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Quantitative Assessment of Extraction Replicas for Particle Analysis

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The errors that may arise from the use of extraction replicas for quantitative measurements of particle-size, density, and volume fraction are considered. It is shown that shadowing the specimen surface before replication allows assessment of the sources of error. Serious errors arise in all particle parameters if sectioned particles are extracted, but irregularities in the matrix surface lead only to systematic errors in particle density and volume fraction.

1. Introduction

The technique of extraction replication is commonly used for the study of second phase particles by electron microscopy. The determination of the number, size, spacing and volume fraction of spherical second-phase particles from such replicas has been discussed recently by Ashby and Ebeling [1], who conclude that the method is suitable for determining particle-size distribution, mean size, and standard deviations of hard or chemically inert particles in the size range 100 to 10 000 Å, but, because of uncertainty about the efficiency of extraction, measurements of particle spacing or volume fraction are unreliable. The advantages offered by this technique over other techniques depend upon the assumption that a replica shows the true distribution of particle sizes on a random plane through the bulk. The comparison made by Ashby and Ebeling between results obtained from replicas and from thin foils, indicates that the assumption may be valid in their case. However, in general a number of factors could invalidate it.

(i) Insufficiently deep etching prior to replication. The depth of etching should be greater than the radius of the largest particles in the distribution, or errors may arise because of particles sectioned during polishing.

(ii) Partial dissolution of particles during preparation of the replica.

(iii) Inadequate rinsing after etching. If all particles etched free are not removed, these will appear on the replica. This problem may be overcome by stripping a plastic replica from the surface before carbon replication, but the danger then arises that particles which just intersect the surface may be ripped out by the plastic replica.

(iv) The etched surface may not be planar on the scale of the particle-size.

(v) All particles which intersect the replicated surface may not be extracted.

(vi) Particles which did not intersect the replicated surface may be freed during re-etching to remove the replica and remain loosely attached to it.

(vii) Non-random sampling of areas to be measured. If the particle size distribution is not uniform throughout the matrix, sampling should be random, e.g. neighbouring areas along random lines.

These effects may be minimised by careful experimental technique, but the errors that they introduce cannot be assessed numerically from normal extraction replicas. We report here a development of the technique which permits such an assessment.

2. Experimental Technique

The modification to the standard procedure for the preparation of extraction replicas is simply to shadow the surface to be replicated at a suitable known angle with gold/palladium before deposition of carbon. The choice of shadowing angle depends upon the features to be examined, but for routine measurements on second phase particles an angle of 50° to the

surface has been found suitable as it gives sufficient contrast to reveal topographical features clearly, but gives a low probability of overlap of shadows from neighbouring particles. For convenience, the replicas produced after shadowing are referred to as *shadowed extraction replicas*, although it is the specimen surface rather than the replica which is shadowed. The second etch to release the shadowed extraction replica takes longer than for an unshadowed replica, but otherwise the shadowing has little effect on the preparation technique.

Details of the procedure used to obtain shadowed extraction replicas from a range of tempered chromium steels are reported elsewhere [2]. The standard procedure was to mechanically polish and deeply etch the specimen surface before shadowing and replication. To study the effect of preparation procedure, a 1.2% chromium 0.2% carbon steel tempered for 10 h at 700° C was electropolished in 5% perchloric acid in glacial acetic acid at 13° C and 22 V, and subsequently etched for different times in 2% nital. The effect of etching on the true surface area was assessed by measuring the cathodic polarisation curve of the as-electropolished surface and of the same surface after etching for 60 sec. The electrolyte, 3% $NaHCO_3$, 0.1% H_2SO_4 solution, was thoroughly deaerated before use by bubbling nitrogen through it. A calomel reference cell was used, and in both cases the probe was in close contact with the specimen so that any resistance polarisation remained the same. Change in current was recorded for a constant rate of change in voltage from −0.70 to −1.10 V, normal hydrogen scale. These limits were necessary to avoid dissolution of the specimen at one extreme, and excessive hydrogen gas evolution at the other.

As the carbide particles in the tempered steels were not perfectly spherical, complementary observations were made on a copper/2 vol % SiO_2 alloy internally oxidised at 1000° C. Shadowed extraction replicas were prepared from a surface electropolished by the jet technique in a solution of 50% H_3PO_4 in water at 80 to 100 V. Replicas were released from the surface by etching in freshly mixed 1:1 concentrated NH_4OH and 1.5% H_2O_2, and were finally stripped in distilled water.

