# PART II

## STUDIES ON TELLURIUM CRYSTALS

# CHAPTER V

## GROWTH AND MORPHOLOGY OF THE VAPOUR-GROWN FILAMENTARY CRYSTALS OF TELLURIUM

The structure and preparation of filamentary crystals from the vapour phase have been studied from as early as 1921[1]. As yet there is no rigorous or complete theory which can explain all the variational and contradictory experimental results. Since whisker crystals grow essentially in one direction, their growth has been explained by the Frank mechanism[2,3], where a screw dislocation provides a self-perpetuating step enabling growth at low supersaturations. Axial screw dislocations have been observed for a few filamentary substances lending support to the Frank

mechanism. However, lately reservations have arisen regarding the universal applications of the theory. Webb and co-workers[4] examined whiskers of nine different metals grown from the vapour and found unequivocal evidence for single axial screw dislocations only in one metal viz. palladium. These considerations have stimulated the present investigations with tellurium filamentary crystals.

It will be advantageous to discuss the various results on whiskers and the theoretical interpretations given to them. Sears[5] observed whiskers and platelets of mercury in a growth cell at -63.5°C. He proposed that the edges of the platelets and the tip of the whiskers are preferred growth sites because they contain one or more emerging screw dislocations, whereas the basal surfaces of the platelets and the lateral sides of the whiskers are free of dislocations. Cabrera[6a] and co-workers[6b] grew Zn whiskers in an atmosphere of helium. In addition to whiskers hexagonal plates, thin ribbons, rhomboids and triangular plates were observed. The whiskers were hexagonal in cross-section and their axes usually made an angle of 30° with the c-direction and in a few cases 42° and 90° with the c-direction. However, growth along the c-axis was never observed.

The growth of Cd crystals was studied by Price[7a,7b] in an atmosphere of helium and under a gradient of temperature and supersaturation. He found that the number and the form of the crystal varied greatly with supersaturation. For $\sigma < 2$ whiskers and thin platelets formed predominantly. For $\sigma > 2$ the density of nucleating points increased and the whiskers and thin plates thickened to give thick hexagonal plates.

The growth of potassium whiskers has been described by Neumann and co-workers[8,9] and Parker and Kushner[10]. The needles were hexagonal in cross-section with their axes along the [110] direction and bounded by six (110) planes. The needles were about 1000 A° thick and 2 mm long.

Howey[11] condensed silver vapour on solidified spherical drops of silver to form whiskers upto 3 mm long and 0.5 mm thick. Their axes were along [110] directions.

Submicron whiskers and platelets of different metals had been grown by many workers for use in field-emission microscopes. Melmed and Gomer[12]

applied the whisker-growth techniques of Coleman and Sears[13] to grow thin crystals of numerous metals. Whiskers grown in high vacuum ($p < 10^{-9}$ Torr) have clean surfaces and the necessary strength to withstand the high stresses caused by the electrostatic field. The substrate temperatures were 0.5 to 0.7 $T_{melting}$ and the source temperatures corresponded to equilibrium vapour pressures of $10^{-5}$ to $10^{-6}$ Torr. The crystals were 50 to 200 A° thick and about 15 $\mu$ in length. Their axes were parallel to one of the low index directions.

Using Gomer's technique, Parker and Hardy[14] had grown potassium field-emitters. So the technique is applicable to alkali metals also. The whiskers were grown with the source vapour pressure between $10^{-6}$ and $10^{-7}$ Torr and substrate temperature as low as 77°K.

The results of Melmed and Gomer and Parker and Hardy show that at low temperatures whiskers can grow at very high supersaturations.

Submicron whiskers of a variety of metals have also been grown by Morelock[15] at higher temperatures

and lower supersaturations. The whiskers grown by him ranged in diameter from 400 to 5000 A° and were upto 300 $\mu$ long.

Parker and Kushner[16] studied the growth rate of Zn crystals from vapour as a function of the supersaturation $\sigma$ at a temperature of 390°C. The results indicate that surface nucleation was not operative in either the nucleation or the growth of crystals.

Twins have been found by field-emission microscopy in Au and Pt vapour-grown whiskers by Melmed[17]. He had shown that twinning occurs during whisker growth. Although the amount of impurities can be kept quite low,in practice it is impossible to eliminate them completely. The structural imperfections might well be expected to occur in the whiskers as a result of the stress due to impurities incorporated into the crystal lattice.

