JOURNAL OF MATERIALS SCIENCE 6 (1971) 252-259

Electrochemically Controlled Growth and Dissolution of Silver Whiskers

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The formation of silver whiskers on the surface of a pressed tablet of α-Ag_2S has been studied. Preferential nucleation of a small number of whiskers was achieved by a novel method involving the direction of a beam of silver vapour on to the surface of the α-Ag_2S. These whiskers were then grown and redissolved electrochemically and the process studied photomicrographically. Current/potential curves indicated that silver crossed the silver whisker/α-Ag_2S interface at current densities as large as 8.7 A cm^{-2} with overpotentials < 5 mV at 300°C. The shapes of the growth and dissolution curves are compatible with the operation of a dislocation mechanism in these processes.

1. Introduction

Between 200°C and 300°C the rate of the reaction $2Ag(s) + S(l) \rightarrow Ag_2S(s)$, as measured during the unidimensional growth of the sulphide [1, 2], has been shown to depend on the transfer process occurring at the solid silver/α-Ag_2S phase boundary. This observation led to further investigations [3-5] of the transfer of metal ions and electrons through this type of phase boundary. Experiments in which the passage of silver, silver ions and electrons were studied electrochemically [3, 4] have shown that electron equilibrium is established at the interface during the transfer of silver but that similar polarisations occur during the passage of Ag^+ ions alone as for the transfer of an equivalent quantity of neutral silver (i.e. Ag^+ ions and electrons). Similar results have recently been obtained for the analogous copper/copper sulphide interface [5]. During the passage of these ionic currents the current-voltage relationships observed were semi-logarithmic [3, 4] indicating non-ohmic polarisation and a transfer process involving an activated step. A simple polarisation model [2] does not explain these findings although the e.m.f.s measured during the passage of silver across the Ag_2S phase boundary have been used successfully in quantitative calculations of the unidimensional growth rate of Ag_2S [4, 6], as well as to explain the linear growth rate observed in the initial stages of the reaction [7]. The most recent and thorough investigation [4] of the Ag/Ag_2S system has shown that the extent of ionic polarisation and also the rate of unidimensional growth of the suphide depend on the particular sample of high-purity silver used and also on its pre-treatment. Increases in the reaction rate were observed when the grain size in the silver was increased by anneal, but neither this factor or the very small differences in their impurity levels could account fully for the experimental behaviour of the different silver samples.

Since the atomistic mechanism of the phase-boundary reactions is not understood, it is important to study the transfer of silver from forms other than block silver to α-Ag_2S in an effort to correlate the atomic arrangement in the silver source with its behaviour. It has long been known [8, 9] that silver whiskers may be formed easily on α-Ag_2S, and since whiskers usually develop well-ordered structures [9] they were an obvious choice for these experiments. Unfortunately, in common with much of the work on proper whiskers, the production of silver whiskers on α-Ag_2S has been virtually uncontrolled. This paper describes a method developed to allow a small number of well-defined whiskers, whose cross-sections could be accurately measured, to be grown on a predetermined location on an α-Ag_2S substrate. This substrate was incorporated in solid-state electro-

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chemical cells which permitted the transfer of silver across the silver whisker/α-Ag_2S phase boundary to be followed. This proved to be a useful method for the investigation of the kinetics of the growth and dissolution of this kind of whisker.

2. Experimental and Results

2.1. Apparatus

The silver sulphide substrate was prepared as a pressed disc 0.3 mm thick and 8 mm diameter from powder obtained from Ag_2S grown in the laboratory from spectroscopically standardized substances by the unidimensional growth method [1]. The substrate arrangement and circuitry are shown in fig. 1. The Ag_2S tablet is a component in two solid state electrochemical cells of the type

$$\text{Pt} \mid \text{Ag} \mid \text{AgI} \mid Ag_2S \mid \text{Graphite}.$$

Wagner [10] has shown that graphite may replace the more usual second platinum electrode.

