JOURNAL OF MATERIALS SCIENCE **25** (1990) 2299–2311

Growth of bi-partite and metallic copper whiskers

ANIMESH JHA*, P. GRIEVESON
Department of Metallurgy and Materials Science, Imperial College SW7 2BP, London, UK

Conditions for the growth of metallic copper and bi-partite whiskers of copper and cuprous sulphide are described with a particular emphasis on the physical chemistry of the growth process. The mechanism of growth of whiskers has been explained and the significance of phase equilibria in determining the morphologies of these whiskers at 1 273 K has been discussed. The length of growing whiskers depends quadratically on time and this has been particularly demonstrated for whiskers of metallic Cu in copper oxide–copper sulphide composites.

---

1. Introduction

The art and science of growing whiskers has been known to material scientists for the past few decades, yet it still remains a fascinating area to discover. A considerable amount of work was done [1–4] during the sixties related to the growth of various types of fibres of metals and ceramics, but nothing is known about the bi-partite whiskers. "Bi-partite whiskers" are composed of two different types of materials which grow together unidirectionally. Earlier the growth of ordinary whiskers was broadly studied under the following conditions: (a) during physical process such as controlled vaporisation and condensation of volatile inorganic compounds, (b) during chemical processes such as thermal decomposition, reduction etc. at high temperatures.

Related to these methods of growing whiskers, a few theories have been proposed [5–10] and these have been modified accordingly to suit the ambient conditions employed during the growth process. A thermodynamic driving force required for an appreciable rate of surface nucleation of lattice layers on a perfect crystal is known to be quite large in many cases and is related to the Gibbs volume free energy as shown in the following Equations 1 and 2. This was suggested by Volmer [5] where the nucleation rate N' is defined as follows:

$$N' = B \exp (\Delta G^*/\mathrm{RT}) \qquad (1)$$

and

$$\Delta G^* = \pi a \sigma^2 \cdot V \cdot N_0 / \Delta G_v \qquad (2)$$

where B is a constant (10^{18} mm^2), ΔG^* free energy increase to form a mole of critical nucleus σ = surface energy (J mm^{-2}), a is the height of lattice steps (mm), V is the molar volume, N_0 is the Avogadro number and ΔG_v is the free energy change to form one mole of solid from a vapour phase.

Based on this classical approach, a few models were then suggested by Sears [6], Frank [7] and Burton and Cabrera [8, 9] subsequently by Wagner [11]. All these models are in general based on the "supersaturation theory" which suggests that each step sweeps the growth surface before a new step is nucleated on a duly completed layer. For sustenance of growth of these steps, it is necessary to maintain a critical level of supersaturation to meet a material demand on these progressing ledges. Likewise, Sears [6] proposed that the "growth is possible under the condition of supersaturation of a growing species and it should be insufficient for a two dimensional nucleation". The need for imperfections such as dislocations to act as nucleation sites was emphasised. Similarly, Cahn [10] and Wagner and co-workers [12] stressed the significance of a second phase or energetically favourable sites during the growth of whiskers. Besides these, the importance of degree of supersaturation was emphasised by Brenner and Sears [13] which has connotations with the model proposed by Sears [6]. The effect of dislocations and impurities were identified during the growth of ceramic and metallic whiskers [2, 12–16].

The growth of whiskers during the reduction of non-stoichiometric oxides and sulphides has also been commonly observed [17–19] and the need for a low value of supersaturation (thermodynamic activity) has been analytically described by Wagner [11]. Wagner and Wagner [20] have shown that the cationic deficiency in cuprous sulphide is dependent on the thermodynamic activity of metallic copper and is expressed as follows:

$$\delta = 2 \cdot x^{\circ} \cdot \mathrm{Sinh}\,(-\ln a_{cu}) \qquad (3)$$

where x° is the concentration of free electrons per atom in ideal Cu_2S and a_{cu} is the activity of copper. In this investigation, we are going to explain a mechanism for the growth of bi-partite whiskers of metallic copper and cuprous sulphide based on the Cu–S–O phase diagram. In addition a possible mechanism for the growth of pure copper whiskers in cuprous oxide–cuprous sulphide composite will also be described. For relevant chemical reactions involved in the process

---

*Present Address: Department of Materials Technology, Brunel University, Uxbridge, Middlesex UB8 3PH.

0022–2461/90 $03.00 + .12

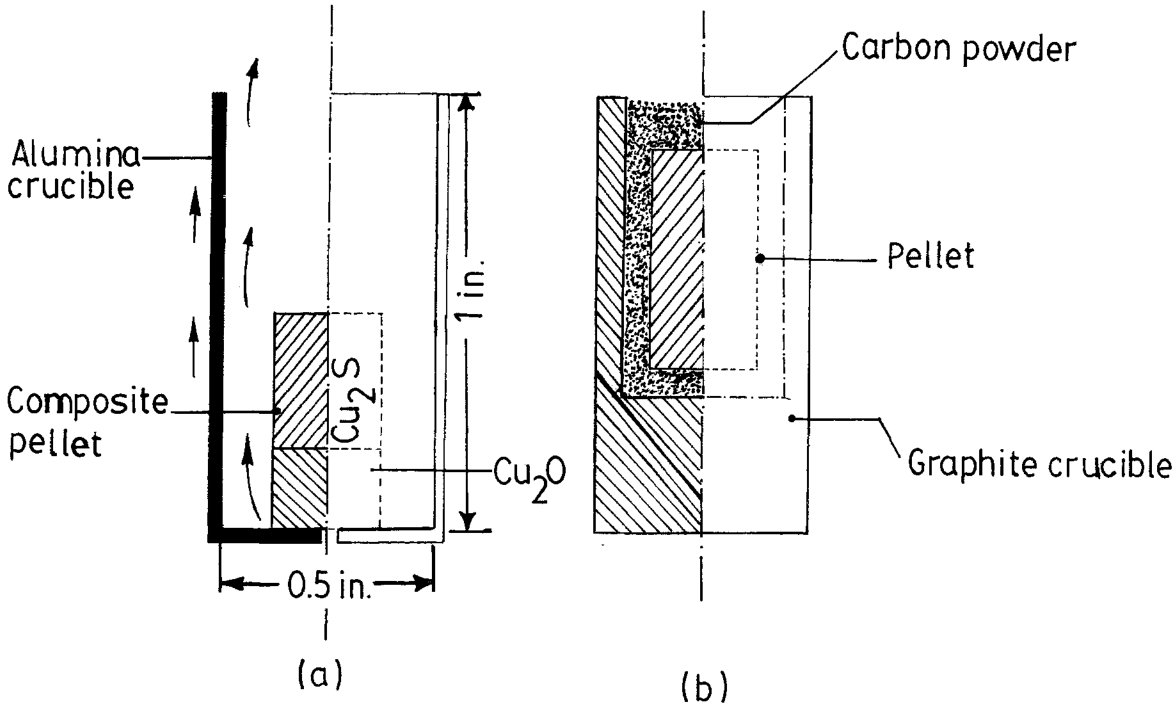

Figure 1 The arrangement of pellets during reduction and heat treatment experiments. (a) the composite pellet inside alumina crucible for heat-treatment (b) heat treated pellets inside graphite crucible.

of whisker growth, the condition of low supersaturation essential for the nucleation of whiskers is also verified in this work by calculating the Gibbs free energy change.

2. Experimental procedure

A thermogravimetric analysis technique was used to monitor any weight changes sustained by pellet samples during the course of reaction. Details of this experimental set up are described elsewhere [21]. Two following types of experiments were carried out at 1273 K: (a) heat treatment of mixtures of copper sulphide and oxide in a flowing stream of scrubbed argon gas followed by a reduction step inside a graphite crucible in the same atmosphere; (b) heat treatment of copper oxide-copper sulphide composites in a flowing stream of scrubbed argon gas.

Pure Cu_2S and Cu_2O (99.99% purity) were used in this work. These two compounds were synthesized in the laboratory by mixing CuS and Cu (99.99% pure), and CuO and Cu for the preparation of Cu_2S and Cu_2O respectively. Followed by pressing these two mixtures into cylindrical shape, these were then sealed under vacuum in silica capsules with about 0.2 atm of pure argon gas (99.999%). Each silica capsule was separately heated at a slow rate from 373 to 823 K in 8 h and then the temperature was raised in steps of 50 K to 1 073 K. At this stage, the temperature was held for 2 h and in the final stage, a homogenisation treatment was given at 1 273 K for 15 h. At the end of heat treatment, these capsules were quenched into an ice bath. Synthesized materials were crushed and examined by the X-ray diffraction technique which confirmed the presence of a single phase and, for example the synthesized Cu/CuS mixture was identified as the stoichiometric cuprous sulphide. Because the powder diffraction pattern of cuprous sulphide varies significantly from Cu/S = 2 to 1.87 and to ensure its stoichiometry, a chemical analysis was carried out to verify the copper content of the sulphide phase. Synthesis of these two stoichiometric compounds in absence of metallic copper is not feasible because of the presence of cationic deficiency in these two crystal lattices.