Webb[18] has grown palladium whisker crystals in which axial screw dislocations are demonstrated to perform their expected role. Dislocations

provide growth steps on the whisker tips and dislocation climb systematically changes the effective growth directions in suitable cases to form helical whiskers. Growth occurs in irrational crystallographic directions so that straight whiskers have irrational axes and helices always have <111> axes formed as the growth direction and gyrates around it.

Crystals of potassium were grown by Dittmar, Meissner and Köhler[19]. These crystals form as needle-like rhombic dodecahedra with a cross-section of either fourfold or sixfold symmetry. The needles increase in length, by an order of magnitude quicker than expected was due to growth by direct collision of atoms at the face. The growth process is therefore thought to be due to surface diffusion. A linear relationship between growth rate and absolute supersaturation was found upto a point where the linear growth stops and the needles begin to thicken. At these higher supersaturations some crystals are formed as plates.

Dendritic crystals of metallic selenium have been grown by Furuta[20]. These crystals, grown with the supersaturation maintained constant, can be

classified into five groups depending on the shape and crystal structure. The growth mechanism of these crystals except one group relates to the twinning. The difference in the shape of these crystals come from the number of twins contained therein and the mutual relation between them. The growth of dendritic crystals containing twin boundaries mainly starts at the steps and kinks formed by overlapping of two twin films originating from twin boundary.

Silicon filamentary crystals have been grown by Wagner *et al.*[21]. The growth of micron crystals and larger whisker crystals from the vapour takes place in two stages. The first is a rapid extension in length of a leader crystal of small cross-section; the second, a slow thickening of the leader through deposition on lateral faces. Initial growth is associated with impurities and does not require an axial screw dislocation. Nodules, ribbons and needles were observed. Ribbons and needles of small dimensions were free of dislocations and imperfections.

Wagner and Ellis[22] in 1964 proposed a new mechanism of growth from the vapour, viz. the VLS or

the Vapour-Liquid-Solid mechanism. There is increasing evidence that most whisker crystals grown from the vapour are dislocation free. Webb and co-workers[4] searched for an Eshelby-twist in Zn, Cd, Fe, Cu, Ag and Pd. They found unequivocal evidence for an axial screw dislocation only in Pd and not every Pd whisker examined contained a dislocation. Since many whiskers are completely free of dislocations an axial screw dislocation does not appear to be an essential requirement for whisker growth of many substances. A significant advance in understanding the whisker growth has been the recognition of the need for impurities. The VLS mechanism differs from the previous theories in that, that a layer of liquid is situated between the vapour and the growing crystal. The source material forms an alloy with an impurity present. This alloy acts as the transport medium between the vapour phase and the solid phase. The alloy becomes supersaturated by adsorption of atoms from the vapour phase. The excess of material is deposited on the growing tip of the whisker crystal. The hemispherical terminations observed at the tip of many whiskers are the solidified alloy. The

crystals grown by this method are free of axial screw dislocations.

From the discussions presented above it is clear that no single theory could explain all the results observed. The three possible mechanisms suggested are: (1) The Frank-mechanism, where an axial screw dislocation emerging at the tip of the whisker provides a self-perpetuating step; (2) The twin mechanism,where, the kinks and steps originating due to overlapping of twin planes provides the sites for growth; (3) The VLS mechanism where a liquid alloy layer acts as the transporting medium. Evidences are found for all the three mechanisms. Which mechanism will be acting in a particular case, depends on the material, the growth conditions and the impurities present.

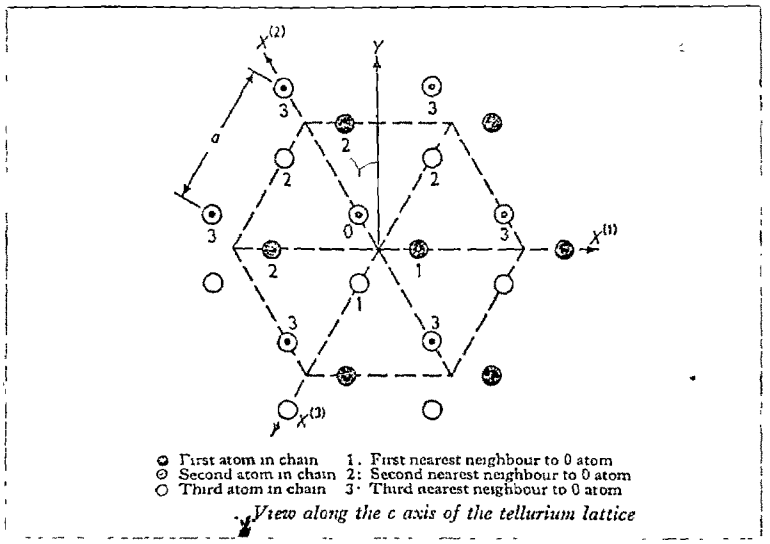
The present work has been taken up with a view to study the growth mechanism of Te crystals grown from the vapour phase. The effect of impurity,temperature gradient and supersaturation ratio on the morphology of the crystals has been studied. Te was chosen because of its relatively high vapour pressure at convenient temperatures, low melting point, a