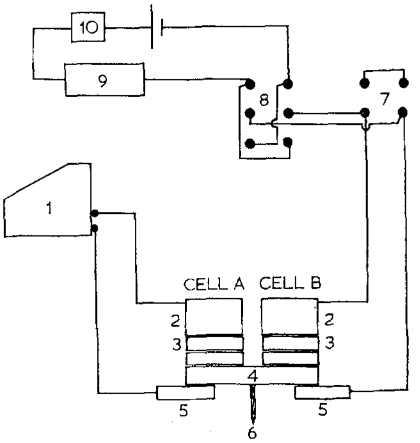

Figure 1 Schematic diagram of the cell assembly and circuitry.
1. Honeywell Electronik 19 Recorder. 2. Silver blocks. 3. Silver iodide tablets. 4. Silver sulphide substrate. 5. Graphite. 6. Silver whisker. 7. Short switch. 8. Reversing switch. 9. Resistance box. 10. Microammeter.

2.1.1. Cell A

When operated under current flow conditions which ensure negligible polarisation or under open circuit, the e.m.f. of this cell, E, as measured by the recorder, is related to the chemical potential of the silver in the silver sulphide $\mu_{Ag}(Ag_2S)$ by the equation [10]

$$\mu_{Ag}(Ag_2S) - \mu_{Ag}{}^0(Ag) = -EF \qquad (1)$$

where $\mu_{Ag}{}^0(Ag)$ is the chemical potential of pure silver at the temperature of the cell and F is the Faraday constant. The activity of the silver in the silver sulphide is given by the relationship

$$a_{Ag}(Ag_2S) = \exp(-EF/RT) \qquad (2)$$

and thus, when measuring E, cell A effectively monitors the metal/non-metal ratio in the Ag_2S tablet.

2.1.2. Cell B

Since, under the conditions of the experiment, AgI is practically a pure cationic conductor, the passage of direct current between the platinum and graphite electrodes and simultaneous electronic conduction in the external circuit result in the transfer of silver to or from the sulphide. When there are silver whiskers on the Ag_2S surface and when the silver transfer process is accompanied by no change in the e.m.f. of cell A (steady state condition) then it will be shown that the current through cell B is a measure of the rate of transfer of silver to or from the whiskers.

The complete cell assembly was held under light spring pressure inside a container machined from spectroscopically pure graphite and heated by alumina insulated nichrome strips. This arrangement proved necessary to eliminate temperature gradients which very rapidly cause spurious whisker nucleation [11]. The experiments were carried out in a metal vacuum system at a residual gas pressure of $\leqslant 1.0 \times 10^{-5}$ torr. The operation of this type of cell at the temperature required here and at significantly lower pressures is not feasible because of the loss of sulphur by evaporation [12]. Temperatures were measured using a platinum/platinum + 13% rhodium thermocouple which was checked against the $\beta \rightarrow \alpha$ phase transition of silver sulphide. The vacuum system contained a controlled source of silver vapour and the substrate assembly could be moved so that the Ag_2S tablet was in the path of the resulting silver beam. Alternatively, it could be placed over a quartz window matched to the lens system of a metallurgical photo-microscope located outside the vacuum system. A suitable focusing device in the substrate support allowed direct viewing of the whiskers during the growth and dissolution process.

2.2. Nucleation Process

α-Ag_2S is non-stoichiometric but only within small limits [10]. When the Ag/S ratio exceeds this range the supersaturation is quickly relieved by the precipitation of the excess silver, usually in whisker form. Schmalzried and Wagner [13] used a cell similar to cell *A* to measure $a_{\mathrm{Ag}}(\mathrm{Ag_2S})$ during and after nucleation of silver in silver sulphide which was being reduced by hydrogen at 400°C. As the Ag/S ratio was increased by removal of sulphur the e.m.f. decreased going to negative values i.e. $a_{\mathrm{Ag}}(\mathrm{Ag_2S}) > 1.0$. It then passed through a minimum between -1 and -2 mV as nucleation of silver was observed, and returned sharply to a value only slightly below zero as the whisker growth continued. When the metal/non-metal ratio was increased in our system by passing a suitable current through cell *B* the e.m.f. of cell *A* was seen to behave in an exactly similar fashion. As with the earlier study [13] the nucleation minima were not reproducible to better than $\pm$ 20% and average values at 220°C and 300°C were -10 mV and -6.5 mV respectively. There is no doubt that precipitation of silver occurs but since the region of maximum supersaturation resulting from this method of silver addition must be close to the $\mathrm{AgI/Ag_2S}$ interface the silver is almost invariably deposited between the silver iodide and silver sulphide tablets and no whiskers were ever observed on the exposed surface of the sulphide. Although the initial deposit most probably forms incipient whiskers, their location means that growth or dissolution probably occurs by the simultaneous migration of silver ions through the iodide to, or from the tips and sides of the whiskers and electrons to, or from their bases.

