ON THE ESTIMATION OF OXIDE/METAL INTERFACIAL ENERGY BY INTERNAL OXIDATION

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Introduction

INTERNAL oxidation is a solid/gas phase reaction in which the stable oxide of a solute metal of high oxygen affinity is precipitated in the matrix of a relatively noble metal by exposing the alloy to a mildly oxidizing atmosphere. The precipitation of the oxide particles occurs uniformly throughout the matrix. Among the various systems studied (such as Ag-Cd,[1] Cu-Al,[2], Cu-Be,[3] Cu-Cr,[4] Cu-Si,[4] Cu-Ti,[4] Ni-Al,[5] etc.), the precipitate oxide particles have been found to be invariably crystalline excepting in Cu-Si alloy where they have been found to be amorphous in nature. The particles precipitated at the grain boundaries have usually the same shape as the one precipitated within the grains except that occasionally they are slightly bigger in the direction of the grain boundary as illustrated in Fig. 1 for Cu–Mg alloy. However, in case of Cu-Ti and Cu-Si alloys, the grain boundary particles have been reported to assume the equilibrium shape which would be a double convex lens bounded by two spherical surfaces of the same radii.

The relationship between various energy terms involved for an equilibrium-shaped grain boundary particle is illustrated in Fig. 2. If the energy of the particle-matrix interface is independent of orientation of the grain boundary, the interfacial energy can be calculated by determining the equilibrium dihedral angle and using the following relationship given by Smith,[6]

$$2\cos\frac{\theta}{2} = \frac{\gamma_{g.b.}}{\gamma_{pm}} \qquad (1)$$

where,

θ is the equilibrium dihedral angle,

$\gamma_{g.b.}$ is the grain boundary energy, and

$\gamma_{p.m.}$ is the particle/matrix interfacial energy.

