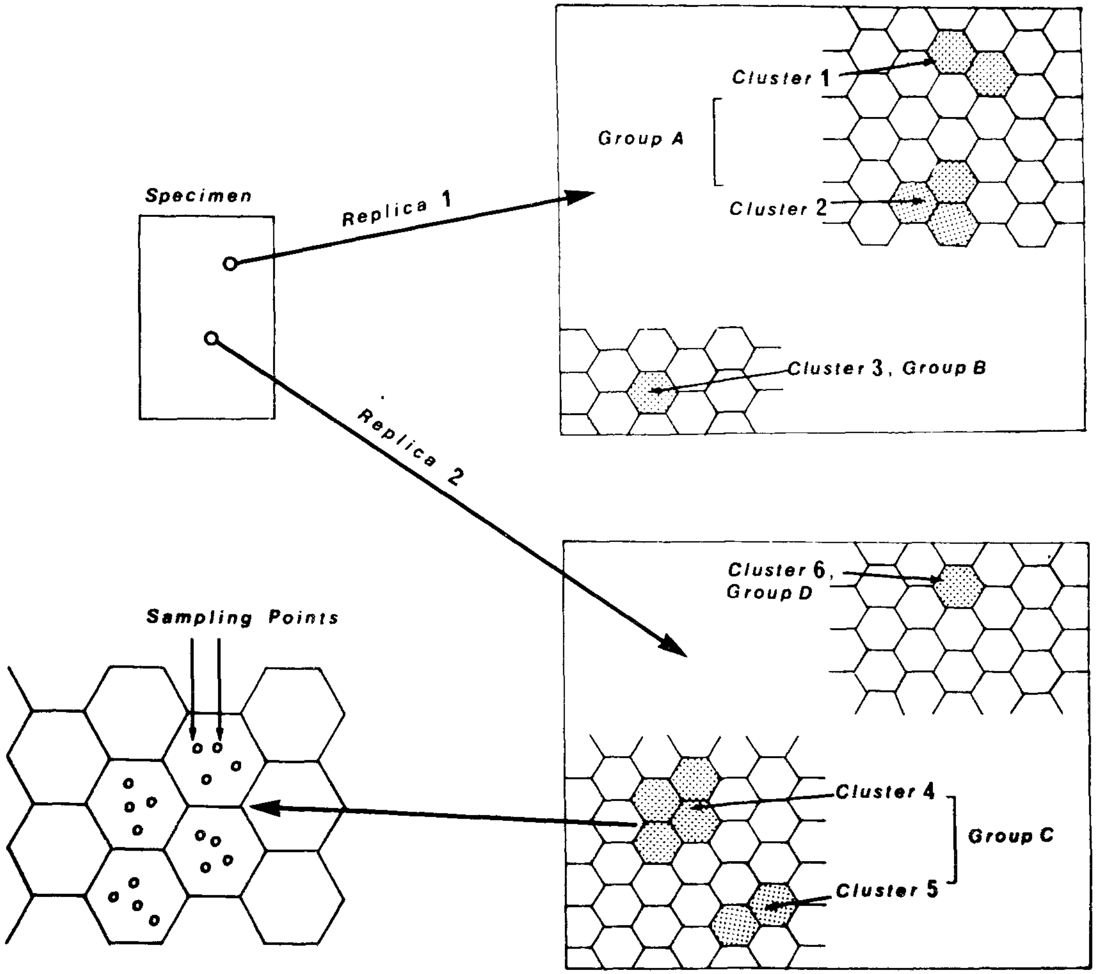

Figure 3 A schematic diagram illustrating the locations on the specimen from which replicas were made. The spatial relationship of the different grains, clusters of grains and groups of clusters are made apparent.

separately after allocating the equivalent circle radius size measurements to one of a number of equally spaced size bins.

A typical example of an area of extraction replica used to provide data for the investigation is shown in Fig. 4. Fig. 5 shows a volume relative frequency/size distribution plot of the data obtained from one of the grains analysed. The individual points on this plot are positioned by the value of each relative frequency and the weighted mean size of the individual particles which constitute that frequency. The size distribution shown is that of a true volume distribution of particles, i.e. correction factors have been applied to convert the frequency of occurrence of individual particle sizes on the replica to those of the true three-dimensional frequency. (The use of correction factors is necessary, since large particles have a greater extraction probability than smaller particles [9].) The volume-size distribution of NbC particles seen in Fig. 5 is close to log-normal in nature. The geometric mean precipitate diameter and standard deviation determined from all particles sampled (in excess of 15000), were found to be 10 and 1.5 nm respectively.

4. Statistical analysis of the data

4.1. Definition of the problem

In order to present the data in a suitable form for statistical analysis, it was necessary to perform a transformation*. For each, grain elements (i.e. particle sizes) were binned according to their observed two-dimensional size. The analysis was

* The statistical analysis was performed on the distributions of particle sizes which were observed on the replica and not on the data obtained after applying the stereological correction.