perfect cleavage and also because Te of quite high purity is available.

The element Te has an unusual crystal structure which is briefly discussed below.

The lattice consists of spiral chains, each spiral having three atoms per turn[23]. The chains lie parallel to one another with corresponding atoms in each chain forming plane hexagonal nets. Looking along the c-axis, only three atoms in each chain are visible since the fourth atom lies directly below the first one. The fifth atom directly below the second, etc. (Figs.V.1 and 2). As regards the lattice constants of Te, the prism edge 'a' and the prism length 'c' parallel to [0001] axis are 4.4 and 5.91 A° respectively.

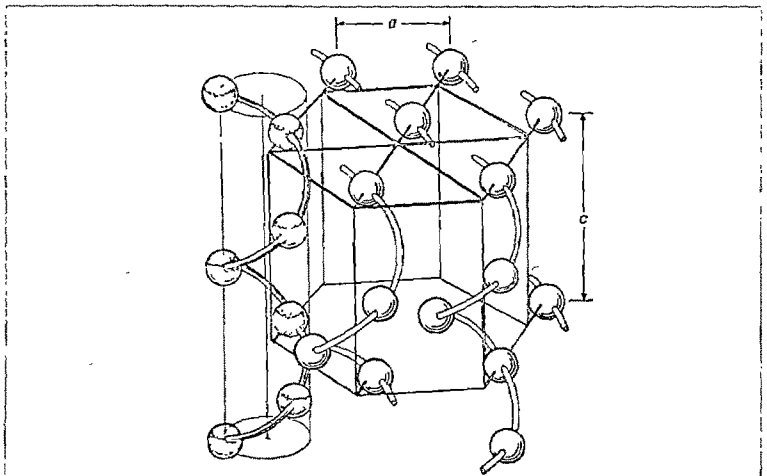
It should be noted that Fig.V.2 arbitrarily shows a right-handed spiral. Both right-handed and left-handed crystals are known to exist. The bonds among atoms on the same chain are believed to be covalent, whereas between chains they are thought to be a weak mixture of electronic and Van der Waals




● First atom in chain 1. First nearest neighbour to 0 atom
◎ Second atom in chain 2. Second nearest neighbour to 0 atom
○ Third atom in chain 3. Third nearest neighbour to 0 atom

*View along the c axis of the tellurium lattice*

**Fig.V-1**




*Perspective view of the tellurium lattice*

**Fig.V-2**

binding. This may account for the fact that Te unlike many hexagonal structures, cleaves most easily along the prismatic $\{10\bar{1}0\}$ plane.

Because of the anisotropic arrangement of atoms, the response of Te to applied stress depends to a large extent on the direction of the applied force. For example it has been found that Te reacts purely elastically to stress along the $[0001]$ direction but the slip readily occurs in directions normal to the c-axis. Te crystals cleave very readily in any of the six planes equivalent to $(10\bar{1}0)$, yielding bright mirror-like surfaces. Slip occurs in the same system of planes along the diretions equivalent to $[\bar{1}2\bar{1}0]$ which lie in the cleavage planes and perpendicular to c-axis.

The crystals were grown as described in Chapter IV, in a bent pyrex tube which was sealed under vacuum of the order of $10^{-4}$ mm of Hg. The crystals grow radially on the cooler part of the tube on and near the notch. Three kinds of crystals are obtained: (1) solid hexagonal prisms, (2) long thin hexagonal needles and (3) long hollow hexagonal crystals.

Crystals have been grown in about 50 to 60 tubes, out of which only 28 tubes yielded good crystals. From each tube some 15 to 20 crystals were obtained which were useful for the work. The short solid prisms had well-developed dome faces and hence they were used to study the dome faces.