Pellets prepared by mixing powdered cuprous oxide and sulphide ($-75\,\mu m$ to $+\ 125\,\mu m$) were heated inside a silica reaction tube in a flowing stream of scrubbed argon gas. A Kanthal-wire resistance furnace was used as a source of heat. The arrangement of the two types of pellets described above during heat treatment is shown in Fig. 1. The weight change sustained by each pellet after reaction was continuously monitored by a chart recorder and a linear voltage digital transducer (LVDT). This was also verified independently by using an analytical balance. To establish whether any phase change had occurred during heat treatment, each pellet was analysed by X-ray diffraction technique. Similarly, the morphological changes occurred during the course of reaction were ascertained by examining these pellets under the scanning electron and optical microscopes. A semi-quantitative chemical analysis of these whiskers was carried out by using an Energy Dispersive X-ray Analysis (EDXA) technique. As an example the typical spectrum of Cu_2S is shown in Fig. 2. From the EDXA spectrum the calibration curves for oxides and sulphides of copper were drawn, see Fig. 3.

3. Results

3.1. Oxide-sulphide mixtures

The data for mass balance and phase analyses for the heat treated oxide and sulphide mixtures are summarised in Table I, whereas Table II lists the weight loss sustained by each of these pellets during the reduction reaction. Therefore from these two sets of data, it is possible to follow the compositional changes occurred

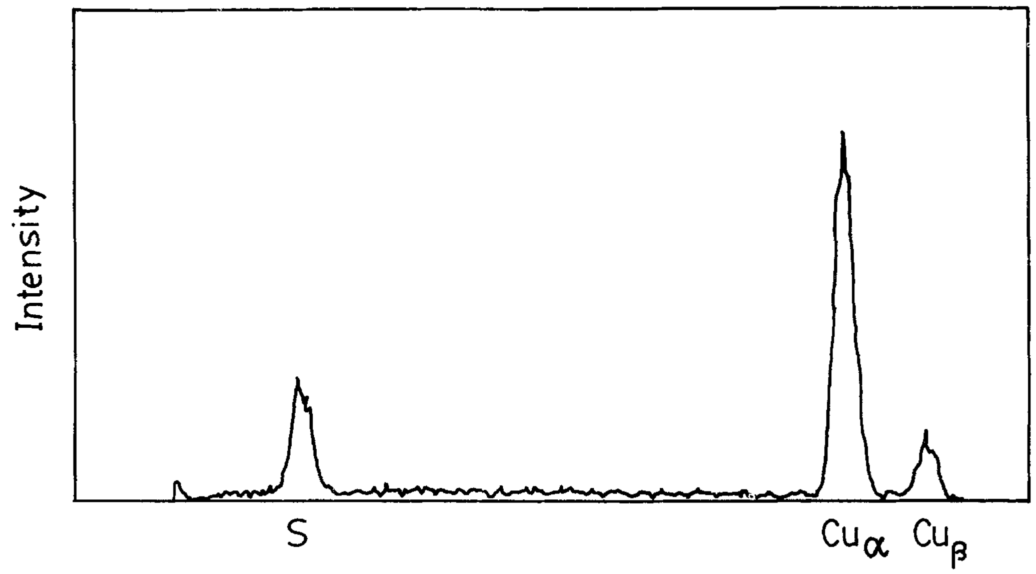

Figure 2 Typical energy dispersive X-ray spectrum of a bi-partite whisker. This particular analysis corresponds very closely to the composition of cuprous sulphide.

at any stage in a particular pellet. The Cu–S–O ternary section reported in one of our earlier works [21] is shown in Fig. 4. In this ternary section at 1 273 K, different mixtures after heat treatment lying in various phase fields are designated by the superscript "h". During the reduction step, when oxygen was removed from these pellets, the composition changes along the oxygen tie lines. The new points are designated by superscript "r" in this text. The reduction reaction usually ceased in 3 to 3.5 h.

A wide range of morphologies of whiskers were observed after the reduction step across the composition range shown in the ternary section and these results are summarized in Table II. Typical scanning electron micrographs are shown in Figs 5a and b from which the dimensions of these whiskers (average 1 000 μm) grown over a relatively short period of time (3 to 3.5 h) can be appreciated. These two micrographs show that there are two types of whiskers–namely long and thin whiskers (Fig 5a) and the other type is relatively shorter and thicker in dimension (Fig, 5b). The unusual morphologies of their tips is an indication that perhaps there was a liquid phase present at the beginning of the growth process, see Fig. 6.

The tips of these whiskers were analysed for their constituents by using the EDXA technique and the calibration curves. This enabled us to get an estimate of Cu/S ratio for each analysis. Results of these semiquantitative analyses are given in Table III. These results were also tested for their reproducibilities. Because these whiskers were often in a plane above the top surface plane of the pellet, a part of the emitted X-ray might not have been received by the detector. Therefore these analyses may have some error incorporated. In Table III, the analysed areas have been summarized.

"Long" and "thin" whiskers (Fig. 5a) observed after the reduction process have varying proportions of copper and sulphur as constituent elements. These specially grew during reduction of mixtures having compositions in the (L + Cu + Cu_2S) phase field. Semi-quantitative analysis of these two types of whiskers given in Table III shows that the whiskers shown in Fig. 5(b) are richer in copper, whereas those shown in Fig. 5(a) have a range of compositions. The Cu-rich type were relatively fewer in numbers. Compositions of heat treated oxide–sulphide mixtures, lying in a two phase field (L + Cu) underwent a different kind of morphological change. Only whiskers of pure copper grew under these conditions. Because the thermodynamic properties of oxides and sulphides in the liquid phase are different in each phase field, in Fig. 4 a range of driving force for the nucleation and growth of these new phases can be expected across the Cu_2S–Cu_2O edge. This could be the principal cause for their morphological diversity.

3.2. Composite pellets

The composites of Cu_2O and Cu_2S shown in Fig. 1 when heat treated in an argon atmosphere at 1 273 K suffered a significant loss in weight, and consequently

TABLE I Phase analysis of heat treated oxide–sulphide mixtures in argon atmosphere at 1 273 K. Argon flow rate – 200 ml/minute. Time – 3 h.

Mixture	Composition	Pct. Wt. Loss	Phase Analysis, Co K-alpha Radiation						
			Cu_2S	$Cu_{1.96}S$	$Cu_{1.93}S$	Cu_2O	CuO	Cu	CuS
1.	CuS : CuO = 3 : 1	15.21	vs	vs	vs	wm	w	–	–
2.	CuS : CuO = 2 : 1	14.72	vs	vs	vs	wm	w	vw	–
3.	CuS : CuO = 1 : 1	18.10	s	s	s	s	m	s	–
4.	CuS : CuO = 1 : 3	19.33	–	–	–	vs	–	ms	–
5.	Cu_2S : CuO = 1 : 1	14.35	m	m	m	s	wm	vs	–
6.	Cu_2S : CuO = 4 : 1	4.30	vs	vs	vs	wm	wm	m	–

Symbols and Acronyms Used: v – very, s – strong, m – medium, w – weak. Therefore, the relative intensity 'vs' means 'very strong'.

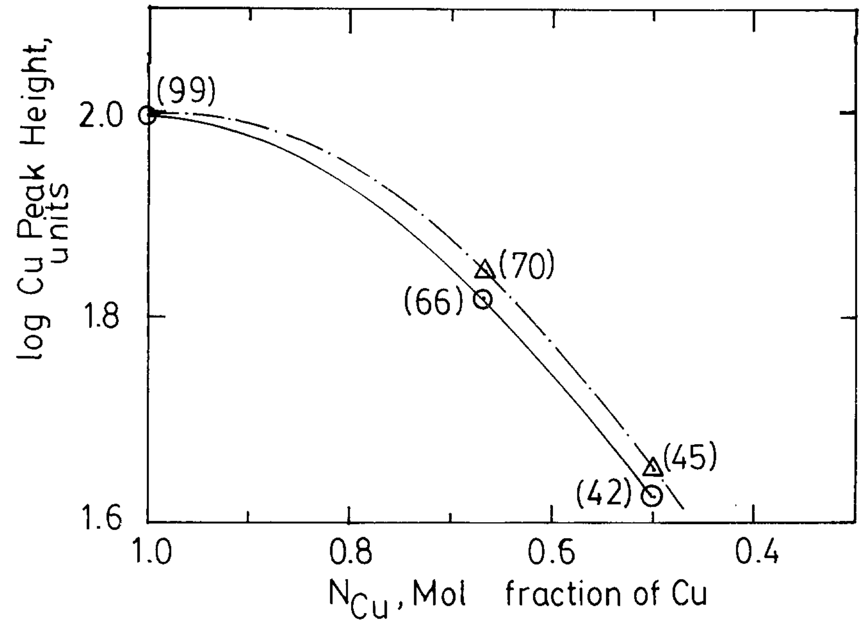

Figure 3 Calibration curves for a semi-quantitative determination of copper, sulphur and oxygen in heat-treated pellets of oxide and sulphide. ⊙ Cu_2S, △ Cu_2O.

had undergone both microstructural and macrostructural changes. These changes were largely due to the presence of a liquid phase in the Cu–S–O ternary at 1 273 K which was in equilibrium with the gas phase. The following visual changes were not observed in pellets shown in Fig. 1 where the Cu_2S part of the composite was on the bottom.