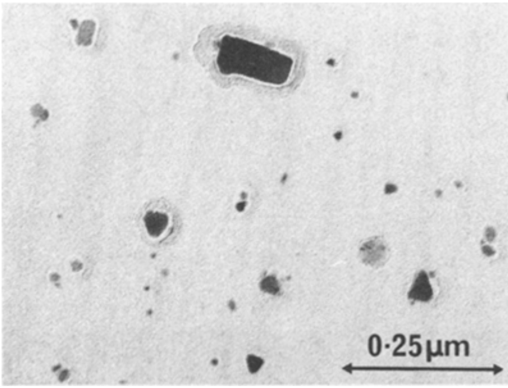

Figure 4 A typical example of a carbon extraction replica used to acquire quantitative data.

performed on the logarithms of the upper limits of each bin, so that (for example) the transformed observation corresponding to an element of projected radius 14.3 nm within the 14 to 15 nm bin is log 15. An examination of the data shows that this manipulation transforms the data for each grain to approximately normal shape. These data are summarized in Table I. The standard deviations of the transformed samples are reasonably homogeneous, vindicating the transformation.

In order to analyse the data, it was first necessary to define a mathematical model. The problem being analysed was essentially a "samples within samples within samples" case (for details see, for example, [10]). An analysis based on such a model gives rise to a nested analysis of variance procedure. The sums of squares are given in Table II.

The analysis proceeds by considering the data in progressively larger groups, so that the effective sample size decreases while the number of elements forming each observation increases. In each case the observed situations are compared for statistical similarity. Thus the grains are initially treated as independent samples, and then within their clusters. The grains within each

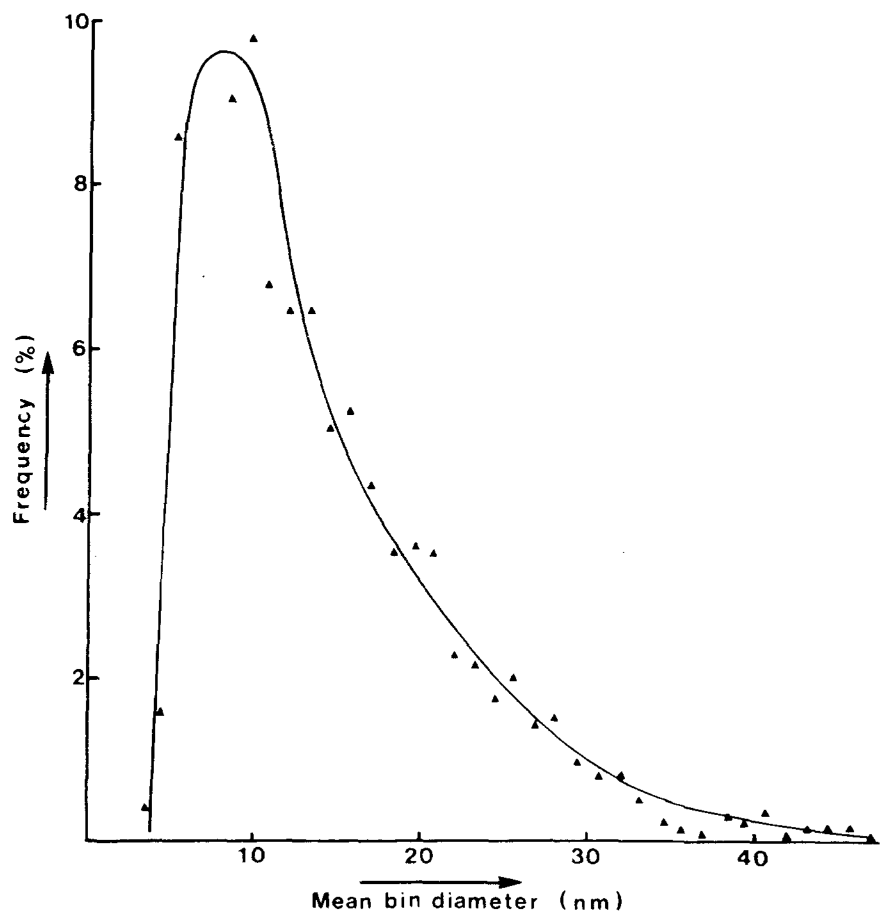

Figure 5 A volume relative frequency/size distribution plot of NbC precipitate data from one grain.