Crystals have been grown in tubes of different diameters and it was found that a tube diameter between 2 to 2.5 cms was the best suitable one. The charge was also to be kept below a particular value to give a limited number of nucleation centres. In all the cases the charge was kept constant, equal to 10 gms.

The effect of source temperature on the morphology of the crystals was also studied. Furuta et al.[24] have grown ribbon like Te crystals in the growth chamber of an electron microscope. They have evaporated Te at a temperature of 275°C. They could not find any growth features on the crystals. They have observed that growth takes place by addition of material to the edges of the growing crystal. The present author has varied the source temperature from 250°C to 530°C. No ribbons

or nodules were obtained in the lower range of temperature. At temperatures below 400°C very small hexagonal prisms were obtained. For temperatures above 450°C long hexagonal crystals were obtained; both hollow prisms and solid prisms. The temperature of the source was kept in the order of 520°C throughout.

The cooling rate of the furnace also affected the morphology of the crystals markedly. With faster rates the crystals are short and the few long crystals obtained do not have all the prism faces developed. With very slow rates the crystals thickened faster and to about three to four times thicker than those grown at normal rates. As a result the crystals clustered together and they are not useful to carry out any studies. A rate of 30°C/hr was found to be the best. It appears that in slower rates, if the nucleation centres can be controlled, it may give larger crystals. It needs a critical temperature gradient and substrate temperature for the crystals to grow with a fairly fast rate and well-developed faces. The large number of nucleating centres makes it difficult to assess the local supersaturation.

The substrate temperature varied between 240° and 270°C. The gradient was in the order of 150°C/cm.

Te metal of two different purities has been used to grow the crystals. With the metal of low purity nucleation rate was very high and as a result the number of crystals grown were very high. The crystals grow very close to each other, finally their tips cluster together towards the centre of the tube. Crystals growing away from the source were separable. These crystals are short and thick, about 0.5 to 0.8 cm long and 1 $mm^2$ area of cross section. All the six prism faces are not developed in most cases. The surfaces are also not very clean. There are too many inclusions and black dots on the surface. No hollow crystals are obtained. Chemical etching has revealed that the dislocation density is much below that in melt-grown crystals.

Remarkably good crystals are obtained from the high purity metal. Crystals as long as 2 to 3 cms with a cross section of about 0.25 to 1 $mm^2$ were obtained. Fig.V.3 shows the crystals inside a tube

and Fig.V.4 shows the long hexagonal crystals obtained. At the farther end of the tube short hexagonal solid prisms are obtained with well developed dome faces. Fig.V.5 is such a crystal with the dome faces. The prism faces are identified as the $(10\bar{1}0)$ planes and the dome faces as $(10\bar{1}1)$ +ve rhombohedrons by back reflection X-ray photographs.

The crystals grow from the sides of the container radially. The nucleation is as a small stalk or from a small lump of metal. The growth in the c-direction is quite fast and the lateral growth is very slow. The lateral growth & subsequent thickening of the crystal continue even after the cessation of growth in c-direction. Wagner et al.[21] observed ribbons, nodules, submicron whiskers and macroscopic whiskers in silicon. But in the present case ribbons, nodules and kinked whiskers are absolutely absent. The few very small whiskers were not used in the work carried out.

The prism faces and the dome faces have been studied in detail. The prism faces are devoid of any conventional growth features. Figs.V.6 & 7 are