Surfaces to be replicated were normally washed thoroughly in running water before shadowing, but, in a few cases, plastic replicas were stripped from the surfaces to determine whether any loose particles still remained. The extraction replicas were sprayed with polystyrene latex particles of standard diameter (0.264 μm) before examination in an EM6 or EM6G microscope to allow direct calibration of magnification.

Particle-size measurements on about 2000 particles were made using a Carl Zeiss TGZ3 Particle-Size Analyser, as reported elsewhere [2]. Shadow lengths and the projected lengths of particles in the direction of shadowing were determined by direct measurement of suitably enlarged photographs. All particles, whether extracted or not, were counted for particle density determinations.

3. Results and Discussion

The advantages of shadowing a specimen before replication are illustrated by fig. 1 which compares plain and shadowed extraction replicas prepared from a tempered chromium steel after mechanical polishing and light etching. The plain extraction replica reveals little about the topography of the replicated surface, or about the efficiency of extraction, whereas both features are immediately apparent from the shadowed replica. As the etching time was short in this case, most of the unextracted particles have flat tops resulting from mechanical polishing. These still reveal polishing scratches, indicating that attack of the particles during etching is negligible. The majority of unextracted particles would have fallen into the larger size ranges, so measurements on extracted particles only could lead to serious errors in particle-size. The assumptions made by Ashby and Ebeling [1] that the efficiency of extraction is independent of particle-size and that hard particles are not sectioned during polishing are thus unfounded in this case.

In the example shown in fig. 1b, it is clear that many of the extracted particles are sectioned as an upper limit to the shadow lengths is set by the length of shadows of the unextracted particles. The product of this length and the tangent of the angle of shadowing gives the depth of etching to be 0.25 μm, which is considerably less than the radius of the largest particles. As the efficiency of extraction and depth of etching increase, it becomes more difficult to assess whether or not sectioned particles are still present, but this can be determined from the frequency distribution of shadow lengths.

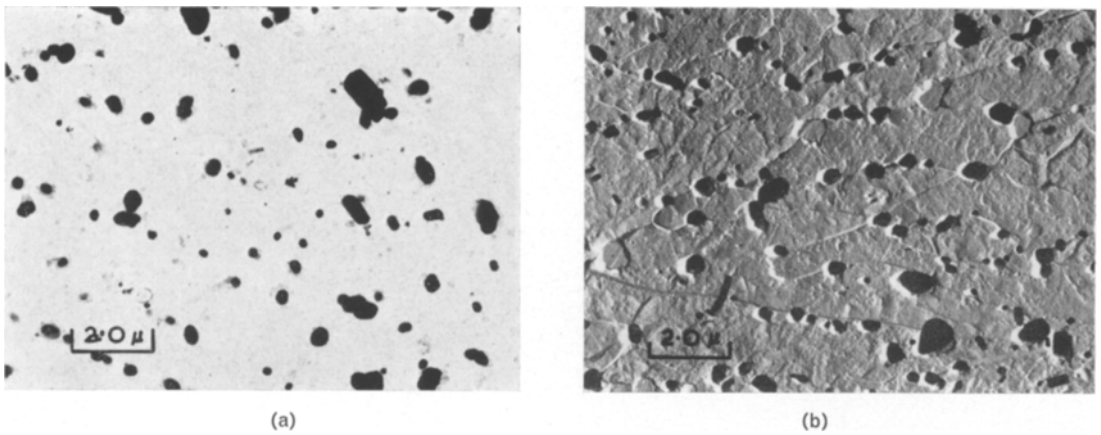

Figure 1 2.4% chromium 0.2% carbon steel tempered for 384 h at 700° C; (a) plain extraction replica, (b) shadowed extraction replica.

3.1. Distribution of Particles

The geometry of shadowing of spherical particles has been considered elsewhere [3], and for a random distribution of unsectioned particles gives that, for a 50° angle of shadowing, 31.8% of particles will not cast a visible shadow. The ratios of visible shadow length (L) to the projected length of particle in the direction of shadowing (D) for the remaining particles should take all values between zero and the maximum of 0.570 with equal probability. As the carbides in the tempered chromium steel are not perfectly spherical, shadowed extraction replicas of Cu/SiO_2 were used to compare with this prediction. The SiO_2 particles are not attacked during electropolishing as they are non-conducting, and they appear on the replicas as complete, virtually spherical particles, as shown in fig. 2. The frequency distribution of shadow lengths is shown in fig. 3. The histogram is in excellent agreement with the predicted form (shown dashed) indicating that the SiO_2 particles are randomly distributed with centres above and below the matrix surface. This agreement between the predicted and observed frequencies in the largest and smallest size groups is direct evidence that particles released during electropolishing and on subsequent etching, respectively, are not attached loosely to the replica in this case.