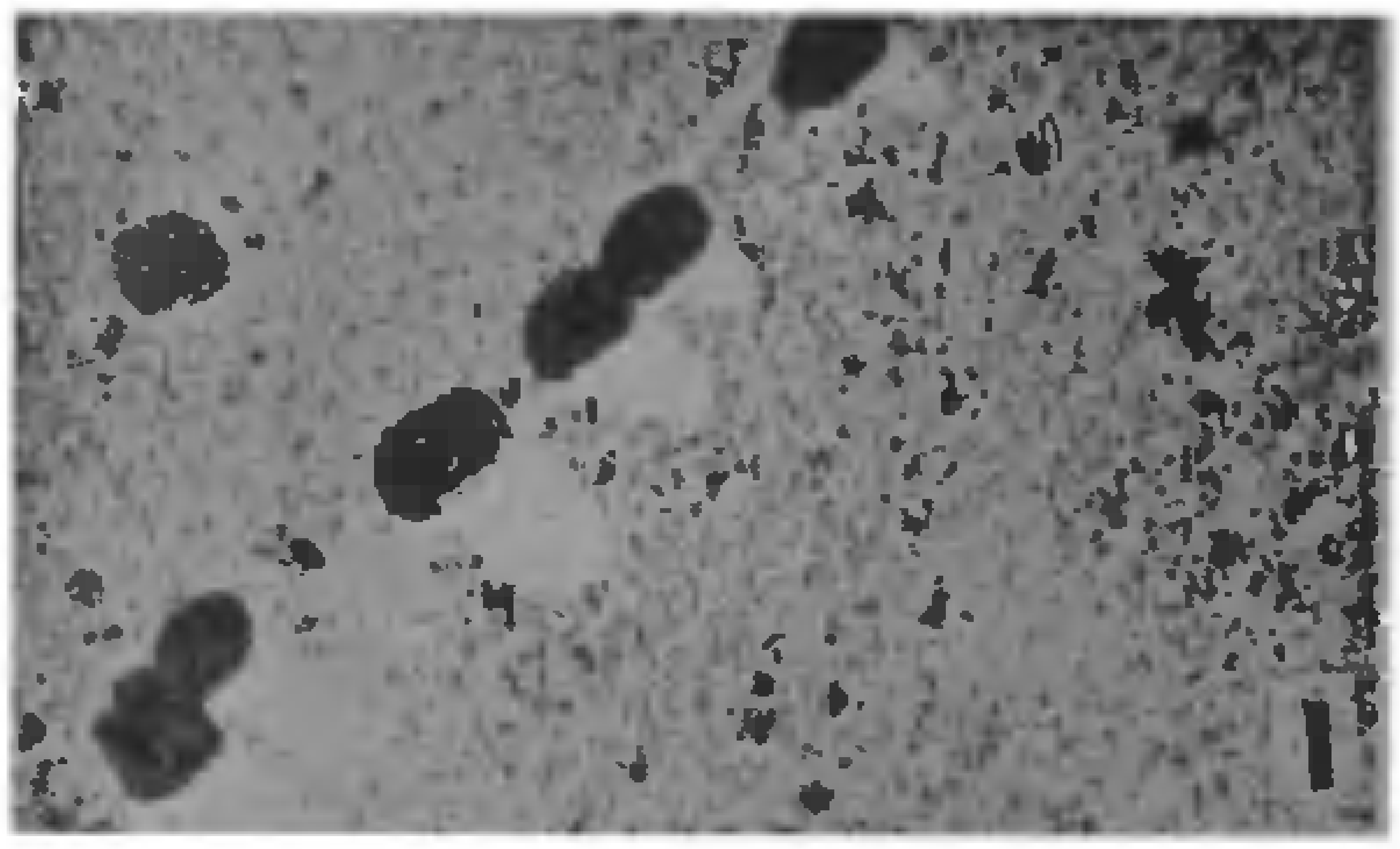
It is essential that true dihedral angles should be measured. If measurements are done on planar metallographic sections, statistical methods must be employed to estimate the correct dihedral angles. However, true dihedral angles can be measured directly, if thin foils of the specimens are used in transmission electron microscopy and care is taken to align the grain boundary parallel to the electron beam. The angles can be determined by a geometrical construction or by the following simple relationship, provided the two spherical surfaces bounding the particles have identical radii.