TABLE I Particle size data after binning and logarithmic transformation

Replica	Group	Cluster	Grain	Number of observations	Sum of transformed elements	Sum of squares	Mean	Standard deviation
1	A	1	1	800	1 562.5	3 189.9	1.95	0.42
			2	756	1 369.8	2 605.9	1.81	0.41
		2	1	1293	2 109.4	3 683.9	1.63	0.43
			2	1217	2 107.0	3 903.6	1.73	0.46
			3	872	1 458.1	2 646.1	1.67	0.49
	B	3	1	752	1 200.0	2 056.9	1.60	0.43
2	C	4	1	1364	2 495.4	4 876.5	1.83	0.48
			2	1184	2 250.7	4 545.3	1.90	0.48
			3	902	1 766.5	3 690.3	1.96	0.51
			4	1242	2 326.5	4 616.7	1.87	0.46
		5	1	1736	2 892.8	5 161.9	1.67	0.44
			2	1759	3 062.0	5 713.2	1.74	0.47
	D	6	1	1207	2 385.6	5 013.1	1.98	0.50
Total				15 084	26 986.2	51 702.4		

cluster are compared with each other, and the clusters as separate entities are compared. Finally the clusters from the two replicas are compared, as individuals and as a group. The analysis can thus indicate over what distance any similarities in the precipitate distribution can be maintained, with both long-range (different replicas) and short-range (adjacent grains) correlations being tested.

4.2. Results of the analysis

The first part of the analysis was to determine whether there was a significant difference between the population of elements drawn from different grains. This problem can be regarded in two ways. Firstly, it was necessary to determine whether the various grains were significantly different as a whole (ignoring the fact that grains were grouped in clusters). Secondly, it was desirable to determine whether grains within each cluster were different. The various ratios for these tests are shown in Table III. It is immediately apparent from this table that there is a very highly significant difference between the precipitate distributions in each grain, both within clusters and viewed as a whole.

The next step in the analysis was to determine whether the clusters of grains were significantly different from one another, i.e. it was necessary to determine whether elements drawn from grains in different clusters could be expected to be more dissimilar than elements drawn from grains in the same cluster. In terms of the model, this was testing for zero the variance in the distribution of random effects. The results of this analysis are shown in Table IV. It follows at once that there was a highly significant difference

TABLE II Sums of squares and degrees of freedom

	Sums of squares	Degrees of freedom
Total	51 702.4	15 084
Due to mean	48 280.1	1
Total corrected for mean	3 422.3	15 083
Replicas	39.2	1
Groups within replica 1	17.2	1
Groups within replica 2	30.2	1
Clusters within group A	45.5	1
Clusters within group C	64.9	1
Grains within cluster 1	7.8	1
Grains within cluster 2	6.3	2
Grains within cluster 4	9.5	3
Grains within cluster 5	4.8	1
Residual sums of squares	3 196.9	15 071

TABLE III Variance ratios for grains within each cluster

	Variance ratio	Degrees of freedom	Significance level (%)
All grains	88.55	12:15 071	99.9
Grains within cluster 1	36.56	1:15 071	99.9
Grains within cluster 2	14.82	2:15 071	99.9
Grains within cluster 4	14.88	3:15 071	99.9
Grains within cluster 5	22.79	1:15 071	99.9

between the population of grains drawn from different clusters.

Further statistical analysis to determine whether there were significant differences between "adjacent" clusters and clusters which were well separated and whether clusters on the first replica were significantly different from those on the second replica proved inconclusive.

5. Discussion

The experimental results of Boas and Hargreaves [6], obtained from an investigation of the deformation behaviour of polycrystalline aluminium, indicated that plastic strain occurred in an inhomogeneous manner during tensile deformation. Individual grains in specimens macroscopically deformed by 5% in tension were strained by amounts varying from as low as ~2% to as high as ~15%. These differences in strain, which appeared as a result of a single tensile deformation, were considered to be a manifestation of the complex constraints imposed on the plastic strain of individual grains within an agglomerate. Although an individual grain within a polycrystal might be favourably oriented for slip, the plastic strain developed will be limited by the accommodation behaviour of the neighbouring grains, and the magnitude and extent of any transgranular slip through the grain-boundary surfaces by which it is encapsulated.

In the present investigation, a polycrystalline sample of an austenitic stainless steel was reduced in thickness by 5% during cold-rolling. While the conditions governing plastic deformation are likely to be more complex during cold-rolling than in uniaxial tension, similar factors should influence local deformation behaviour in both cases. Therefore, grain-to-grain differences in the levels of plastic strain are to be expected in the cold-rolled steel specimen.