Because our primary concern was to study the transfer of silver across the Ag(whisker)/α-$\mathrm{Ag_2S}$ interface and since it is known that the presence of free silver can aid whisker nucleation [11], an attempt was made to shift the site of nucleation to the exposed surface of the silver sulphide tablet. A beam of silver vapour of intensity $\sim 5.0 \times 10^{14}$ atoms cm^{-2} sec^{-1} was allowed to impinge on the α-$\mathrm{Ag_2S}$ for a short time either before or during the electrochemical addition of silver. Little change in the nucleation pattern was observed but microscopic examination revealed that the whiskers, which first appeared as *E* of cell *A* passed through its minimum, were now on the $\mathrm{Ag_2S}$ surface. When the silver beam was confined to a small area of the surface, 0.3 mm diameter in our case, nucleation occurred in that area only and a small number, usually between three and seven, of well-defined whiskers appeared. Similar preferential nucleation resulted when a tablet which had been supersaturated to an extent insufficient to cause nucleation by electrochemical addition of silver (e.g. *E* cell *A* at -4.0 mV at 300° C) was exposed to the restricted silver beam for 2 to 3 minutes. Figs. 2 and 3 are scanning electron micrographs showing whiskers grown after general and preferential surface nucleation respectively. (Figs. 4 and 5 show detail.) They were taken when the samples had been removed from the vacuum system as the conventional photomicrograph used for the *in situ* observations lacked the depth of focus necessary to photograph complete whiskers. All the whiskers whose growth and dissolution were studied originated from preferentially nucleated sites.

2.3. Growth and Dissolution Procedure

Addition of silver to the whisker-bearing α-$\mathrm{Ag_2S}$ by a suitable fixed current flow through cell *B* caused the potential of cell *A* to vary with time as shown in fig. 6. The potential fell initially as the thermodynamic activity of the metal in the sulphide increased. Then, without any nucleation minimum, a steady state was attained at a potential which was dependent on the magnitude of the growing current used. Switch-off of this current gave a relaxation curve characteristic of the sample being studied. Microscopic observation during the steady state showed that the whiskers were growing from the base and that when formed from preferentially nucleated sites they were unusually straight and free from kinks (Fig. 3). A simple test was used to prove that the current through cell *B* during the steady state condition was a true measure of the rate of transfer of silver to the whiskers. A number of groups of whiskers were grown at a fixed rate for a known period of time so that the weight of silver transported through the cell could be calculated using Faraday's Law. The whiskers, usually 2 to 3 mm long, were then removed from the growth substrate, from which they broke cleanly, and weighed in the micro-analytical laboratory. Agreement between calculated and observed weights was better than 0.5% in the samples measured. Reversing the current through cell *B* gave a potential vs. time curve which was the mirror image of the curve shown in fig. 6. The steady state now indicated that silver was entering the sulphide from the whiskers at a rate exactly compensating the electrochemical withdrawal. Under these conditions the

Figure 2 Silver whiskers grown without preferential nucleation on α-Ag_2S substrate (×40).