1. Whiskers of pure metallic copper were observed on the top of cuprous sulphide portion of each composite, see Fig. 7.
2. Nuclei of metallic copper in the form of a protruded surface appeared on the peripheral surface of sulphide, see Fig. 8.
3. Voids were observed at the oxide-sulphide interface, see Fig. 9.
4. The deposition of copper occurred on the peripheral surface of oxide. Due to reaction a significant amount of a volumetric shrinkage was also observed in the oxide portion of the pellet. Various data related to the growth of these whiskers in the composite pellets are summarized in Table IV. From this table, it is apparent from a sample of 20 to 25 whiskers that their average length '*L*' increases with increasing time for reaction. These lengths and the rate of change of length 'd*L*'/d*t* are plotted against time '*t*' in Fig. 10.

Observations under the optical and scanning electron microscope were also carried out on these pellets and the following inferences were drawn:

1. Both whiskers of copper on the peripheral surface of cuprous sulphide and particulates within the matrix of cuprous oxide had a dense structure, (see Figs 7 and 9) suggesting that these could have grown involving a diffusive process and not directly via chemical reaction (described in the next section).
2. The deposited layer of copper on the peripheral surface of oxide had many micropores. These were produced due to the evolution of a gaseous species during the nucleation and growth of copper.
3. The interfacial cracks observed in Fig. 9 could have opened as a result of high internal partial pressure of gases. Areas at the interface where the contact between Cu_2S and Cu_2O had been lost during the reaction, on the corresponding parallel plane at the top surface of these pellets whisker did not grow. This is shown schematically in Fig. 11. From this it can be inferred that there was a unidirectional flux of material maintained through the sulphide pellet which contributed to the growth process. From this optical examination, the population density of these whiskers grown on the free surface was estimated to be inversely proportional to the amount of copper deposited at the interface.

4. Discussion

4.1. Thermodynamics of growth of bi-partite whiskers:

The compositions of various oxide–sulphide mixtures after heat treatment, as shown in Fig.4, are thermo-

TABLE II The structural changes observed during the reduction of oxysulphide mixtures inside a graphite crucible at 1 273 K. Time – 3 h. Argon flow rate – 200 ml/min.

Mixture	Composition	Pct. wt. Loss during red^n	Phase Field after heat-treatment	Structural Changes			
				Thin Whiskers	Thick Whiskers	Faceted Shape	Liquid Phase
1h	CuS:CuO = 3:1	0.113	L + Cu_2S	–	–	–	–
2h	CuS:CuO = 2:1	0.791	L + Cu_2S + Cu	yes	yes	yes	yes
3h	CuS:CuO = 1:1	3.740	L + Cu	–	yes	–	yes
5h	Cu_2S:CuO = 1:1	0.236	L + Cu + Cu_2S	–	yes	–	yes
6h	Cu_2S:CuO = 4:1	0.295	L + Cu + Cu_2S	yes	yes	–	yes

"yes" means the particular structure grew or developed during the process of reduction.

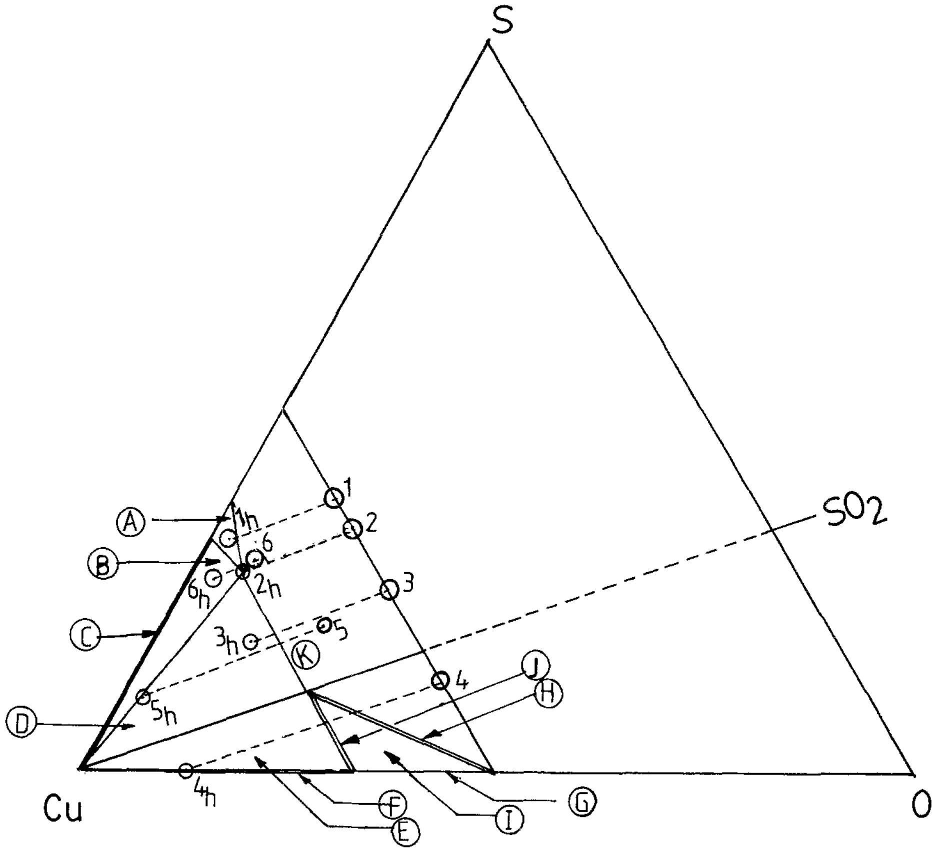

Figure 4 Phase relationship in Cu–S–O ternary section [21]. (A). L + Cu_2S (B). L + Cu + Cu_2S (C). Cu + Cu_2S (D). L + Cu (E). L + Cu + Cu_2O (F). Cu + Cu_2O (G). CuO + Cu_2O (H). L + CuO (I). L + Cu + Cu_2O (J). L + Cu_2O (K). Liquid. T = 1273 K.

dynamically unique. Under the reducing condition, there is negligibly small contribution of any other liquid (or solid)–gas reaction to the removal of oxygen because the reaction primarily proceeds at the liquid–graphite interface. Thermodynamic properties in an invariant phase field (L + Cu + Cu_2S) are constant at a given temperature and pressure. A composition in this phase field is therefore in equilibrium with pure solids such as metallic (Cu), metal sulphide (Cu_2S), the liquid (*L*) and a gas phase. During the reduction of oxysulphide liquid present in these pellets at 1 273 K its oxygen content changes. This means that in order to maintain the invariance of this phase field, both copper and cuprous sulphide must precipitate from the liquid phase during oxygen removal and therefore simultaneously maintain the thermodynamic activities of different components in this liquid at a constant value. The co-precipitation of these two phases is therefore the cause for the growth of bi-partite whiskers.

A variation in the composition of bi-partite whiskers, given in Table III, along its length can be explained as follows: (1) If a copper whisker grows beside a

TABLE III The semi-quantitative analysis of metallic copper and the bi-partite whiskers using the energy dispersive X-ray technique. The relative heights of copper and sulphur intensity peaks are given below for Cu_2S and CuS.

	Peak Heights, units		
	Cu	S	Cu/S ratio
Cu	99.0	–	99.0
Cu_2S	66.0	39.0	1.692
CuS	42.0	53.0	0.792
Cu_2O	70.0	–	–
CuO	45.0	–	–

Typical analysis of microscopically accessible parts of different types of whiskers

Type	Related Phase Field	Analysis in terms of Cu/S ratio	
		Tip	Stem
Bi-partite	L + Cu + Cu_2S	2.20, 2.66, 2.72 4.60, 5.51	3.05, 3.46, 3.75 4.40, 1.33
Thick Cu	L + Cu + Cu_2S	73.0, 14.93, 25.0 35.0	77.0, 25.0, 25.0 35.0
Thick Cu	L + Cu	81.0, 85.0	81.0, 85.0
Whiskers of Metallic	Cu	88.0, 90.0 75.0, 68.0	88.0, 90.0 75.0, 69.0

Note:- There is a possibility of an error in this analysis, because not all the emitted X-rays might have been received by the microscope detector.

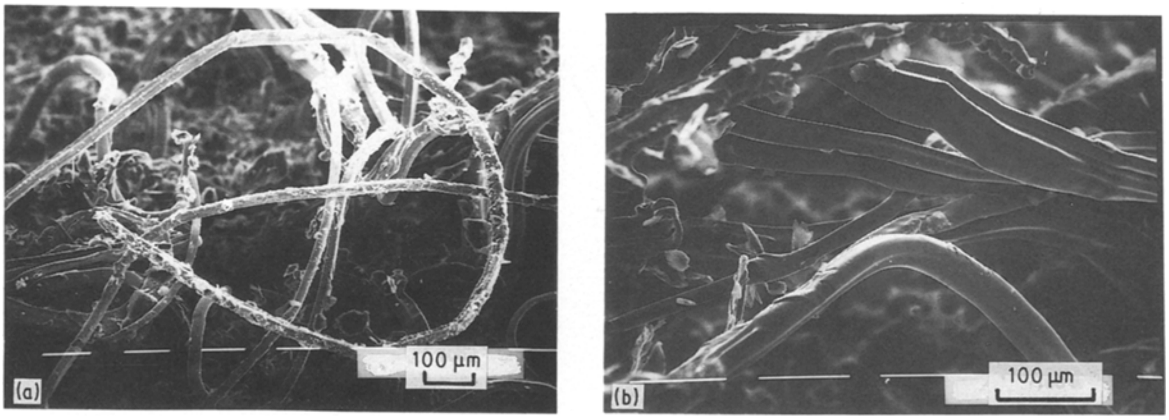

Figure 5 Low magnification scanning electron micrograph of bi-partite whiskers. Initial compositions of oxide–sulphide mixtures prior to the heat treatment is given below. Reduction carried out inside a graphite crucible at 1 273 K. (a) long and thin whiskers (b) shorter and thicker whiskers.

bi-partite one, a significant amount of copper will be deposited on the metallic whisker, leaving a surplus sulphur rich liquid from which cuprous sulphide will precipitate. This will give a high sulphur to copper ratio along the lengths of bi-partite whiskers. (2) If the evolution of sulphur dioxide also takes place, the deposition of material will be governed not only by the oxygen tie line but also by the SO_2 line. Therefore, a resultant tie line will run between these two composition paths. This could also give rise to a variation in the composition of whiskers along their lengths.