The relationship between the density and arrangement of dislocations in a deformed specimen and the different patterns of precipitation which will result from heterogeneous nucleation followed by growth/coarsening during subsequent ageing is likely to be complex. Grains containing identical dislocation densities may well produce dissimilar precipitate distributions, even though the nucleation density of particles may actually be similar in both cases. Differences in the configuration of the dislocation networks in two such grains may exert a strong influence on the initial pattern of precipitate growth/coarsening. Any rearrangements of existing dislocation substructures, on dissolution of smaller pinning particles during coarsening, might even accentuate the disparity between the two particle size distributions. Hence, the wide variations in plastic strain between different grains and the close correlation between the dislocation substructures and the subsequent development of NbC precipitate distributions, should combine to produce an overall particle-

TABLE IV Analysis of variance

	Sums	Degrees of freedom	Variance ratio	Significance level (%)
Sum of squares between clusters	197.1	5	9.7	99
Sum of squares between clusters within groups	110.4	2	13.6	99
Residual sum of squares (= sum of squares between grains within clusters)	28.4	7		

size distribution in a specimen which consists of an agglomeration of many individual precipitate populations.

Statistical analysis of the results of the present investigation has shown conclusively that precipitate distributions do differ significantly from one grain to another in the deformed and aged stainless steel specimen material examined. This result is almost certainly a direct consequence of the different densities and arrangements of the dislocations in the individual grains of the polycrystalline aggregate. The additional conclusion of the statistical analysis – that grains within clusters contain precipitate distributions that are less dissimilar than precipitate distributions from grains in random positions – correlates with a further feature of the experimental work of Boas and Hargreaves [6]. These workers found that strain levels did not vary from grain to grain in a random fashion, but that more or less continuous fluctuations in the levels of strain were observed to extend over numbers of grains. Hence, one group of neighbouring grains might contain dislocation densities scattered about a different mean value to that for another group of grains some distance away: the correlation between such fluctuations in plastic strain and the consequent development of precipitate populations follows directly.

Further, the results of the present investigation indicate that, for the alloy studied, a single value quoted for the mean particle size developed during an ageing treatment is only a general indication of the underlying precipitation behaviour. Such values will be of limited use in determining any local mechanisms governing precipitate growth/coarsening kinetics. Conversely, the results obtained indicate that for reasonable comparisons of precipitate sizes in specimens of different thermomechanical histories, the quantitative information obtained should be selected from a number of well separated sampling points in each specimen studied.

6. Conclusions

The distributions of sizes of heterogeneously nucleated NbC precipitates have been investigated in a deformed and aged austenitic stainless steel. The main points arising from the investigation are as follows:

(1) there is a highly significant difference in the precipitate size distributions developed in different grains in the specimen;

(2) clusters of neighbouring grains contain precipitate populations which differ significantly from those of other grain clusters;

(3) it is considered that the precipitate-size distributions evolved during ageing reflect variations in the plastic strain generated in different grains during room-temperature deformation.

The above three results lead to two more general conclusions concerning the quantitative analysis of precipitate-size distributions which evolve by heterogeneous nucleation, followed by growth/coarsening on dislocation substructures. These conclusions are:

(1) the sampling of precipitate sizes must be carried out in a number of widely separated areas of a specimen to determine a mean particle size characteristic of a single thermomechanical treatment;

(2) for precipitate particles which nucleate heterogeneously on dislocation substructures, a single mean particle size, obtained from a large number of disparate measurements, cannot be used to provide accurate local information on the rate determining processes involved in precipitate growth/coarsening.

Acknowledgements

The authors are grateful to Professor R.W.K. Honeycombe for the provision of laboratory facilities. The experimental assistance of Mr J. Ward during quantitative analysis is also acknowledged. Financial support during the research was provided by the S.R.C. and the Springfield laboratories of the U.K.A.E.A.

References

1. R. SUMERLING and J. NUTTING, *J.I.S.I.* **203** (1965) 398.
2. M.A.P. DEWEY, G. SUMNER and I.S. BRAMMAR, *ibid* **203** (1965) 938.
3. A. R. JONES, P. R. HOWELL, T. F. PAGE and B. RALPH, 4th Bolton Landing Conference on Grain Boundaries in Engineering Materials, J. L. Walter, J. H. Westbrook and D. A. Woodford (eds.) (A.I.M.E., A.S.M. Claitor, 1975) p. 629.
4. A. R. JONES, P. R. HOWELL and B. RALPH in "Grain Boundaries" (Proc. of Conf. held at Jersey organized by Institution of Metallurgists) paper B1 (1976).
5. H. KREYE, *Z. Metallkunde* **61** (1970) 108.

6. W. BOAS and M. E. HARGREAVES, *Proc. Roy. Soc.* **193A** (1948) 89.
7. A. R. JONES, Ph.D. Thesis, University of Cambridge (1974).
8. J. GAHM, *J. Microscopy* **95** (1972) 368.
9. M. F. ASHBY and R. EBELING, *Trans. Met. Soc. AIME* **236** (1966) 1396.
10. G. W. SNEDECOR and W. G. COCHRAN, "Statistical Methods" (6th edn.) (Iowa State University Press, Ames, Iowa, 1967) Ch. 10.

Received 8 May and accepted 10 July 1978.