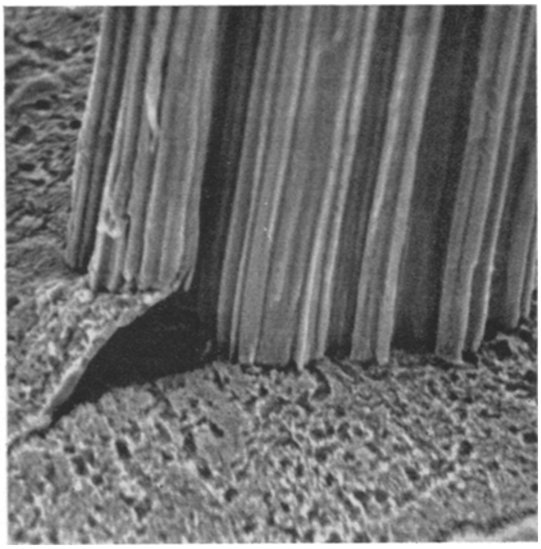

Figure 4 Similar to Plate 2 in detail (×1200).

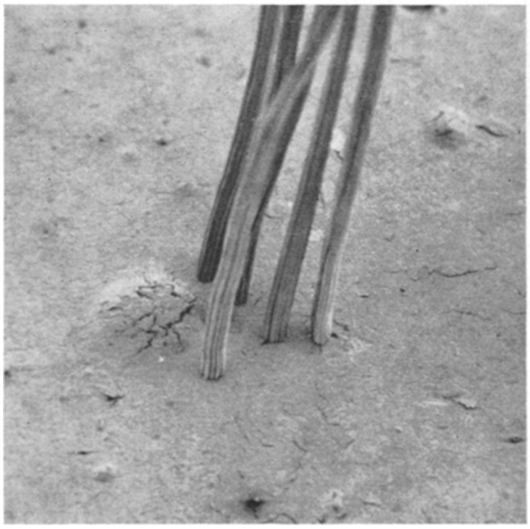

Figure 3 Group of whiskers grown with preferential nucleation on α-Ag_2S substrate (×40).

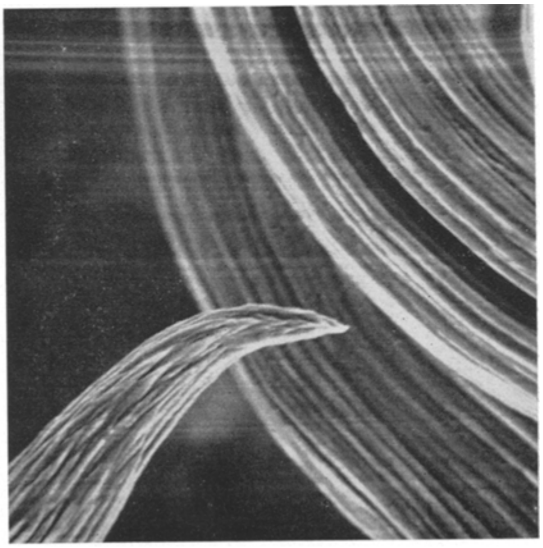

Figure 5 Detail of whisker tip (×1100).

whiskers, which were hanging downwards from their substrates, were seen to redissolve sometimes rotating about an axis drawn through their length as their tips were incorporated into the silver sulphide. This dissolution process was similar to that carried out by Rickert and O'Briain [3] and by Warde [4] in their phase boundary studies, the difference being that the silver was now migrating into undersaturated sulphide from silver whiskers rather than from block silver.

The following was the procedure adopted to carry out the silver transfer processes necessary to obtain data for the current vs. potential curves shown in fig. 7. After nucleation the whiskers were grown using a fixed current, usually 1.0 mA, until they had attained a length of 2 to 3 mm. They were then partially redissolved using a series of reverse currents which were varied step-

