GROWTH FEATURES OF SINGLE CRYSTALS OF SILVER AMALGAM IN THE PRESENCE OF COPPER

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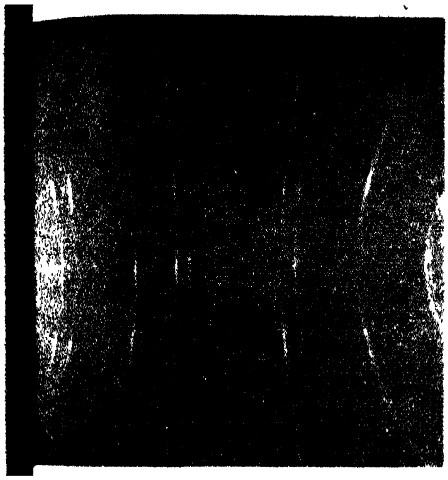
(Plate 10)

ABSTRACT. In the absence of copper, the growth of single crystals of silver amalgam from $AgNO_3$ solution and mercury drop takes place on the mercury surface. In the presence of copper, in the form of wire in contact with mercury drop placed in the solution of $AgNO_3$, the single crystals do not appear on the drop but grow radial to the wire. The growth features of these crystals depend on the strength of the solution as well as the quantity of mercury. There seems to be a critical concentration of $AgNO_3$ solution above which the growth of crystals on the wire is favoured and below just the amalgamation.

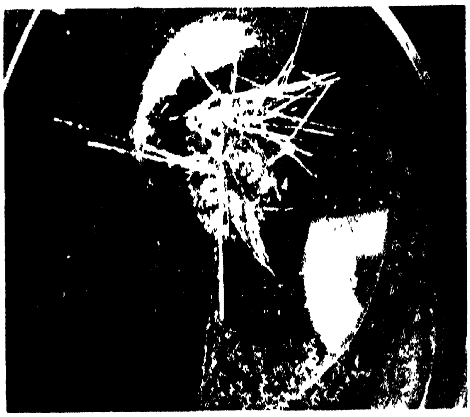
INTRODUCTION

Crystals are grown from solution, vapour and melt. The growth of crystals and the growth mechanism has been pursued by many from time to time. It appears from an article on metal filaments, reported by Hardy (1956), that Henkel and Wallerius, as early as 1720 noticed for the first time the growth of single crystals from a drop of mercury placed in the solution of silver salt and of silver filaments by heating Ag_2S. The formation of silver whiskers by electrolysis by Aten *et al* (1920) has been studied. Generally the nucleation for the growth of whiskers from solution has been attributed to screw dislocation (Newkirk *et al*, 1955). Sears (1957) in his work on the fibrous growth of $NaClO_3$ has observed that surface tension and the consequent gradient in surface tension of the solution due to different rates of evaporation as the cause for fibrous growth.

The growth of single crystals of silver amalgam using N/50 $AgNO_3$ solution and a globule of mercury and a particular aspect of the effect of heat on the structure of single crystals of silver amalgam has been published by Rama Swamy *et al* (1965). In the present work an attempt has been made to study the growth peculiarities of single crystals of silver amalgam in the presence of copper using $AgNO_3$ solution of different concentrations and mercury globules of different amounts. A striking contrast has been observed in the growth of single crystals of silver amalgam in the presence of copper as compared to that in the absence of copper.



X-ray diffraction photograph of silver filament



(3½×)

Fig. 2. Silver amalgam crystals in the absence of copper.

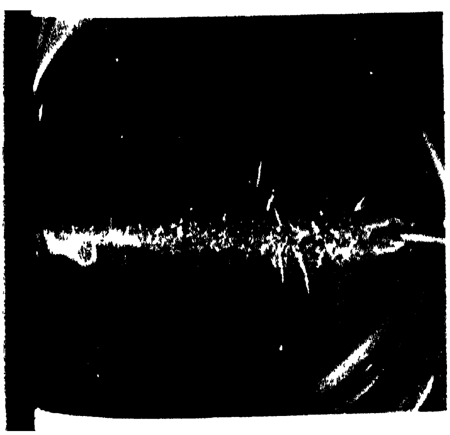


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Fig 3. Radial growth of silver amalgam crystals in the presence of copper in contact with mercury drop at extreme left.