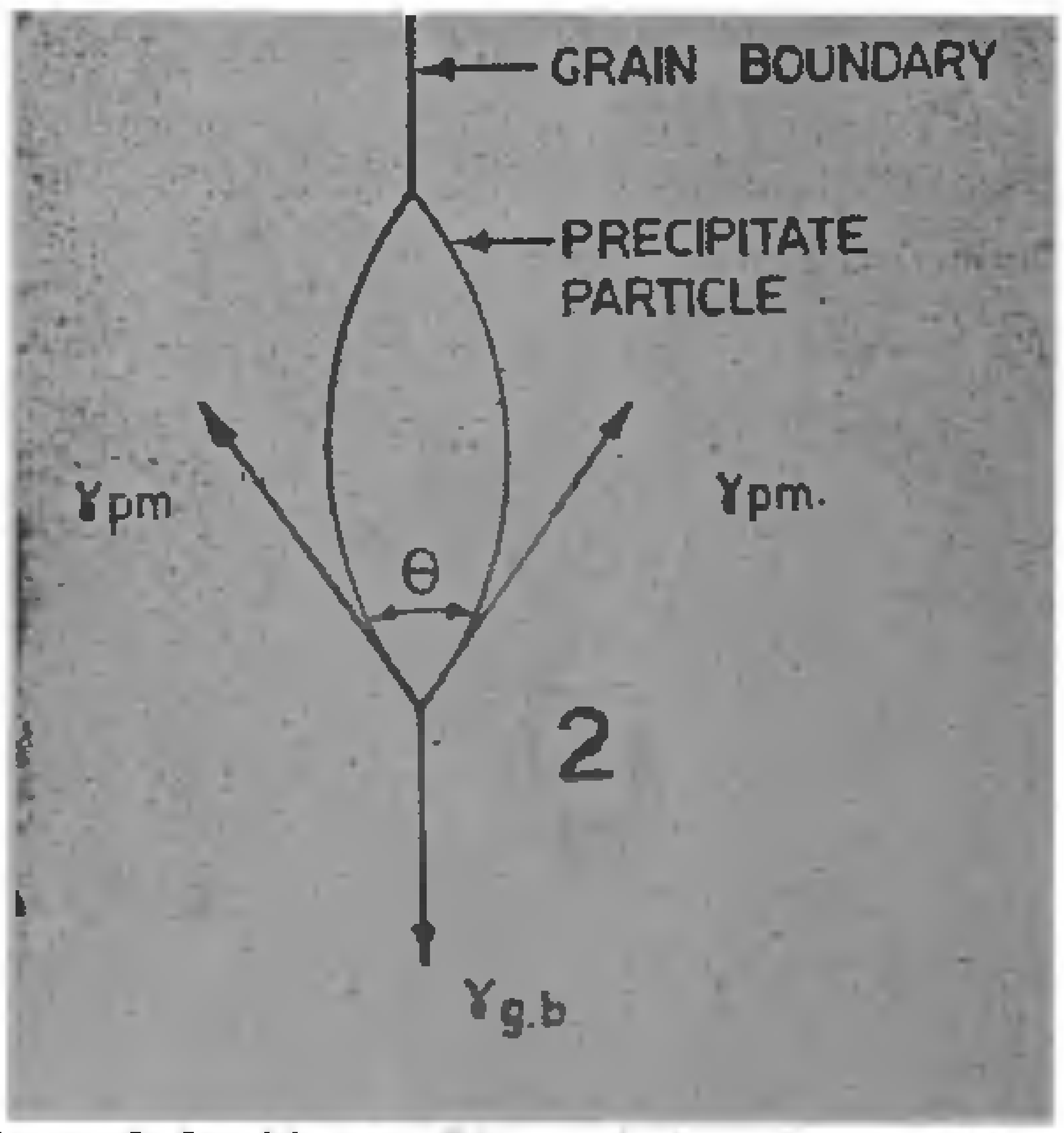
$$\cot\theta/4 = d/t \qquad (2)$$

where,

d is the diameter of the lens-shaped particle, and

t is the thickness of the lens.





FIGS. 1–2. Fig. 1. The grain boundary precipitation in Cu–Mg alloy internally oxidized at 800° C., × 28,000. Fig. 2. Relationship between grain boundary energy and particle-matrix interfacial energy for an equilibrium-shaped grain boundary particle.

Experimental

Copper-silicon alloys containing 0·12% and 0·25% silicon, and copper-magnesium alloy containing 0·21% magnesium were melted in

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a high purity graphite crucible in a vacuum induction furnace under argon atmosphere. The alloys were vacuum cast into suitable ingots and then subsequently reduced to strips of about 1 mm. thickness by hot extrusion, cold rolling and intermediate vacuum annealing. OFHC copper and high purity silicon and magnesium were used for making the alloys.