However, in a two phase field such as (L + Cu), the removal of oxygen is not governed by the Gibbs invariance rule. Here the composition of liquid changes univariantly until it reaches the phase boundary of a three phase field (L + Cu + Cu_2S). The energetics of the growth and nucleation processes are explained below in terms of the Gibbs Volume Free energy change (ΔG_v) which is expended to create a surface. A calculation for such a change can be carried out from the knowledge of the thermodynamics of the Cu–S–O melt. During the reduction of this liquid, the following reaction takes place.

$$(O)_{\text{sol}} + C(gr) = CO(g) \tag{4}$$

and the equilibrium constant K_4 is defined in Equation 5;

$$K_4 = \frac{P_{co}}{a_{(o)}\, a_c} \tag{5}$$

where $a_{(o)}$ is the activity of oxygen in the liquid phase and a_c is the activity of pure carbon and is equal to unity. Thus for any phase field, the deviation of 'K_4' from a value greater than unity would determine the necessary driving force for both the nucleation and growth processes and this is also a measure of the Gibbs volume free energy change. From Fig. 4, for each composition, a change in the driving force can be determined from compositions before and after the reduction process. The calculated values of ΔG_v for different compositions in (L + Cu + Cu_2S) phase field are given in Table V.

$$\Delta G_v = -RT \ln \frac{\{a^h(o)\}}{\{a^r(o)\}} \tag{6}$$

where R is the universal gas constant = 8.314 Joules per Kelvin per mole and T is the absolute temperature. The activity values in this equation can be written in terms of the partial pressure of sulphur dioxide gas using Schmiedl's empirical relationship [22] (see

TABLE IV Conditions for the heat treatment of copper oxide–sulphide composite and the results of morphological changes observed. Diameter of composite–6.35 mm, length–10 mm. Argon and Carbon Dioxide flow rate–200 ml per min.

Temperature, T	Atmosphere	Time, t hour	Moles of SO_2 $\times 10^3$, lost	Morphological & Physical Changes	
				Length 'L' mm.	Liq. Phase
1273	argon	0.75	–	–	√
1273	argon	7.25	0.180	0.650	√
1273	argon	8.00	1.023	0.925	√
1273	argon	15.00	2.706	2.250	√
1273	argon	20.00	0.195	3.100	√
1273	argon	24.00	0.572	3.600	√
1023*	CO_2	15.00	0.925	0.15–0.25	x
1273	CO_2	24.00	0.756	–	√
1273†	argon	7.250	0.182	–	?

*means that the growth of whiskers was observed at the Cu_2S–Cu_2O interface.

†means that the Cu_2O portion of the composite was positioned up.

√ = present

x = absent

? = doubtful

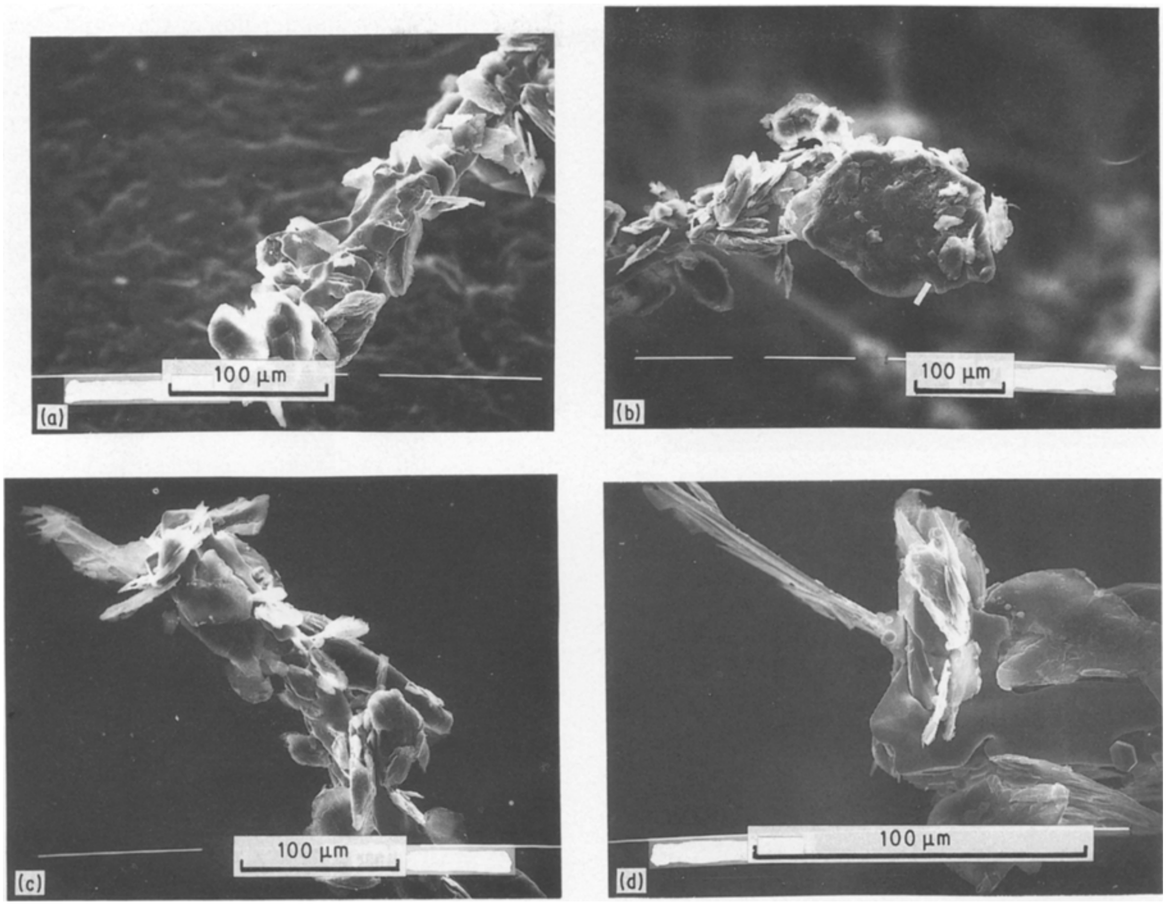

Figure 6 Various morphologies of the tip of a bi-partite whisker. Compositions of oxide–sulphide mixture before heat-treatment (a) and (b) CuS : CuO = 2 : 1 (c) and (d) Cu_2S : CuO = 4 : 1. Mixtures reduced at 1 273 K inside graphite crucible.

Equation 7) and the equilibrium relationships (see Equations 8 and 9).

It is evident from the computed ratio of the partial pressures of SO_2 in Table V that this value is seldom far away from the value at unity thus satisfying the necessary condition of "slight supersaturation" required for such a unidirectional growth. This was further ascertained in our work when the mixture with CuS : CuO = 1 : 3 was heat treated and reduced, no whisker growth was observed. For this composition, the phase field is (L + Cu + Cu_2O) and the driving force for the nucleation of copper (ΔG^*) is small because $a_{cu} \gg 1$ i.e. ΔG_v is large.

$$(\text{wt \% O}) = [10^{-(1.95989+1013.2/T)}]p_{SO_2}^{1/2} \quad (7)$$

$$Cu_2S(l) + Cu_2(l) = 6Cu(S) + SO_2(g) \quad (8)$$

$$a_{Cu_2O} = \left(\frac{p_{SO_2}}{K_8}\right)^{1/2} \quad (9)$$

For (L + Cu + Cu_2S) phase field, the activities of Cu and Cu_2S are unity, hence Equation 9 can be written as shown above. This relationship does not hold true for the (L + Cu) phase and therefore for pellets 1 h and 3 h in Table II, the value of the Gibbs volume free energy change cannot be determined from