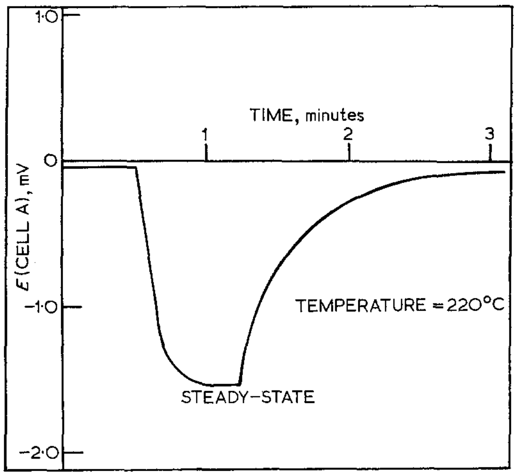

Figure 6 Curve showing typical behaviour of potential *E* (*Cell A*) during the short-term growth (also regrowth) of silver whiskers on an α-Ag_2S substrate. This curve is from a recorder trace and the growth current = 0.12 mA.

wise in the range 0.02 mA to 0.60 mA, the smallest current being used first. In every case the current was allowed to flow only for a time sufficiently long enough to characterise the steady state potential attained and hence the activity of the silver in the sulphide. It was then switched off and the trace of the relaxation curve recorded. While these measurements were made the whiskers were under continuous microscopic observation to ensure that the dissolution process was confined to the long straight portions of their length. The partially dissolved whiskers were then regrown using a similar series of currents and measuring the corresponding $a_{Ag}(Ag_2S)$ values. This method was found preferable to a growth and dissolution cycle at each chosen current because (a) growing the whiskers at a steady initial growing current provided the best possible means of dissolving them across a non-changing interface and (*b*) by regrowing at currents which were always smaller than the initial growing current the danger of producing new nuclei was minimised. All the relaxation curves pertaining to any sample of whiskers were found to be exactly superimposable indicating that the state of the silver whisker/solid silver sulphide interface remained unchanged during the growth and dissolution process. This is in direct contrast to the other transfer studies [3, 4] and it is significant that in the course of some of our less successful early experiments when the interface was changed by completely dissolving some of the whiskers during dissolution or by producing new whiskers during regrowth (as observed microscopically) it was immediately possible to correlate such changes with changes in the shapes of the observed relaxation curves.

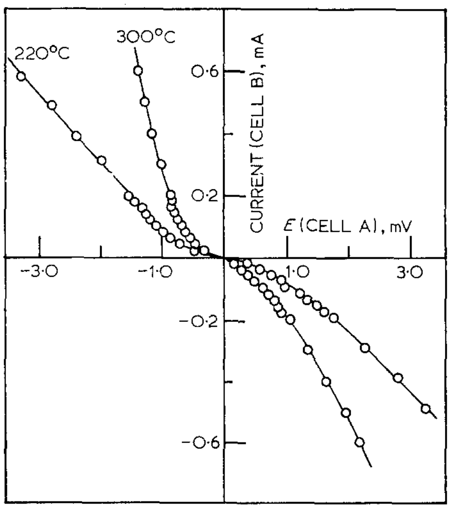

Figure 7 Current-potential curves for the transfer of silver in both directions across the silver (whisker)/α-Ag_2S interface at 220° C and 300° C.

To obtain current density measurements for the silver whisker/α-Ag_2S transfer process, thereby permitting direct comparison with available data [3, 4] the cross-sectional areas of the whiskers were determined by a method similar to that of Brenner *et al* [14]. When the whisker-bearing substrate had been embedded in resin the silver sulphide tablet was machined away and the bases of the whiskers were then exposed by grinding and polishing with diamond paste. To ensure clear definition a final polishing was carried out as recommended by Darling [15]. Using the photomicrograph, the bases were photographed at ×400 onto a grid which had been calibrated against an objective micrometer and their areas were measured. Fig. 8 is a scanning electron micrograph of the base of a whisker which had been removed from its growth substrate. As is evident from the fine structure shown in this sample, the whiskers were composed of a number of smaller fibres and their overall shapes were roughly cylindrical. Extension of the cross-sectioning technique showed that the whiskers were of constant cross-section over their straight portion and that any voids, like the one in the base of the whisker shown in fig. 8, extended right through this length. Examination of the whisker tips showed that

Figure 8 Base and lower section of a silver whisker which has been detached from its α-Ag_2S substrate (× 350).

they were most probably formed by the joining together of the smaller fibres (a commonly observed phenomenon [16]) just after nucleation. This formation and growth process would explain both the presence of voids and the constant cross-section of the whiskers. Whiskers grown at 300° C tended to be smaller with typical cross-section of 1.5×10^{-5} cm^2 which corresponds to a diameter of ~ 40 μm. Those grown at 220°C had cross-sections 4 to 8 times larger than this and among the hundreds of whiskers examined during this study three were found with cross-section of approximately 70×10^{-5} cm^2. These large whiskers had rather blunted heads but their growth and dissolution behaviour was exactly similar to that of the more usual-sized whisker.