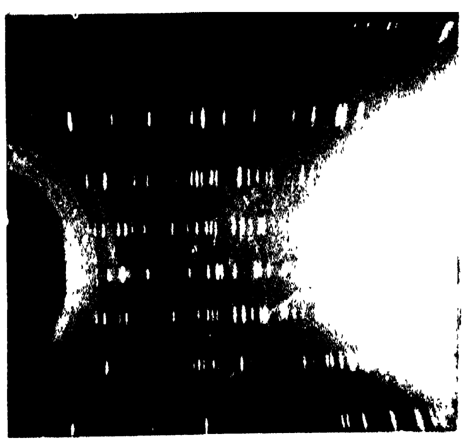

Fig. 4. Rotation picture of silver amalgam crystals grown in the absence of copper.

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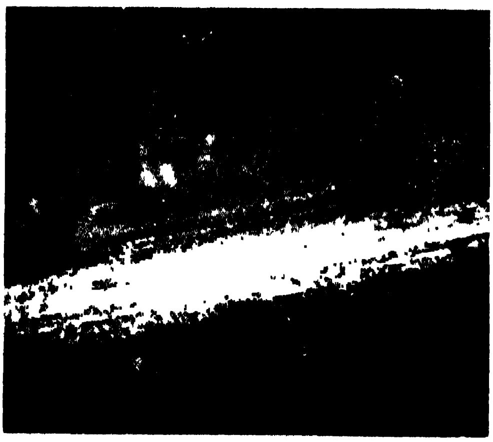
Fig. 5. Rotation picture of silver amalgam crystals grown in the presence of copper.



(36×)

Fig. 7. Streaks seen on copper surface after the completion of reaction with $AgNO_3$ solution in the absence of mercury.

(36×)

Fig. 8. Copper surface as seen after the completion of reaction in the presence of mercury.

EXPERIMENTAL

Experimental observations fall into three parts. In (A) we describe the growth of silver fibres from $AgNO_3$ solution and copper wire; in (B), the growth of silver amalgam crystals in the presence of copper and in (C), the growth of the same crystals by varying the concentration of silver nitrate solution and the quantity of mercury.

(A) When a copper wire of 0.162 cm. thick is kept inclined in a crystallizing dish containing N/50 $AgNO_3$ solution at room temperature, bright fibres of silver are seen all along the immersed portion of the wire within a few minutes and the growth is radial. The fibres, separated after the completion of the reaction, are cleaned with distilled water and dried. The X-ray diffraction photograph (figure 1, plate 10A) of the silver filaments taken reveals that the powder lines are not continuous. Also the analysis of X-ray picture gives the structure as f.c.c. and the lattice constant as 4.095 Å which agrees with that of silver. This indicates that the silver filaments grown on the copper surface are due to the replacement of copper by silver.

(B) Long needle-like single crystals of silver amalgam shoot out from different points of the surface of the mercury drop (figure 2, plate 10A) placed in a dish containing N/50 $AgNO_3$ solution. The presence of copper wire touching the mercury drop in the same system has completely changed the initiation of nucleation on the surface of mercury. The fact is that no crystals appear on the mercury surface (figure 3, plate 10A) but on the immersed portion of the wire and radial to it. These crystals a few mms. in length are thin pointed needles. The rotation picture (figure 4, plate 10A) is of single crystals of silver amalgam grown in the absence of copper and of (figure 5, plate 10B) is of the same crystals grown in the presence of copper. The layer line spots of the latter are quite sharp compared to those of the other.

(C) The observations made in the presence of copper are repeated with 5gms. and 10 gms. of mercury taking equal volumes (200 c.c.) of $AgNO_3$ solution of different concentrations in long identical cylinderical jars 4 cms. in internal diameter. The crystals do not appear all along the length of the wire but only up to a certain point of the immersed wire. This reveals that the appearance of crystals on the wire as well as the surface nucleation length is a function of concentration. The relationship is graphically represented in (figure 6, plate 10B) by the curves shown side by side to bring out the similarity between the two cases. In both cases the surface nucleation length is minimum at some concentration. With large quantity, this minimum occurs at a lower concentration. Above the concentration at which the minimum occurs, mostly micro-crystals grow and below that only the amalgamation of the surface with no crystals.