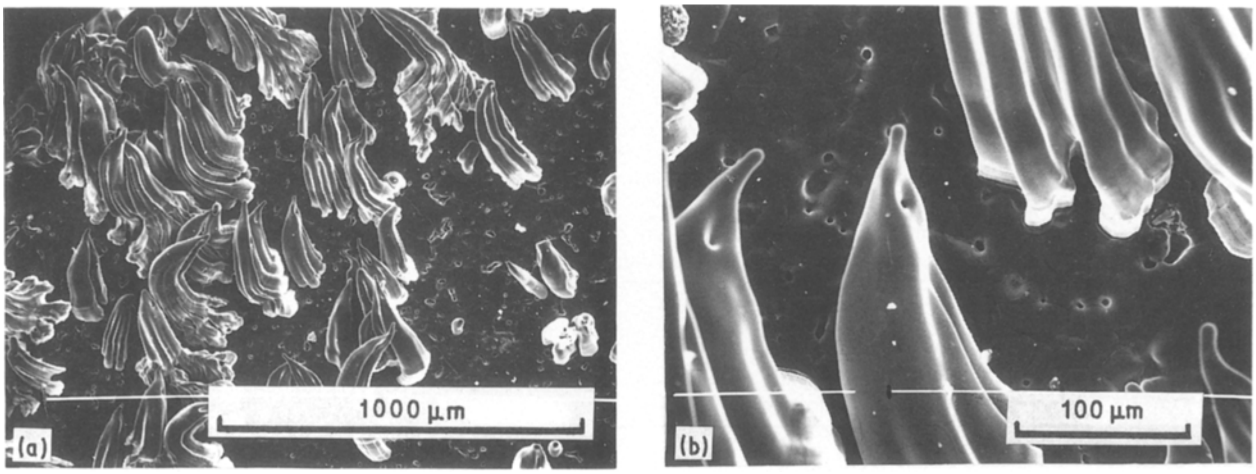

Figure 7 Whisker growth in an oxide–sulphide composite. (a) Low magnification, (b) high magnification.

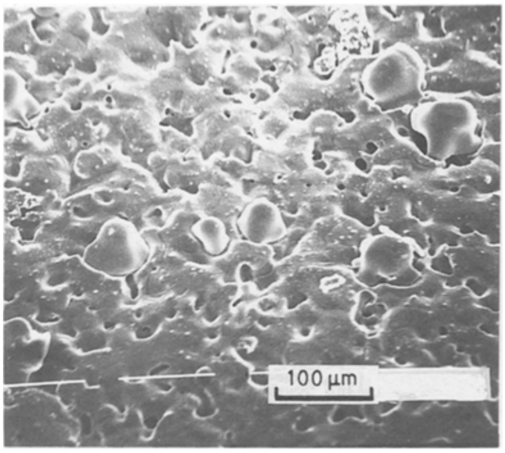

Figure 8 Growth of nuclei on the peripheral surface of Cu_2S in the composite.

the measured weight loss. In this univariant phase field, for calculating the value of ΔG_v, it is necessary to know the activities of sulphur and oxygen (or oxide and sulphide) in the liquid phase.

Mechanistically the liquid phase must be present at the beginning of the nucleation and growth process at energetically favourable sites, because it is from this phase the transport of material will continue for the sustenance of the growth process. As soon as the reduction process ceases, both the nucleation and growth of new whiskers stop.

4.2. The nucleation and growth of metallic copper whiskers during heat treatment of oxide–sulphide composite pellets:

The liquid phase characterized in the previous section also forms during heat treatment at the interface of composite pellets. In the beginning, the formation of a sulphur rich liquid takes place and as the time progresses both the volume and the oxygen content of this liquid rises as a result of oxide dissolution thus raises the equilibrium partial pressure of SO_2 in the system (see Equations 8 and 9). When the volume of this liquid becomes unsustainable at the interface, it drains over the peripheral surface of oxide and produces metallic copper. The drainage of liquid does not occur when the pellet is in the inverted position, as explained earlier. Due to evolution of SO_2, the pellet loses its weight during the course of reaction.

The nucleation of whiskers, however, does not depend upon the magnitude of weight loss but on a mechanism illustrated below. The formation of liquid at the interface initiates the diffusion of S^{-2} and O^{-2} anions in stoichiometric Cu_2S and Cu_2O respectively. This results into a counter-flux of Cu^{+1} and electrons which is essential to balance the electroneutrality of the dissolution reaction. The flux of cations and electrons sets up in the longitudinal direction of the pellet and is assisted by the presence of Schottky defects present in the sulphide and oxide crystal lattice [23]. It has been also suggested by Swalin [23] that the species which has the lowest partial pressure in the gas phase, will be deficient in that crystal lattice at equilibrium. The presence of SO_2 in the gas phase thus creates an anionic excess in these two stoichiometric solids according to following reactions:

$$SO_2\,(g) = \tfrac{1}{2}S_2(g) + O_2(g) \tag{10}$$

$$\tfrac{1}{2}S_2(g) = S_{Cu_2s} + V'_{cu} + h \tag{11}$$

$$\tfrac{1}{2}O_2(g) = O_{Cu_2O} + V'_{cu} + h \tag{12}$$

where h is an electron hole in the valence band and V'_{Cu} is a vacant cationic interstitial with a negative charge in the lattice. In this way, the defect structure and the ionic species maintain an equilibrium with the gas phase.

It is evident from our results and the thermodynamic analysis of Schmiedl [22] that it is the dissolution reaction of anions which controls the partial pressure of gaseous species and hence the thermodynamic activity of Cu at the interface. Therefore it is important that the activity of copper in the liquid at the interface should not exceed the critical limit so that cationic transport for whisker growth remains sustained.

4.3. Analysis of diffusive process during growth

Steele [24] has measured the chemical diffusivity of copper in cuprous sulphide and oxide. In polycrystals of sulphide at 713 K and 100 mv, the diffusivity of copper is of the order of 7-8 mm^2 sec^{-1}, whereas for cuprous oxide single crystal, this value is 0.03 mm^2 sec^{-1} at 1 273 K. At a given temperature, T, the chemical diffusivity Cu^{+1} can be defined in terms of its mobility and the slope of a variation of its activity coefficient (γ_{Cu}) with mole fraction of Cu in the sulphide [25] and which is equal to

$$D_{Cu} = B_{Cu} \cdot RT \cdot \left[1 + \frac{d(\ln \gamma_{Cu})}{d(\ln N_{Cu})}\right] \tag{13}$$

where D_{Cu} is the chemical diffusivity of copper (mm^2 sec^{-1}), B_{Cu} the mobility of Cu in sulphide lattice and N_{Cu} is the mole fraction of Cu in Cu_2S crystal. Evidently the value D_{Cu} will depend upon the extent of non-stoichiometry in Cu_2S.

The value of the term within the parenthesis can be

TABLE V Relationship between the composition, partial pressure of $SO_2(P_{SO_2})$ and ΔG_v for various compositions in Cu–Cu_2S–Cu_2O ternary at 1 273 K. Atmosphere of argon was maintained at a flow rate of 200 ml min^{-1}.

No.	After heat-treatment (h) Oxygen Content					After Reduction (r) Oxygen Content				ΔG_v Joules
	Mole % O	Wt. % O	$P_{SO_2}^{h\times 10^3}$ atm.	% Wt. loss, SO_2		Mole % O	Wt. % O	% Wt. Loss CO	$P_{SO_2}^{r\times 10^3}$	
2 h	6.8	2.28	0.519	14.72	2 r	6.772	2.27	0.791	0.514	−105.31
5 h	2.4	0.805	0.065	14.35	5 r	2.391	0.803	0.236	0.064	−167.99
6 h	3.2	1.073	0.115	4.3	6 r	3.189	1.071	0.295	0.114	−94.83

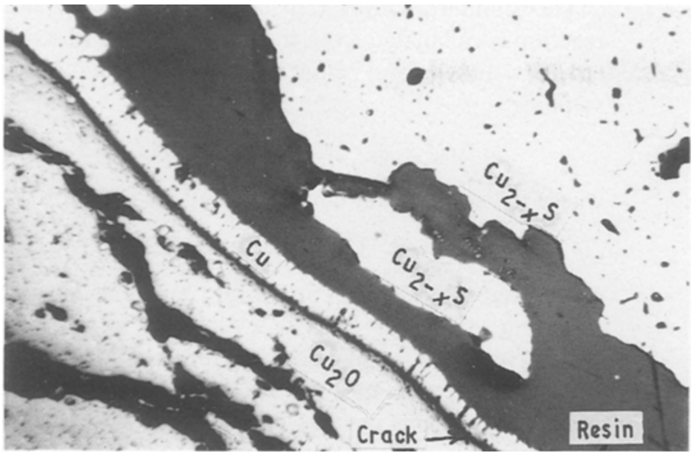

Figure 9 Optical micrograph of a heat treated composite pellet. × 100.

evaluated from the slope of an extrapolated straight line shown in Fig. 12 and is obtained from the data of Blanks and Willis [26]. By substituting the value of the slope in Equation 11 at 713 K, the value of D_{Cu} can be expressed in terms of its mobility which is

$$D_{\mathrm{Cu}} = 1\,2310\, B_{\mathrm{Cu}} \qquad (14)$$

where the mobility is in mm ampere unit and is a direct indication of the velocity of diffusive species at a given temperature. These values represent the transport processes in cuprous sulphide. The corresponding value of mobility obtained is 1.550×10^{-5} in mm ampere units.