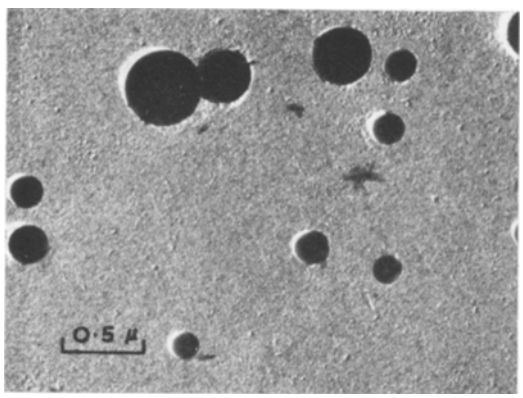

Figure 2 Copper/2 vol % SiO_2 electropolished and shadowed at 50°.

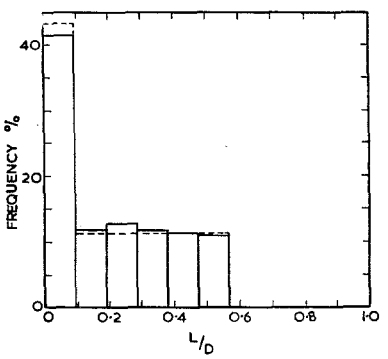

Figure 3 Histogram of shadow lengths on replicas of copper/2 vol % SiO_2. Dashed curve predicted for randomly distributed spheres.

Preparation of the surface of the Cu/SiO_2 by etching rather than by electropolishing led to preferential attack of the matrix adjacent to the particles, which was easily detectable by spurious shadowing effects. This resulted in discrepancies between the predicted and observed histograms of shadow lengths, and could