The transfer of silver across the Ag(whisker)/α-Ag_2S interface at a current density of 0.5 A/cm^2 was found to occur in typical cases with overpotentials of $\sim$2.9 mV and 2.2 mV at 220°C and 300° C respectively. The same silver transfer rate from block silver was accomplished [3] only when overpotentials greater than 220 mV and 160 mV were applied at these same temperatures. The greatest rate of silver transfer measured at a Ag(whisker)/α-Ag_2S interface in this study was 8.7 A/cm^2 and this took place with an overpotential of less than 5 mV at 300° C.

3. Discussion

In the operation of solid-state electrochemical cells, as in all applications where a solid metallic electrode is pressed against another solid, good contact is important. Solid electrolytes, in general, have little or no tendency to flow and although the simple expedient of using moderate contact pressure is often successful it can hardly be regarded as an ideal arrangement. Thus the large difference in the results obtained for the transfer processes across the silver (block)/α-Ag_2S and silver(whisker)/α-Ag_2S phase boundaries might possibly be explained in terms of the microcontacts made at each of these interfaces. As discussed by Raleigh [17] the pressure-dependent effects observed by Rickert [3] as well as his failure to obtain reproducible relaxation curves strongly suggest that microcontact problems were involved in his case. In the present study where the silver whiskers were first grown *in vacuo* on the α-Ag_2S surface, the contact must be expected to be almost ideal and the facility with which the silver transfer occurs suggests that this is indeed true. This explanation can only be partly satisfactory, however, since the work of Warde [4], as described earlier in this paper, shows clearly that in the case of a block silver source the mosaic structure of the silver is also a determining factor in the magnitude of the observed overpotentials. Because several mm thickness of silver (either block or whisker) are transferred into the silver sulphide during a typical experiment of this kind the process under study really involves the dissolution of one solid into another. The crystal structure of the α-Ag_2S [18] is especially well-suited to accept silver since the effective number of sites available to silver ions has been estimated [19, 20] at almost six per unit cell with only four silver ions to be accommodated. The unusually high interdiffusion coefficient for silver in the sulphide [10] ($\sim 3 \times 10^{-2}$ cm^2 sec^{-1} at 400° C) ensures that concentration gradients are quickly eliminated and the silver dissolution process should continue provided only that the atomic arrangement in the dissolving silver crystal facilitates the removal of its silver atoms. Although the dissolution of a solid under these conditions is not common, two mechanisms are known to operate when solids evaporate or dissolve in solution. The two-dimensional nucleation model [21] requires continuous nucleation of an atomically smooth face and growth and dissolution curves show critical super and undersaturation characteristics [22]. In the dislocation model introduced by Frank [23], in which crystal imperfections provide perpetual steps in the crystal surface, growth and dissolution processes may take place much more easily. Vermilyea [24] has extended these theoretical considerations to electrolytic crystal growth and using copper whiskers has observed [25] variations in overpotentials for electrolytic growth and dissolution in solution which he ascribes to the relative perfection of the samples used.

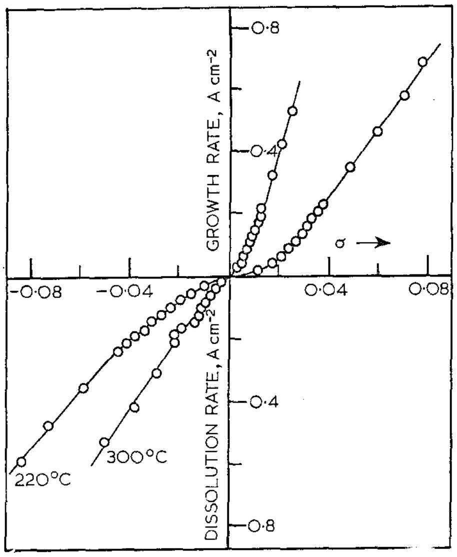

Figure 9 The growth and dissolution rates of silver whiskers against the supersaturation σ at temperatures of 220° C and 300° C.