Wagner [27] worked on the growth of Cu in copper

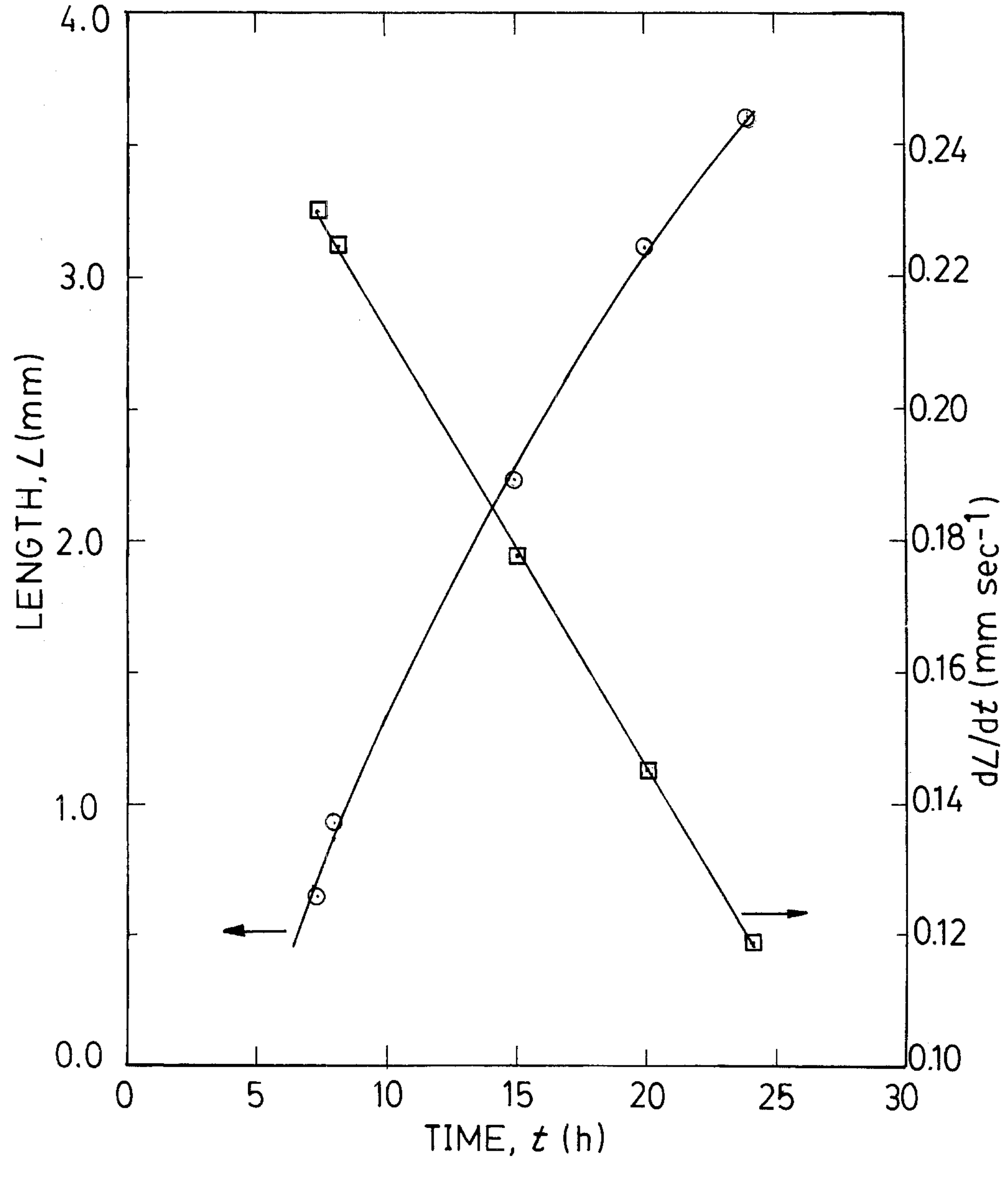

Figure 10 The variation in the length (L) and $\mathrm{d}L/\mathrm{d}t$ of metallic copper whiskers (μm) with time (h). Argon flow rate — 200 ml min^{-1}.

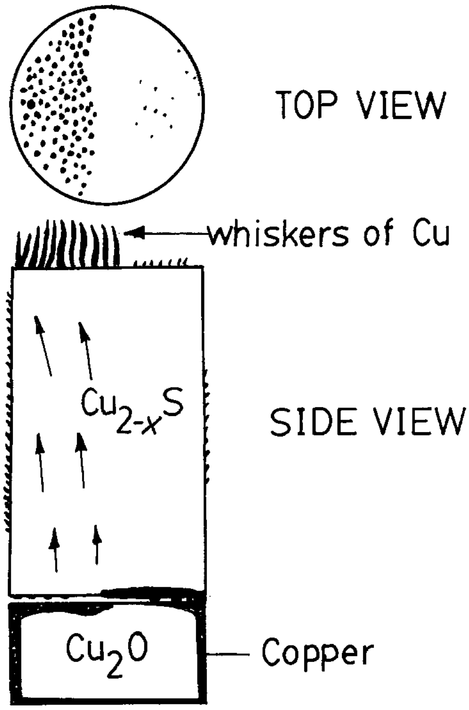

Figure 11 Schematic diagram for the areas of preferential growth of whiskers (not to the scale).

oxide–copper sulphide composite which is shown in Fig. 13. This composite was heated in a CO_2 atmosphere at 1 023 K for 2 h. An increase in diameter by 0.49 mm was observed over this period. Wagner suggested that the equilibrium described by reaction (8) influences the chemical diffusivity of Cu^{+1} cations from the periphery of the composite to the core.

The standard Gibbs free energy change for this reaction is calculated from the data available in reference (28) and is given below in Joules for each mole of sulphide.

$$\Delta G_{v,8} = 212\,495 - 199.94T \qquad (16)$$

where the equilibrium constant, K_8 is given below:

$$K_8 = \mathrm{Exp}\,(-\Delta G_{v,8}/\mathrm{R.T}) \qquad (17)$$

Calculated values of the equilibrium constant, K_8, and the value of a_{Cu} at 1 023 K are 0.6245 and 0.9245 respectively. The activities of the sulphide, oxide and the partial pressure of SO_2 are assumed to be equal to unity which yields a value of driving force equal to $-\mathrm{RT}.\ \ln a_{Cu} = 664.5$ Joules and is positive. Hence the nucleation of Cu is thermodynamically not possible.

We, however, propose that it is the equilibrium between cuprous oxide and CO_2 shown below which is established during heat treatment.

$$Cu_2O(S) + CO(g) = 2Cu(S) + CO_2(g) \quad (18)$$

and the value of $\Delta G_{v,17}$ in Joules is:

$$\Delta G_{v,17} = -112\,522 + 15.06T \qquad (19)$$

For $a_{Cu_2O} = 1$ and $P_{Co} = 1.1 \times 10^{-5}$ atm, the value of a_{Cu} reaches unity at 1 023 K. If P_{co} exceeds this value, the nucleation of Cu will be thermodynamically favourable. From the observed growth of copper in Wagner's experiment, the chemical diffusivity of copper in polycrystalline cuprous sulphide has been calculated and is shown below by assuming that the

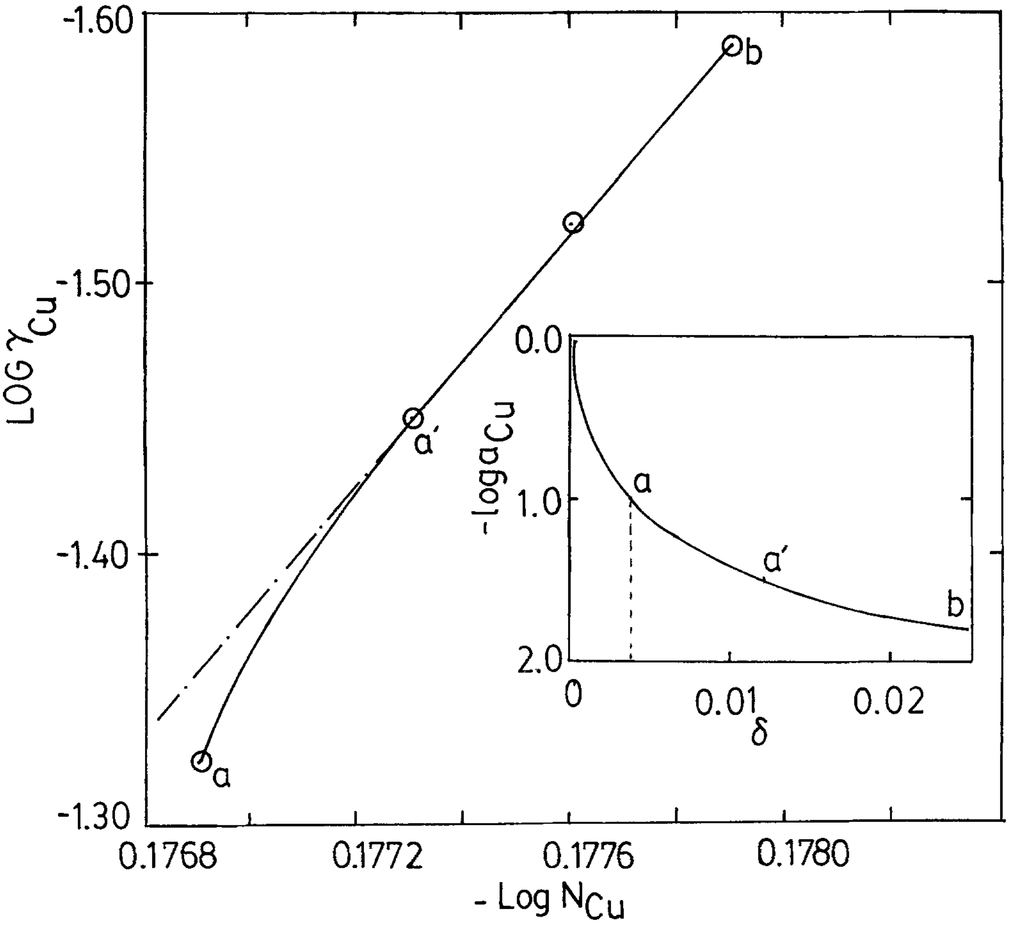

Figure 12 The variation of $\ln \gamma_{Cu}$ with $\ln N_{Cu}$ in Cu–Cu_aS system at 713 K [19].