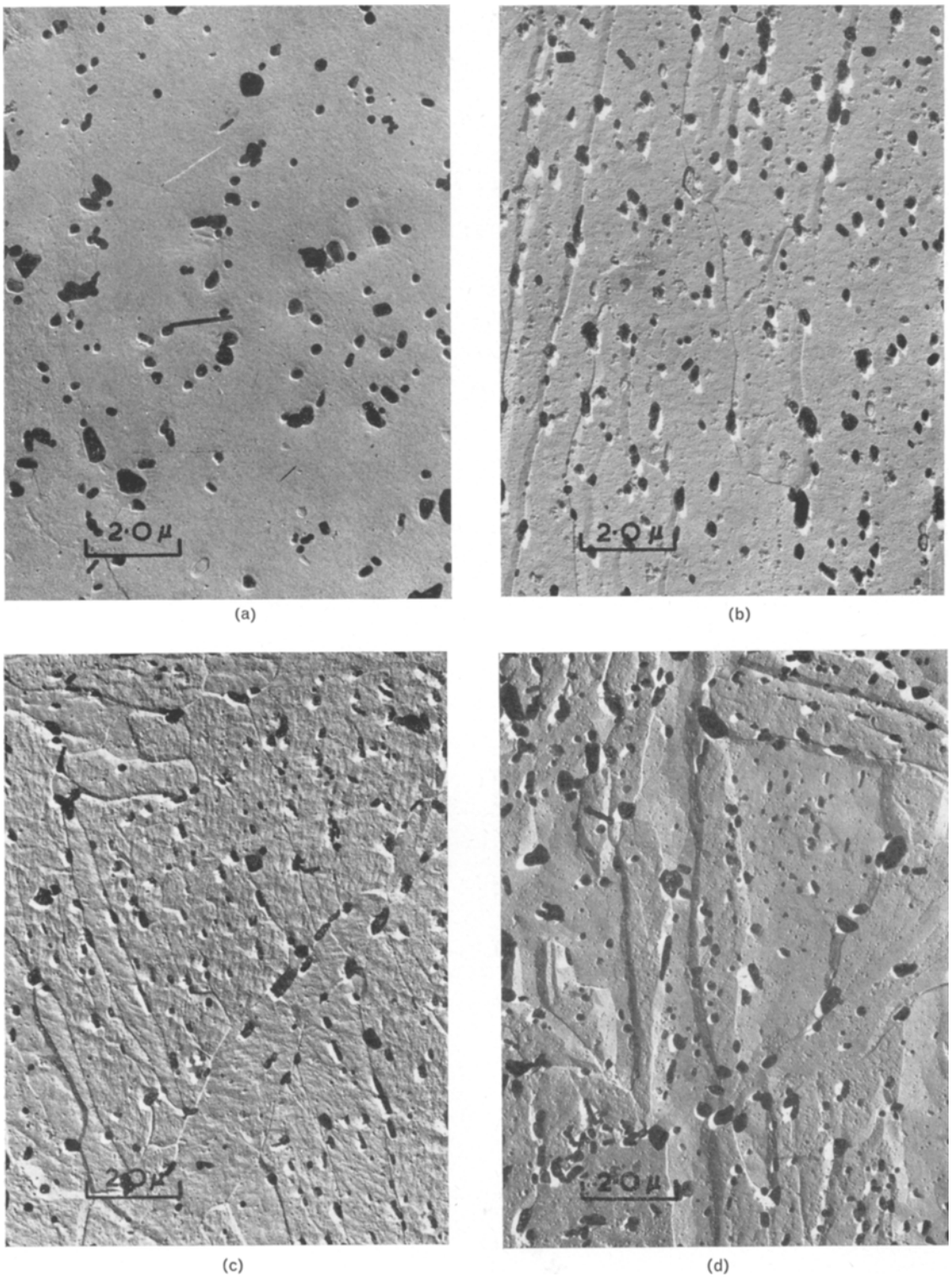

Figure 4 1.2% chromium 0.2% carbon steel tempered for 10 h at 700° C. As-electropolished (a) and etched for 8 sec (b), 15 sec (c), and 60 sec (d), in 2% nital.

lead to errors in particle-size and density measurements.

The effect of surface topography and of sectioning of particles was studied on a tempered chromium steel by varying the initial etching time. The matrix surface prepared by electropolishing alone was virtually flat, and became increasingly irregular with time of etching, as shown in fig. 4. In this case, no spurious effects associated with preferential etching near the particles were detectable. As carbides are conductors, the particles are attacked during electropolishing. From the restricted distribution of shadow lengths after electropolishing, and after light subsequent etching, it is clear that the attack of the particles results in sectioning which is qualitatively similar to that after mechanical polishing and light etching (fig. 1b). This results in difficulties in obtaining high extraction efficiencies after the shorter etching times.

The importance of sectioning of particles is shown quantitatively by the frequency distributions of shadow lengths given in fig. 5. The geometrical arguments used to predict the histograms for spherical particles were extended to the case of randomly oriented ellipsoids as shown in the appendix. Since calculation of the frequency functions for ellipsoids of all axial ratios from 1:1 to the observed maximum is tedious, the theoretical distribution curve given as dashed lines in fig. 5 is an approximation made on the assumption that half the the particles are spherical and half are randomly oriented ellipsoids of axial ratio 1.4:1. The histogram observed after 60 sec etching (fig. 5b) is in reasonable agreement with the predicted form, apart from a discrepancy in the number of unshadowed particles. This discrepancy is considered later. The histogram after light etching (fig. 5a) shows a marked restriction in the maximum shadow length, and a systematic trend for particles to have shorter shadows than expected, indicating that a significant fraction of the particles are still sectioned. As the tendency will be for the majority of particles sectioned below their diameter to belong to the larger size ranges, this leads to a systematic error in the measured particle-size distribution. The magnitude of this error is shown by the size distribu-

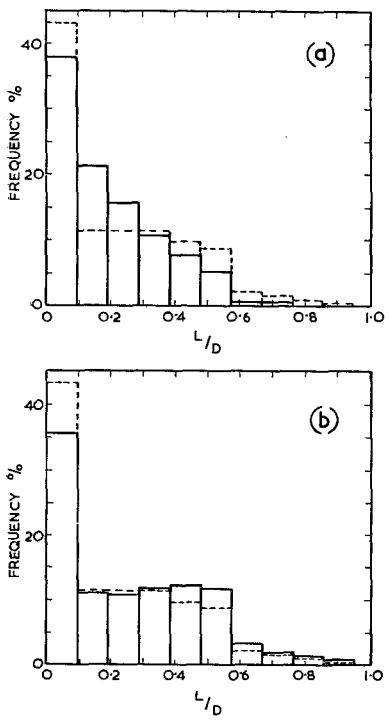

Figure 5 Histograms of shadow lengths on replicas of 1.2% chromium 0.2% carbon steel tempered for 10 h at 700° C. Etched for 8 sec (a), and 60 sec (b).