Since Rickert [26] has observed screw dislocations in silver whiskers grown on an α-Ag_2S substrate in a manner similar to that described here it is proposed that it is the presence of these imperfections in the whiskers which is mainly responsible for their growth and dissolution behaviour and consequently for the very low overpotentials required to effect the passage of silver across the Ag(whisker)/α-Ag_2S interface. Fig. 3 shows that the whiskers do not grow over the total area exposed to the nucleating silver beam but are confined to specific sites where dislocations are presumably introduced during growth by dislocation ends existing in the crystallites which form the surface of the pressed α-Ag_2S disc. Such a mechanism has been proposed by Sears [27] for the growth from the vapour on glass of mercury whiskers. The silver whiskers in this study must contain multiple dislocations since they are larger than the size usually associated with perfect whiskers [16] and are composed of numerous fibres. Further evidence for a dislocation mechanism is shown in the growth and dissolution curves for the whiskers shown in fig. 9. The current through cell *B* has already been shown to be a measure of the rate of growth or dissolution of the whiskers and a current density of 1 A cm^{-2} corresponds to a growth rate of $\sim$ 1 μm sec^{-1} in whisker length. The thermodynamical activity of the silver in the silver sulphide measured by cell *A* during the growth and dissolution process is analogous to the saturation ratio $\alpha = p/p_0$ usually used to define the magnitude of the driving force in the discussion of the growth of crystals from their own vapour. Following Burton *et al* [28] the supersaturation σ is defined as

$$\sigma = \alpha - 1 \qquad (3)$$

and the curves in fig. 9 are of the growth and dissolution rates of the whiskers in A cm^{-2} at two temperatures against the supersaturation calculated using equations 2 and 3. These curves show no critical super or undersaturation characteristics and approach linearity at larger σ values. The rates of growth and dissolution increase with temperature and the curves are qualitatively very similar to those obtained by Kitchener and Strickland-Constable [29] for the growth and evaporation of polycrystalline benzophenone and interpreted by these authors in terms of the Frank theory of crystal growth.

Attempts have been made using a modified apparatus, to distinguish the part played in the silver transfer process by the presence of dislocations in the whiskers from that resulting from the nature of the contact at the whisker/α-Ag_2S interface. Whiskers were removed from their original growth sites and replaced (a) vertically but with their bases in contact with a different site and (b) horizontally with their sides pressed against the α-Ag_2S surface. These experiments were difficult to do without upsetting the temperature equilibrium of the cell assembly and no conclusive results could be drawn since the magnitude of the overpotentials observed in both cases proved to be extremely sensitive to the pressure applied to the sample. This effect was more pronounced than has been reported for the experiments using block silver [3] and was further aggravated by the extremely small size of the whiskers which made even estimates of the applied pressure doubtful. It is concluded therefore that the results reported here for the passage of silver across the Ag(whisker)/α-Ag_2S phase boundary are due to a combination of the dislocation structure of the whiskers, which always ensures the availability of silver atoms at sites from which they are easily removed, and the special nature of the microcontact achieved by growing the whiskers on the substrate. Of these factors, the degree of perfection in the crystal structure of the silver, which has also been shown to influence markedly the transfer process from block silver [4] and which is known to produce similar effects when whiskers are electrolytically dissolved in solution [25] is probably more important.

Acknowledgements

Thanks are due to Dr Hans Rickert, Dr C. J. Warde and Dr E. P. O'Neill for valuable discussions and to Dr D. Cansfield and Mr D. L. Scott for the scanning electron micrographs.

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Received 7 December and accepted 24 December 1970.