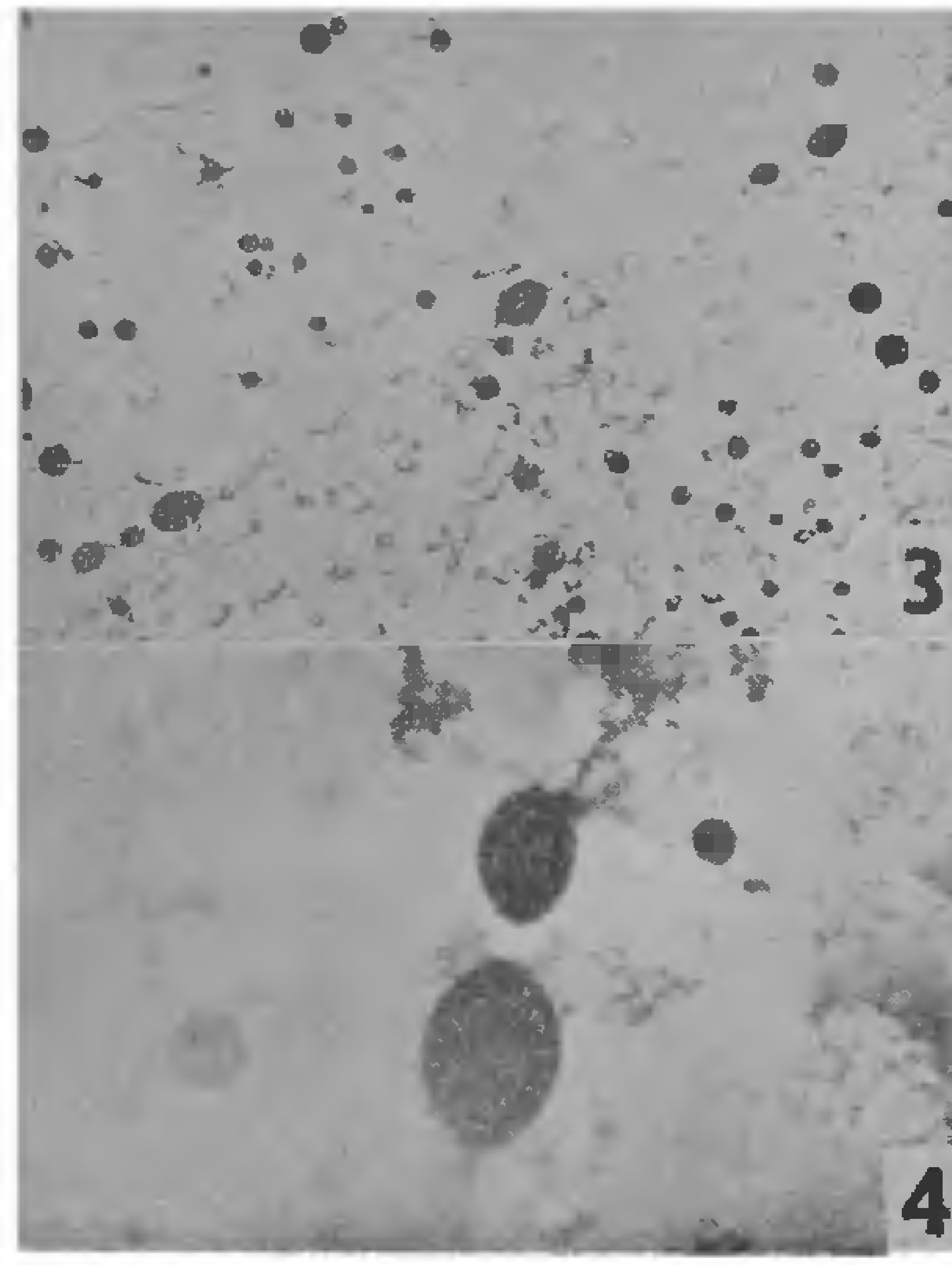
For internal oxidation specimens of about $1 \times 1 \times 0{\cdot}1$ cm. size were packed in a mixture of alumina, cuprous oxide and copper powder in the ratio of 2 : 1 : 1 and annealed in argon atmosphere at the desired temperature for a predetermined time to effect complete internal oxidation throughout the section.[7] The copper/copper oxide mixture provides the necessary oxygen partial pressure for internal oxidation while alumina powder prevents the sintering of the mixture to the sample. The oxidized samples were cleaned with fine emery-paper and electropolished in a D-2 solution. Carbon extraction replicas from these samples were prepared in the usual manner. To obtain the thin foils, coupons about 3 mm. dia. were trepanned from the specimen by spark machining. They were then dished on both the sides by jet polishing in an electrolyte of 50% orthophosphoric acid and then subsequently polished in D-2 electrolyte until a small hole just appeared in the centre. Both replicas and the thin foils were examined at 100 KV in EM-6/JEM-7 electron microscope.