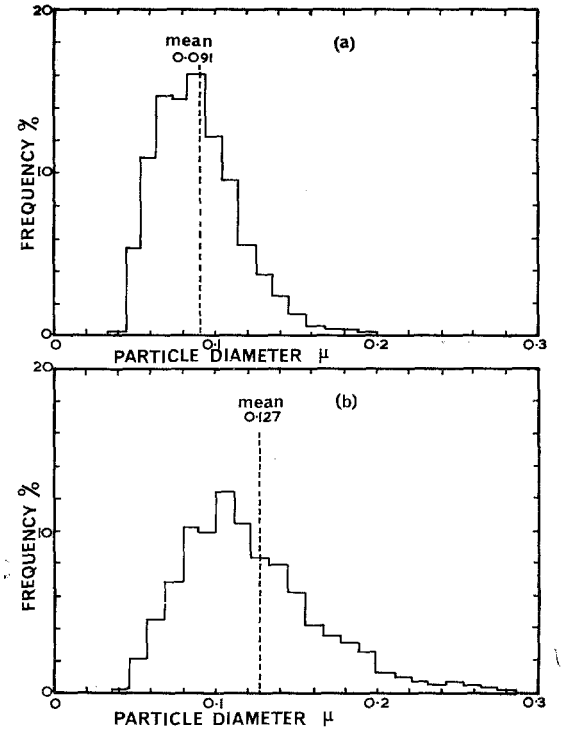

Figure 6 Planar size distribution curves for carbides in 1.2% chromium 0.2% carbon steel tempered for 10 h at 700° C. Etched for 8 sec (a), and 60 sec (b).

tion curves, fig. 6. The absence of particles in the larger size ranges after only 8 sec etching may be exaggerated by the difficulty in obtaining high extraction efficiencies in this condition, which, as pointed out previously, results in the largest particles being preferentially unextracted. Thus, for accurate quantitative measurements it is necessary to ensure that the extraction efficiency is high (>99.5% has been adopted as the criterion in current work), and that no sectioned particles appear on the replica.

3.2. Effect of Angularity of Particles

The reason for the discrepancy between the observed and predicted frequency of unshadowed particles even after 60 sec etching was examined by measuring the distribution of shadow lengths on replicas of a 6.1% chromium 0.2% carbon steel, tempered for 100 h at 700° C, and of a 0.87% chromium 0.2% carbon steel recrystallised and tempered for a further 950 h at 700° C [2]. Specimens were heavily etched before replication, but the former retained a relatively smooth matrix surface, and contained non-spherical particles (fig. 7a), while the latter developed a more irregular surface and contained more nearly spherical particles (fig. 7b). The histograms of shadow lengths in the two cases are shown in fig. 8. The irregular particles in the 6.1% chromium steel lead to a discrepancy in frequency of unshadowed particles, almost as large as that observed in the 1.2% chromium steel (fig. 5b), whereas the more nearly spherical particles in the recrystallised 0.87% chromium steel give a result in good agreement with the predicted one. It thus appears that angularity of the particles, and not irregularities in the matrix surface, cause the discrepancy, and that particle centres are randomly distributed above and below the replicated surface, even when this is very irregular.

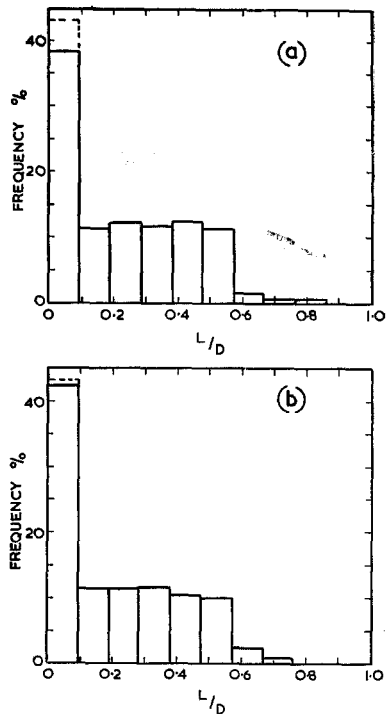

Figure 8 Histograms of shadow lengths on replicas of (a) 6.10% chromium 0.2% carbon and (b) 0.87% chromium 0.2% carbon steels tempered at 700° C.