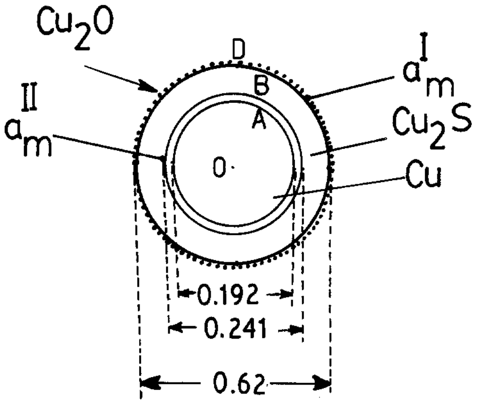

Figure 13 The composite Cu-Cu_2O-Cu_2S in Wagner's experiment [27].

weight gained by the copper rod varies linearly with time. The rate of growth ($\overset{n}{\text{Cu}}$) therefore can be directly determined from the mass of copper deposited over a period of time '*t*'. To calculate the chemical diffusivity of Cu^{+1} cations in Cu_2S, the following equation suggested by Wagner [11] is used.

$$\overset{n}{\text{Cu}} = \frac{4AC_{\text{Cu}}\,D^*_{\text{Cu}}}{r \cdot f_{\text{Cu}}}\, ln\left[\frac{a^{\text{I}}_{\text{Cu}}}{a^{\text{II}}_{\text{Cu}}}\right] \tag{20}$$

Also we know that

$$D_{\text{Cu}} = \frac{3D^*_{\text{Cu}}}{\delta^*} \tag{21}$$

Substituting Wagner's result in Equation 19, (see Appendix), D^*_{Cu} is 0.117 mm^2 sec^{-1}. For a value δ^*, the deviation from stoichiometry equals to $0.035 \ll 1$, the chemical diffusivity (D_{Cu}) from Equation 20 is then equal to 9.86 mm^2 sec^{-1}. By plotting D_{Cu} in polycrystalline cuprous sulphide against $1/T$ in Fig. 14 and 713 and 1023 K and by extrapolating it to 1273 K yields a value diffusivity which is equal to 11.85 mm^2 sec^{-1}. Below we will be calculating the value of D_{Cu} from our whisker growth rate data at 1273 K. If however we consider Wagner's equilibrium (Equation 8), the value of D_{Cu} becomes negative for $a_{\text{Cu}} = 0.9245$ which is physically impossible. This suggests that reaction (8) does not govern the growth of Cu and the radial growth of copper rod at 1023 K in CO_2 gas (occurs due to reaction 17.)

For the data shown in Fig. 10 a second order polynomial curve has been fitted using curvillinear regression analysis and is shown in this figure. The equation for this curve is shown below for which the first derivative decreases with increasing times, see Equation 22.

$$L = -1.4105 + 0.278\,t - 3.325 \times 10^{-3}\,t^2 \tag{22}$$

$$\mathrm{d}L/\mathrm{d}t = 0.278 - 6.62 \times 10^{-3}t \tag{23}$$

The decrease in the rate of growth is attributed to an increasing diffusion path for mobile cations in Cu_2S. If we assume that the growth of whisker follows Wagner's parabolic oxidation rate law as shown above for which the rate constant, λ, is described by Turkdogan [29] in Equation 23.

$$\lambda = 2L\frac{\mathrm{d}L}{\mathrm{d}t} = 2.\int_{a_{\text{int}}}^{a_{\text{cu}}=1} D_{\text{Cu}} \cdot \mathrm{d}lma_{\text{Cu}} \tag{24}$$

which upon integration gives

$$\lambda = -2D_{\text{Cu}}\ln\left[\frac{a_{\text{int}}}{a_{\text{Cu}}}\right] \tag{25}$$

Here the subscript 'int' defines the activity of metallic Cu at the interface of whisker and copper sulphide. If we assume that in Equation 24 with increasing time, a_{int} will decrease gradually to a value of unity such that D_{Cu} is fixed with respect to L then for sulphide containing 66.37 mol% of Cu and $L = 0.65$ mm after 7.25 h, the diffusivity of Cu in sulphide at 1273 K is 11.22 mm^2 sec^{-1} for $a_{\text{int}} = 1.01$. This value of activity of Cu at the interface is comparable with the corresponding values of ΔG_v given in Table V. The values of D_{Cu} obtained from our growth data and that from the extrapolation of low temperature diffusivity data are in good agreement. Plotting $\log D_{\text{Cu}}$ against $1/T$ at 1273 K in Fig. 14, we obtain a relationship for D_{Cu} with temperature from which the activation energy for the diffusion process can be derived:

$$D_{\text{Cu}} = D_0 \exp\left(-E_{\text{diff}}/R.T\right) \tag{26}$$

The derived value of E_{diff} from the slope of straight line in Fig. 14 is 7000 Joules per mole of Cu_2S. This value corresponds to a relatively small thermally activated barrier, which could be due to the combined effects of

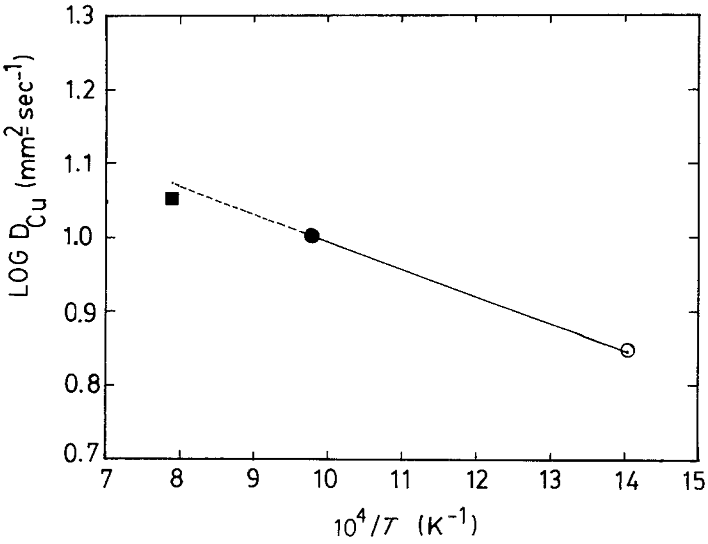

Figure 14 Log D_{Cu} against $1/T$ curve for diffusivity of Cu in polycrystalline Cu_2S. ○ Steele [24]; ● – Wagner's work [27]; ■ – this work.

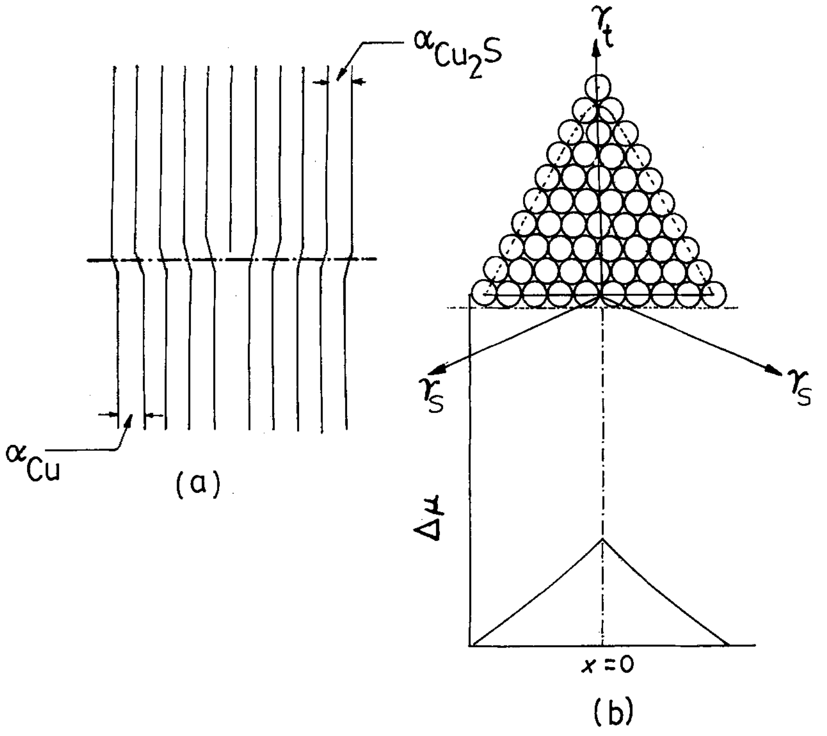

Figure 15 (a) Schematic diagram of mismatch between a substrate (Cu$_2$S) and nucleating phase (Cu) planes, (b) schematic representation of atomic roughness of a screw dislocation and variation of $\Delta\mu$ with thickness x [33].

a large grain boundary area in cuprous sulphide, and a relatively large number of cationic vacancies in this material. It is, however, not possible from these results whether the surface diffusion (grain boundary effect) or the lattice diffusion (cationic vacancies) governs the growth process. In general the activation energy for lattice diffusion is much larger than the surface diffusion. The mechanism of whisker growth, however, is believed to be ostensibly governed by a surface diffusion process involving screw dislocation(s) and is explained below in the next section.