The dihedral angles were measured on the enlarged photographs by drawing tangents to the particles as well as by measuring the '*d*' and '*t*' values. A good agreement was obtained between both the values which indicates that the two faces bounding the particle have identical radii.

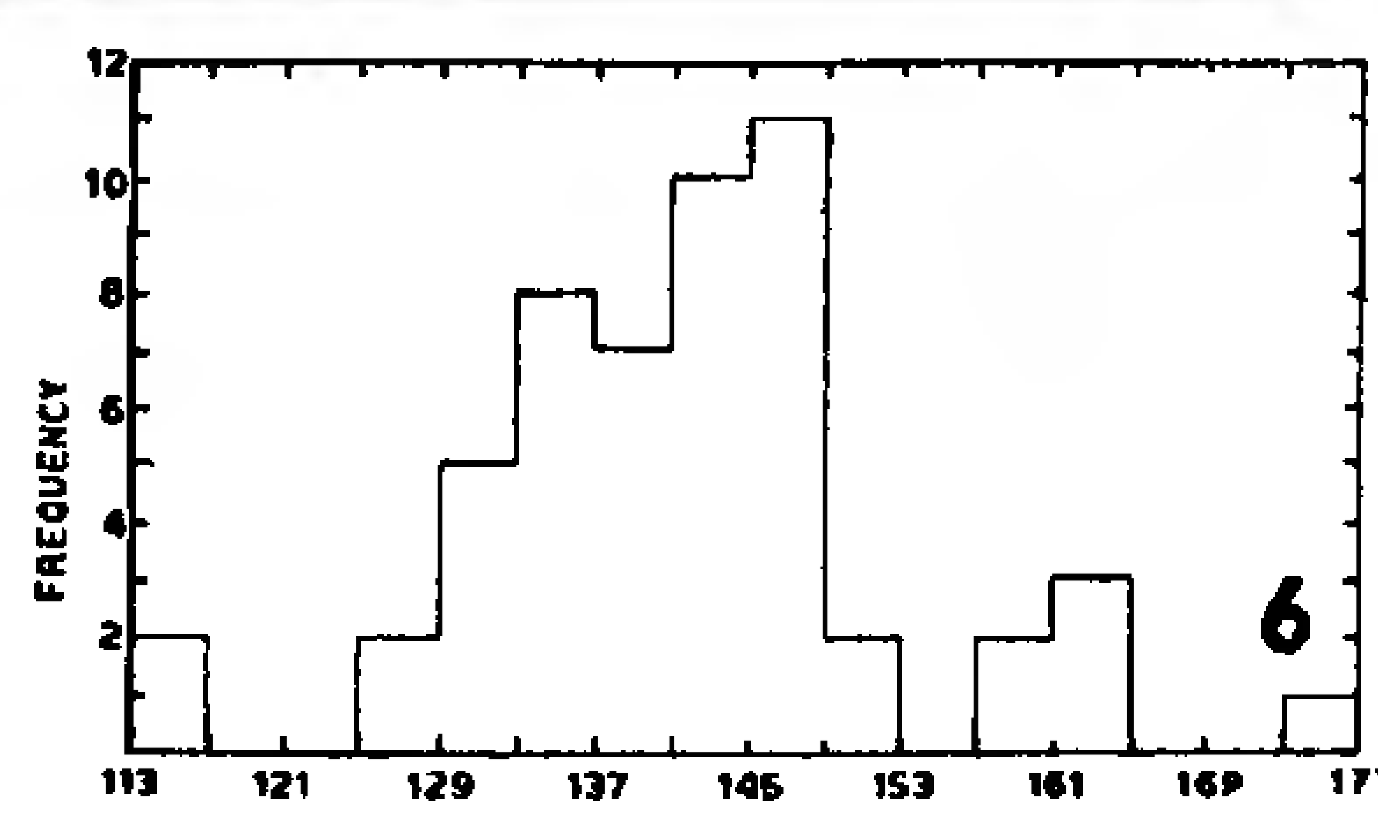
Results

The typical photographs of the grain boundary precipitates are illustrated in Figs. 1, 3 and 4. The grain boundary particles of silica were invariably lenticular in shape. However, occasionally few faceted particles (Fig. 5) were also observed. The grain boundary particles of magnesia were slightly elongated in the direction of the grain boundary but apparently they did not assume the equilibrium shape and hence could not be used for estimation of interfacial energy.