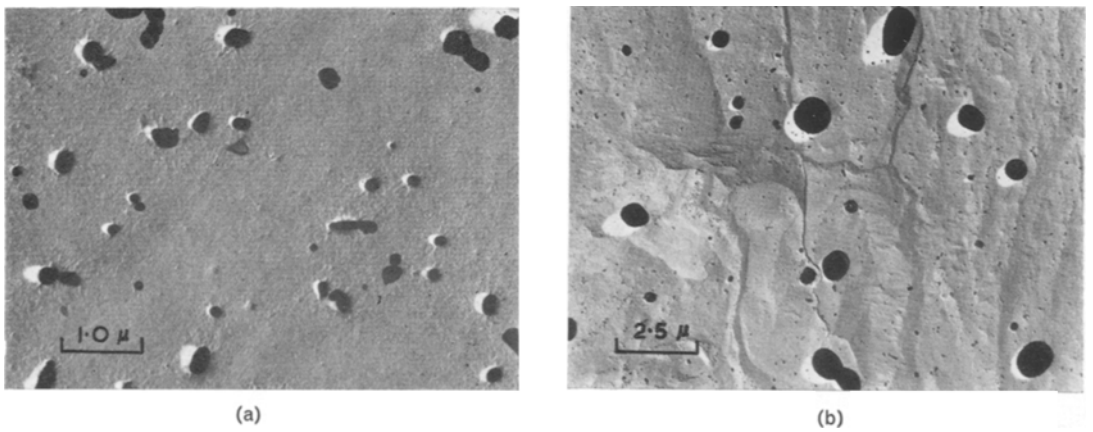

Figure 7 (a) 6.10% chromium 0.2% carbon steel tempered for 100 h at 700° C. (b) 0.87% chromium 0.2% carbon steel recrystallised and subsequently tempered for 950 h at 700° C.

3.3. Effect of Surface Irregularities

A noticeable feature of the structures shown in fig. 4 is that the apparent number of particles per unit area (N_S) increases with etching time. This increase is shown in fig. 9. The frequency

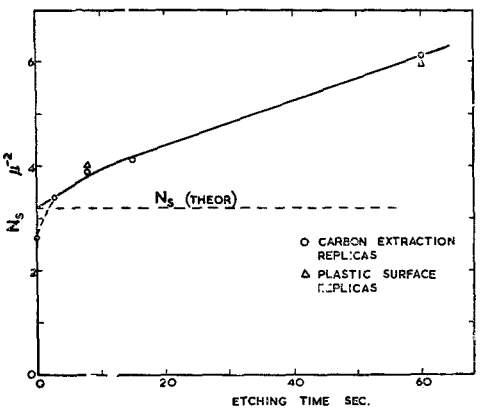

Figure 9 Dependence of number of particles per unit projected area (N_S) on time of etching for 1.2% chromium 0.2% carbon steel tempered for 10 h at 700° C.

distributions of shadow lengths, already considered, indicate that this is not associated with extra particles attached loosely to the replicas. Confirmation that extra particles do not arise from the initial etch was obtained by stripping plastic replicas from the specimen surface before shadowing. This resulted in no change in appearance of the extraction replicas, and only one or two particles were found adhering to areas of plastic replica, in which 1000 to 2000 were observed on the extraction replicas. As confirmation that no extra particles result from the second etch, the density of particles was determined from shadowed plastic surface replicas as well as from the extraction replicas, for the specimens etched for 8 and 60 sec. The close agreement of these results indicates that the measurements reflect the true numbers of particles intersected by the replicated surface. The theoretical value of N_S shown is derived from the particle-size distribution determined after 60 sec etching, and the theoretical volume fraction. The low value observed on the as-electropolished specimen probably results from the poor extraction and the sectioning of particles as, with the high angle of shadowing used, some unextracted particles may not give detectable contrast.