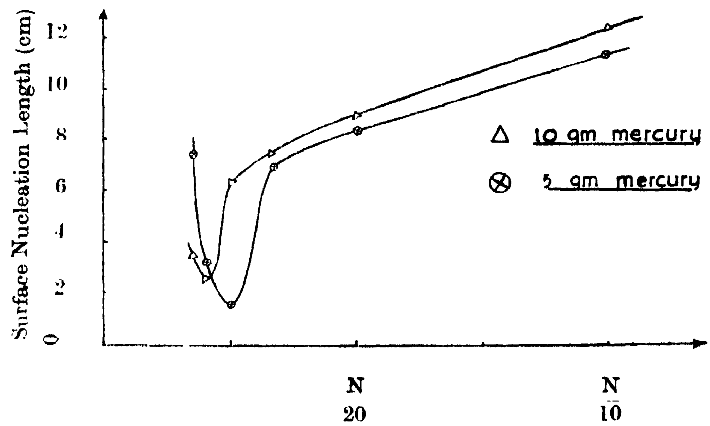


Fig. 6. Curves showing the variation of surface nucleation length with concentration of $AgNO_3$ solution.

DISCUSSION

The growth process of silver filaments can be explained as follows: The replacement of copper by silver during chemical reaction between copper and $AgNO_3$ solution, renders possible the initiation of nucleation on copper itself. Once the nucleation occurs the growth of silver filaments may be attributed to screw dislocation that is favoured by the transport of silver ions from the surrounding medium towards the nucleation sites by diffusion process and simultaneous replacement of copper. Observing under a microscope a well-cleaned surface of copper subjected to chemical reaction using dilute solution of $AgNO_3$, irregular streaks or channels (figure 7, plate 10B) are noticed along the immersed wire. Due to nonuniformity in the density distribution of silver ions as they approach the copper wire, these channels are not uniform either in depth or in width. This perhaps is an indication of randomness in rapid crystallization that results in the growth of silver filaments. Also the discontinuity of the lines in the X-ray picture of these filaments shows the tendency of the growth towards crystallinity.

The radial growth of crystals along the wire and none on the mercury globule is a very striking observation which is explained below. The chemical reaction between $AgNO_3$ solution and copper is more predominant than nucleation taking place first on the mercury surface. Consequently, the silver ions are adsorbed in the regions wherever copper is replaced. The mercury ions themselves creep along the channels formed on the wire and migrate into the adsorbed layer of silver (figure 8, plate 10B). The creeping of mercury is very conspicuous even to the bare eyes. This is due to the existence of some kind of capillary forces probably related to interfacial tension that will produce acute angle of contact of mercury with the adsorbed layer of silver and not due to electrical forces since the standard electrode potentials of silver and mercury are the same ($= -0.799$ volts). With the surface migration of mercury ions, the nucleation for the growth of silver amalgam crystals takes place and further growth requires the presence of screw dislocation as suggested by Sears to provide self-perpetuating growth steps at which the atoms can be easily attached.

With $AgNO_3$ solution of varying concentration there seems to be a critical concentration above which the crystals appear and below no crystals. At higher concentrations, as mercury creeps up and single crystals shoot up radial to the wire, the tendency of the silver ions above is to move towards the crystals already formed. From a similar observation made by Aten *et al* (1920) in their studies of silver whiskers formed by electrolysis using silver nitrate solution as electrolyte, during deposition of silver ions on cathode consisting of a ring on which silver fibres are already formed (by an earlier experiment) and a fresh flat disc in contact with the ring, most of the silver ion current was towards the whiskers on the cathode ring.

At lower concentrations the available silver ions are few in number and probably just enough for the replacement of copper. The process is too slow and the mercury creeps at a very slow rate and spreads over the adsorbed layer of silver without the formation of crystals. The fact that the length of amalgamation increases with further lowering of concentration seems to indicate the amlgamation process or otherwise surface nucleation itself may be a prior stage for the growth of crystals.

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REFERENCES

Aten, A. H. W., and Boerlage, 1920, *Report of the International Conference on "Growth and perfection of crystals" held at Cooperstown*, New York, Aug. 1958, p. 85.

Hardy, H. K., 1956, *Progress in Metal Physics* 6, 45.

Newkirk, J. B. and Sears, G. W., 1955, *Acta Met.*, 3, 110.

Rama Swamy, S. and Sake Gowda, D. S., 1965, *Proc. Indian Acad. Sci.* 61, 301.

Sears, G. W., 1957, *J. Chem. Phys.*, 26, 1549.