Both replicas and thin foils were used to calculate the dihedral angles. While examining thin foils, care was taken to align the grain boundary parallel to the electron beam as judged by the thickness of the grain boundary. The



FIGS. 3–4. Fig. 3. Grain boundary precipitation in Internally oxidized Cu-Si alloy (Carbon extraction replica), $\times$ 5,000. Fig. 4. Grain boundary precipitation in internally oxidized Cu-Si alloy (thin foil), $\times$ 10,000.



FIGS. 5–6. Fig. 5. Faceted grain boundary particles of silica observed in Cu-Si alloy, $\times$ 34,000. Fig. 6. A typical distribution of dihedral angles observed in case of internally oxidized Cu-Si alloy.

results obtained from the replicas as well as thin foils were handled separately by statistical methods. However, since both the results yielded identical values for the dihedral angles, they were combined together in the final plot. Figure 6 shows a histogram for dihedral angles observed in Cu-0·25 Si alloy oxidized at 1,000° C. It is seen that most of the values for dihedral angles fell between 124° and 153° C. However, occasionally much lower or higher angles were also encountered.

To calculate the interfacial energy of copper-silica interface, the grain boundary energy of copper was assumed to be 600 ergs/cm^2.[8] The results for dihedral angles and calculated interfacial energies are summarized in Table I. The dihedral angle was found to be independent of the silicon content of the alloy and to increase slightly with decrease in the oxidation temperature. No significant precipitate-free zones adjacent to grain boundaries were observed.

interfacial energy. This was ostensibly done to avoid any errors caused by the grain boundary being inclined to the electron beam. The procedure, however, does not seem to be justified because apart from the above variation caused by inclination of the grain boundary to the electron beam, there is a 'true' variation of the dihedral angle from particle to particle and grain boundary to grain boundary. The latter arising from the slight dependence of the dihedral angle on the misorientation across the grain boundary. Hence, statistical methods seem to be the best way of arriving at the correct estimate of the dihedral angle.

A much lower value of 564 ergs/cm.^{2} for copper-titania interfacial energy has been reported by Williams.[4] This was attributed by the author to the possible presence of certain impurities. However, Palmer[11] has subsequently shown that the presence of impurities affects the interfacial energy as well as the grain boundary energy to the same extent so that the dihedral angle remains unchanged. A more plausible explanation seems to be that the grain boundary titania particles do not assume the equilibrium shape because they are, unlike silica particles, crystalline in nature.

TABLE I

Interfacial energy of Cu/SiO_2 interface

Alloy		Temperature of oxidation (°C.)	Dihedral angle	Interfacial energy ergs/cm.^{2}	Reference
Cu-0·25% Si	..	1000	142±3°	921	Present work
Cu-0·12% Si	..	1000	144°	971	"
Cu-0·12% Si	..	800	147±3°	1056	"
Cu-Si	..	800	152	1000-1200	Ashby and Smith[10]
Cu-0·3% Si	..	800	135	780	Palmer[11]
Cu-0·3% Si	..	1000	135	684	"

DISCUSSION

Electron microscopic examination of the magnesia oxide particles in the matrix revealed that they were coherent with the matrix. A complete orientation relationship has been determined by Lewis.[9] A coherent interface suggests that the interfacial energy of copper-magnesia is probably very low.