The increasing value of N_S with etching time is associated with an increase in severity of irregularities in the matrix surface. These will lead to an increasing difference between the true and projected surface areas. The cathodic polarisation curves determined on the electropolished surface, and on the same surface after heavy etching, are shown in fig. 10. The dis-

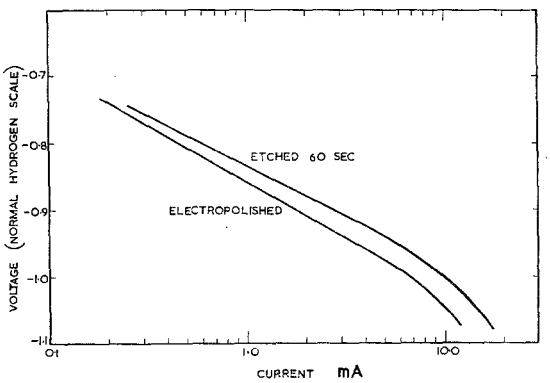

Figure 10 Cathodic polarisation curves in 3% $NaHCO_3$, 0.1% H_2SO_4 solution of 1.2% chromium 0.2% carbon steel tempered for 10 h at 700° C.

placement of the two curves cannot be correlated directly with the change in true surface area because of autocatalytic activity of the roughened surface [4], and unknown effects of the carbide particles. However, it does indicate that the ratio of the true to the projected surface area is of the same order as the ratio of the observed and expected density of particles after etching for 60 sec. Thus, even when the extraction efficiency is high, the true density of particles is only obtained when the matrix surface is nearly planar, and if extraction efficiencies are low, it is necessary to shadow at a low angle to ensure that all unextracted particles give detectable contrast.

Experimental volume fractions are determined from measured particle-size distributions, and the apparent number of particles per unit area, and so will be in error unless the matrix surface is flat. If the extraction efficiency is high, the experimental value (f_{exp}) should always be higher than the theoretical value (f_{theor}). Results obtained on a range of chromium steels tempered for different times at 700° C [2] are shown in fig. 11. In all cases the value of f_{exp} is higher than expected.

The frequency of unshadowed particles, an easily determined parameter, was obtained for each of these specimens. If particles are spherical or ellipsoidal, this gives a rapid check on the

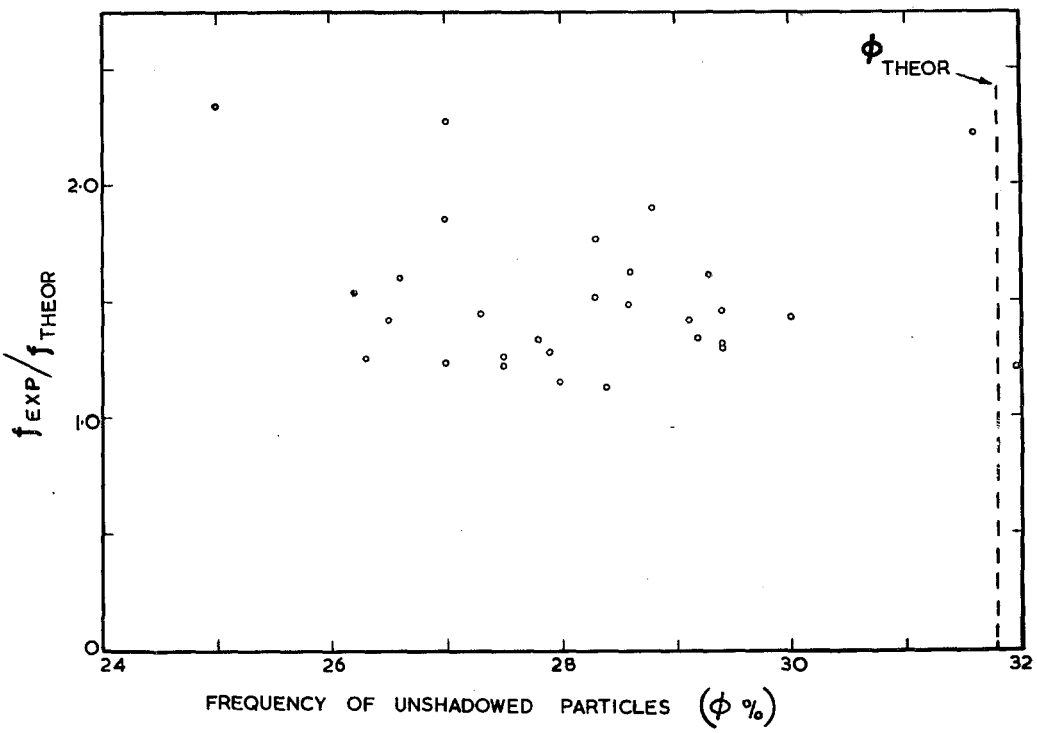

Figure 11 Relationship between ratio of experimental to theoretical volume fraction and frequency of unshadowed particles. Angle of shadowing 50°.

absence of extra particles resulting from the second etch. In the present case, the lack of correlation between this frequency and the volume fraction indicates that extra particles are not significant. It also demonstrates that the frequency is independent of surface irregularities, and that errors introduced into the determination of volume fraction because of angularity of the particles are probably small.