4.4. Possible mechanism of nucleation and growth of whiskers–a hypothetical approach

It was established in the previous section that the magnitude of the volume free energy change (ΔG_v) determines the surface created. If whiskers are believed to have fewer defects and imperfections, it is then necessary that these must have been kept at a minimum from the beginning of the growth process. This is only possible when the change in volume free energy is small and hence the barrier to the nucleation of metallic copper is large (cf. Equation 1). Also, when the nucleation begins on the substrate, the new phase must wet the substrate plane to minimize the interfacial tension between these two phases. It is therefore required that the very first layer must have a close crystallographic plane identity with the substrate plane. Invariably such planes are nearly close packed during the nucleation of whiskers [30, 31] and any mismatch of the first few planes with the substrate would create defects which later on participate in the growth process. In the initial stage of growth, the possible defects could be the vacancies or dislocations at the interfacial plane. The degree of mismatch between the crystallographic planes of a substrate and a new phase produces a lattice disregistry and is believed to be responsible for the formation of screw dislocation(s) during the growth process, see Fig. 15(a). The value lattice disregistry, β, between copper and cuprous sulphide in this case can be evaluated from the equation proposed by Turnbull and given by Swalin [32].

$$\beta = \frac{\alpha_{Cu_2S} - \alpha_{Cu}}{\alpha_{Cu_2S}} \qquad (27)$$

Here α designates the lattice parameter. For the growth direction along the C-axis in Cu$_{1.96}$S crystal lattice, the value of β is 0.0954 and corresponds to 1 dislocation at every 4.206 nm. Screw dislocations during the growth process act as a potential sink for material and this can be explained on the basis of the Gibbs-Thompson equation. A schematic diagram of atomic arrangement around a screw dislocation at the tip of a whisker is shown in Fig. 15(b). The presence of large numbers of unsaturated bonds between the atoms at the tip of whiskers is believed to be the cause for material transport during the growth process.

This material transport occurs along the surface and is commonly known as "surface diffusion". The driving force for this material transport is therefore a measure of unsaturation and is explained by the Gibbs-Thompson chemical potential, $\Delta\mu$, [33] which is defined below for a curved surface shown in Fig. 15b.

$$\Delta\mu = \Gamma\Omega K_0 \qquad (28)$$

where Γ is the surface energy. Ω is the volume per atom and K_0 is related to the radius of curvature, and is roughly equal to d^2y/dx^2.

Therefore, it is evident from these equations that the flux of material depends upon the position "x".

Conclusions

The growth of bi-partite whiskers of Cu and Cu$_2$S in the Cu–S–O system is possible if oxygen is removed from the liquid lying in the three phase field (L + Cu + Cu$_2$S). The rate of growth of bi-partite whiskers is faster than the growth of pure copper whiskers. It is explained that a critical value of supersaturation is

TABLE VI The computed values of length 'L' in mm of metallic whiskers for different time 't' (hours) from the following equation.

$$L = -1.1405 + 0.278\,t + 3.325 \times 10^{-3} t^2 \text{ mm}$$

$$T = 1273\,\text{K}$$

Time "t", h	Average Measured Length "L" mm	Computed Length "L" mm	dL/dt, mm hr^{-1}
7.250	0.650	0.6968	0.2294
8.000	0.925	0.8670	0.2244
15.00	2.250	2.275	0.1778
20.00	3.100	3.081	0.1445
24.00	3.600	3.606	0.1180

required for the growth of bi-partite whiskers. The supersaturation is related to the thermodynamic activity of the growing phase. In a similar way, the growth of pure copper whiskers was also found to be dependent on the activity of copper at the oxide–sulphide interface in the composite.

The diffusivity of Cu in cuprous sulphide is of the order of 11.2 mm^2 sec^{-1} in Cu_2S at 1273 K. The rate of growth has a parabolic dependence on time at this temperature.

Appendix

From Fig. 14 and Equation 19.
r = BD radial distance = 3.79 mm.
A = π. OB radius. unit length = 3.75 mm^2.
$f_{Cu} = 1.0$.
density of copper = 8.95 mg per (mm^3).
change in diameter of Cu rod = (OB − OA) = 0.49 mm.
$\dot{n}_{Cu} = 3.23611 \times 10^{-5}$ mg mol sec^{-1} per unit length.
$C_{Cu} = 0.070$ mole (mm)$^{-3}$ per unit length.
$a^{1}_{Cu} = 1.001$ for equilibrium reaction (17).

Acknowledgements

Animesh Jha particularly acknowledges financial supports from the INLAKS Foundation, the IMM London and the RTZ company.

References

1. H. W. RAUCH SR, W. H. SUTTON and R. M. CRIGHT, in "The Fabrication, Testing and Applications of Fibre-reinforced Materials – a survey". (Space Science Laboratory, General Electric Company, TR AFML-TR-68-162, September 1968 p. 5.
2. F. R. N. NABARRO and P. J. JACKSON, in "The Growth and Perfections of Crystals" edited by R. H. Doremus, B. W. Roberts and D. Turnbull (Wiley, New York, 1958) p. 13.
3. S. S. BRENNER, in "The Art and Science of Growing Crystals" edited by J. J. Gilman (Wiley, New York, 1963) p. 30.
4. R. V. COLEMAN, *Met. Rev.* **9** (1964) 35.
5. M. VOLMER, *Z. Physik. Chem.* **119** (1926) 277.
6. G. W. SEARS, *Acta Metall.* **3** (1965) 361, 367.
7. F. C. FRANK, *Phil. Mag.* **44** (1953) 854.
8. W. K. BURTON and N. CABRERA, Diss, Faraday Society **No. 5** (1949) on "Crystal Growth", p. 33.
9. N. CABRERA and W. K. BURTON, *ibid* p. 40.
10. J. W. CAHN, *Acta Metall.* **5** (1957) 169.
11. C. WAGNER, in "The Physical Chemistry of Steel Making – The Chipman Conference" edited by John F. Elliot (MIT Press, 1962) p. 19.
12. R. S. WAGNER and C. J. DOHERTY, *J. Electrochem. Soc.* **115** (1968) 93.
13. S. S. BRENNER and G. W. SEARS, *Acta Metall.* **4** (1956) 268.
14. R. S. WAGNER and W. C. ELLIS, TMS-AIME **233** (1965) 1053–64.
15. D. R. HAMILTON, *J. Appl. Phys.* **31** (1960) 112.
16. W. W. WEBB and W. D. FORGENG, *ibid.* **28** (1957) 1449.
17. R. E. CECH and T. D. TIEMANN, TMS-AIME **245** (1969) 1727.
18. J. D. FORD and F. A. FAHIM, *Metall. Trans.* **6B** (1957) 461.
19. P. M. PRASAD and T. R. MANKHAND, *Trans. IIM 32* **No. 3** (1979) 253.
20. J. B. WAGNER and C. WAGNER, *J. Chem. Phys.* **26** (1957) 1602.
21. A. JHA, P. GRIEVESON and J. H. E. JEFFES, *Scan. Jl. Metall.* **18** (1989) 31–45.
22. J. SCHMIEDL, in "The Physical Chemistry of Process Metallurgy – the Richardson Conference" edited by J. H. E. Jeffes and R. J. Tait (IMM, London, 1973) p. 127.
23. R. A. SWALIN, "Thermodynamic of Solids" (Wiley, New York, 1972, 2nd Edition) p. 366.
24. B. C. H. STEELE, *Scan Jl. Metall.* **18** (1989) 1.
25. P. G. SHEWMON, "Diffusion in Solids" (McGraw Hill, 1963) pp. 124–5.
26. R. E. BLANKS and G. M. WILLIS, *Trans Faraday Soc.* **57** (1961) 999.
27. C. WAGNER, *Jl. Metals, Trans AIME* (1952) 214.
28. E. T. TURKDOGAN, "The Physical Chemistry of High Temperature Technology" (Academic, 1st edition, 1980) pp. 5–21.
29. *Idem, ibid.* p. 260.
30. W. C. DASH, *Jl. Appl. Phys.* **29** (1958) 597, 30 (1959) 1748.
31. E. E. JENKINSON and A. R. LANG, in "Direct Observations of Imperfection in Crystals" (Interscience, Wiley, New York, 1962) p. 471.
32. R. A. SWALIN, "Thermodynamics of Solids" (Wiley, New York, 1972, 2nd Edition) p. 255.
33. P. G. SHEWMON, "Diffusion in Solids" (McGraw Hill, 1963) pp. 180–182.

Received 2 February
and accepted 24 July 1989