The interfacial energy for copper-silica was found to be 950 ergs/cm.^{2} at 1,000° C. and 1,050 ergs/cm.^{2} at 800° C. Thus, interfacial energy shows a behaviour similar to that of surface energy of pure metals in that it decreases with increase in temperature.[8] However, the data are insufficient to estimate the temperature coefficient of the interfacial energy.

The above results are in good agreement with the earlier values reported by Ashby and Smith[10] for Cu/SiO_2 alloys. Palmer,[11] however, reported values of 680 and 780 ergs/cm.^{2} for temperatures of 1,000° C. and 800° C. respectively. The author chose the minimum values of dihedral angles to calculate the

Interfacial energy is a measure of the binding force between the surfaces. The greater the interfacial energy, the smaller will be the work of separation required to rupture the interface. During plastic deformation, extensive cavitation occurs at the interface to relieve the stress concentration at the particles. The incidence of such a cavitation process, which may affect the final fracture, will, therefore, be related to the magnitude of the interfacial energy. Studies on interfacial energy would, thus, provide a good insight on the role of dispersed particles in the fracture of materials.

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STERILIZING EFFECT OF A DIETARY SURPLUS OF BIOTIN IN *TROGODERMA GRANARIUM* EVERTS

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INTRODUCTION

INSECTS in general are known to require biotin in their diet for normal growth and development.[1] Recently, it has been shown in a few insect species that an excess of biotin in the diet causes reduction in their fertility.[2-5] It is of interest to know if biotin will elicit similar reactions in insects in general. Hence, such studies were conducted with Khapra beetle, *Trogoderma granarium* Everts, which is a serious pest of stored cereals.

MATERIALS AND METHODS

T. granarium were normally cultured on broken wheat and 5% brewer's yeast at 35 ± 1° C. and a relative humidity of 65% to 70%. For biotin treatment, a chemically defined diet was used.[6] Biotin was dissolved in 0·1 N sodium hydroxide and the known amounts added to the diet. The diet was allowed to equilibrate for 48 hours with the experimental conditions. One gm. diet was kept in a glass vial of 2·5 × 5·0 cm. In each vial, 20 ten-day-old larvae were introduced. Each treatment was replicated 10 to 12 times. The adults were removed from the diet soon after emergence and the period recorded. The males and females were separated and subsequently used for appropriate crosses. The diet containing only sodium hydroxide solution was used as controls. Additional controls using broken wheat flour and 5% brewer's yeast were also kept. Crosses were made between treated males and treated females, treated males and normal females and normal males and treated females. The eggs were scored at frequent intervals for ten days and allowed to hatch. The number of eggs hatched was also recorded.

RESULTS AND DISCUSSION

Higher doses of biotin, such as 0·5% and 1·0% inhibited further development of the larvae ultimately causing complete mortality. However, there was no mortality at the lower doses of biotin even upto 90 days of treatment. Higher levels of biotin treatment resulted in mortality in house-flies[3] and in *Aedes aegypti*.[5] *Dermestes maculatus*, a closely related species, however, was apparently able to tolerate upto 1% dietary biotin.[4] Comparison of toxicity based on such treatments may be taken with caution as it is possible that the amount of biotin uptake may vary in different cases as it is dependent on the period of treatment and the actual amount of food consumed by the insect. It is evident from Table I that the lower levels of biotin reduced the number of adult emergence. It was observed that this was due to a retarded development of the larvae. In all the treatments, the time taken for adult emergence increased with an increase in the biotin content of the diet (Table I). Such a growth inhibition was not recorded in other insect species studied.[2-5] The treatments in general reduced the fecundity, but the sodium hydroxide controls also showed a similar reduction. This will mean that the fecundity reduction may be due to sodium hydroxide treatment rather than the biotin overdosage. However, sodium hydroxide has been shown to have no effect on fecundity and fertility in house-flies.[3] Biotin did cause a reduction in the number of eggs laid in the insects studied so far.[2-5]

In *T. granarium*, the primary effect of biotin treatment was found to be on the fertility of eggs. A large number of eggs were sterile and