4. Conclusions

(i) Extraneous particles attached loosely to extraction replicas can be avoided by careful technique.

(ii) Serious errors may arise in measurement of particle-size distributions if the extraction efficiency is poor, or if sectioned particles are present on the replicas.

(iii) Provided that the depth of etching is sufficient, particles are randomly oriented about the replicated surface, even when severe irregularities are developed in this.

(iv) When irregularities are developed in the matrix surface, the true surface area may be considerably larger than the projected surface area, causing systematic errors in determinations of particle densities and volume fractions.

(v) Shadowing the surface of the specimen prior to replication allows assessment of the possible sources of error in quantitative measurements.

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Appendix

The geometry of shadowing an ellipsoidal particle can be represented by the section taken on a plane normal to the matrix surface in which

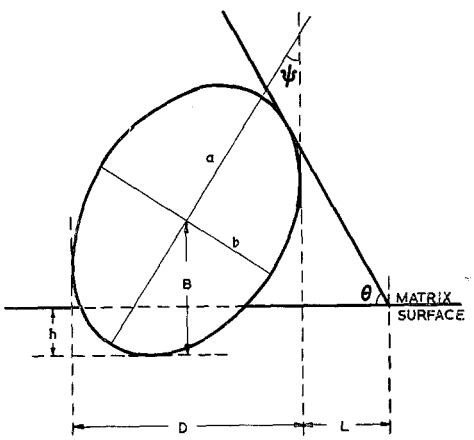

Figure 12 Geometry of shadowing an ellipsoidal particle. Section normal to the matrix surface containing the direction of shadowing.

the direction of shadowing lies, as shown in fig. 12. The angle of shadowing, θ, leads to a visible shadow of length L when the centre of the particle is at a height $(B - h)$ above the matrix surface. If the major axis of the ellipse is inclined at an angle ψ to the surface normal, the projected length of the particle in the direction of shadowing is D. Considering the semi-axes of the ellipse, a and b, are related by $a^2 = \gamma b^2$,

$$B = b\cos\psi\,(\gamma + \tan^2\psi)^{\frac{1}{2}}$$
$$D = 2b\cos\psi\,(1 + \gamma\tan^2\psi)^{\frac{1}{2}}$$

Putting $h = \alpha B$,

$$L/D = \tfrac{1}{2}\left\{\frac{[\tan^2\theta(1+\gamma\tan^2\psi)+\gamma+\tan^2\psi+2(\gamma-1)\tan\theta\tan\psi]^{\frac{1}{2}}+(1-\alpha)[\gamma+\tan^2\psi]^{\frac{1}{2}}}{\tan\theta[1+\gamma\tan^2\psi]^{\frac{1}{2}}} - 1\right\}$$

Computing this for values of ψ from 0 to 180°, values of α from 0 to 2, and values of γ from 1 to the maximum for the ellipsoid, and considering that the probability of the particle being cut by the surface is proportional to B, the frequency function of L/D for randomly oriented ellipsoids can be determined.

The condition for visibility of a shadow is that $L > 0$, or

$$h/B < 1 + \frac{[\tan^2\theta(1+\gamma\tan^2\psi)+\gamma+\tan^2\psi+2(\gamma-1)\tan\theta\tan\psi]^{\frac{1}{2}}-[1+\gamma\tan^2\psi]^{\frac{1}{2}}\tan\theta}{[\gamma+\tan^2\psi]^{\frac{1}{2}}}$$

Computing this for values of ψ from 0 to 180°, and considering that the probability of a particle being cut by the surface is proportional to B, gives the proportion of randomly oriented particles which will cast visible shadows for a given angle of shadowing. For 50° shadowing angle this is 68.2%, independent of the value of γ, and is thus the same as for spherical particles.