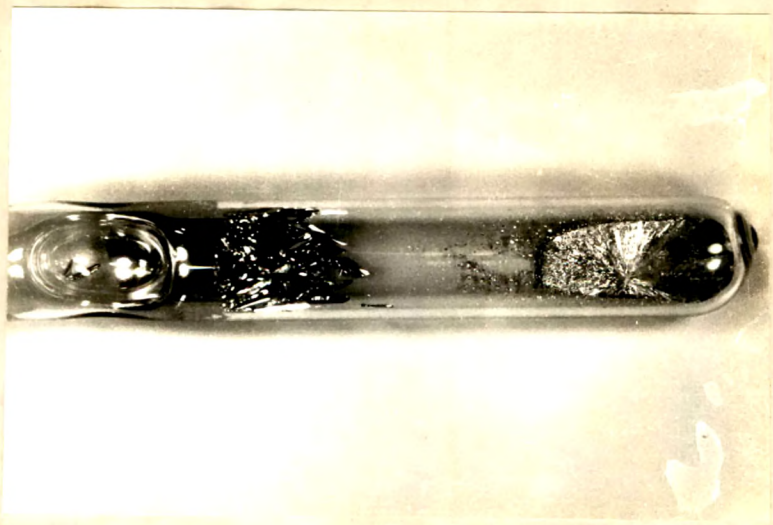


Fig.V-3

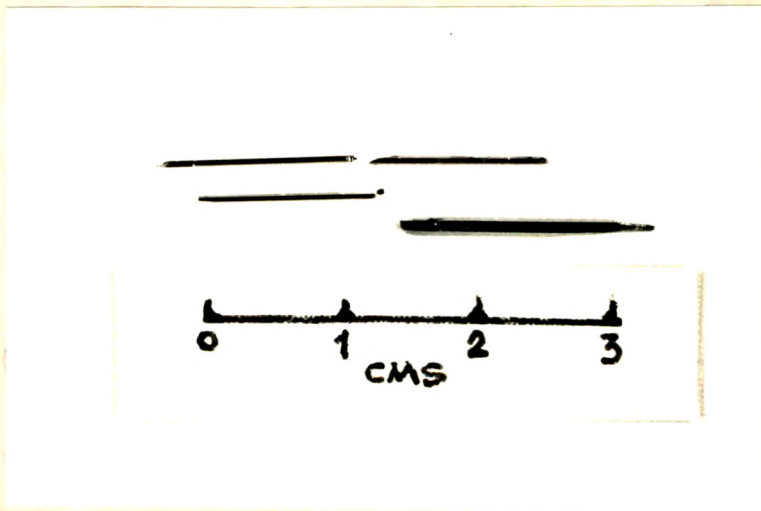



Fig.V-4

Fig.V-5

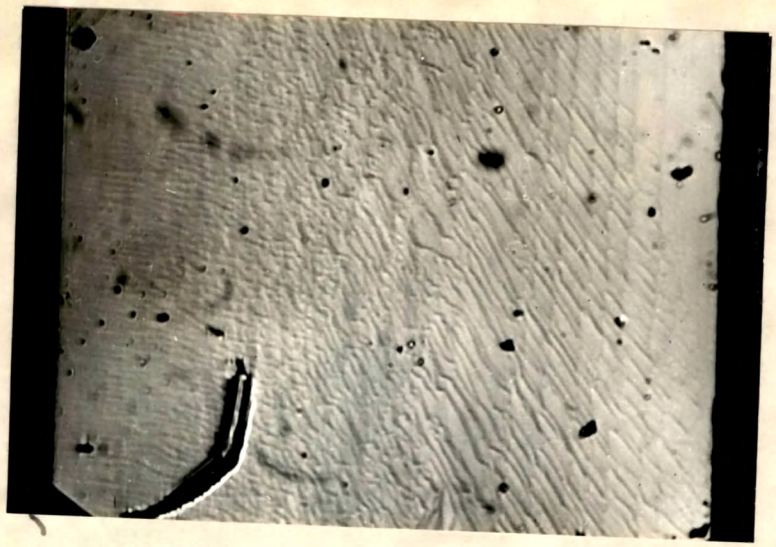


Fig.V-6 X170

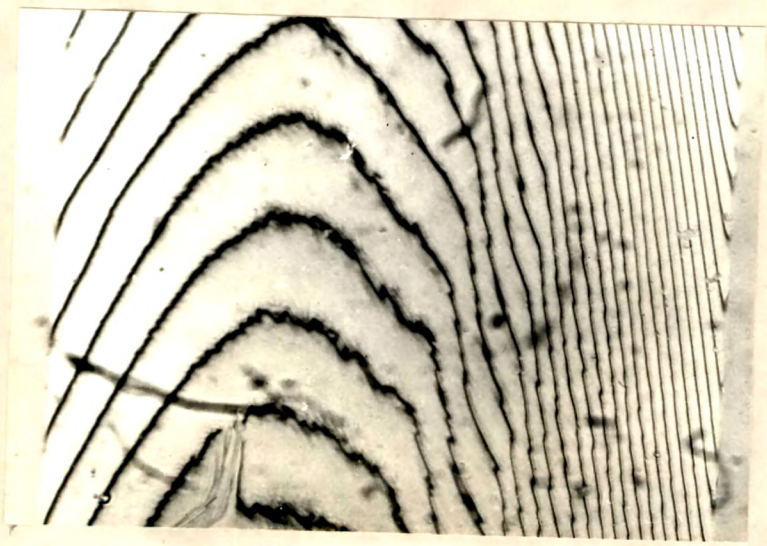


Fig.V-7 X170

the photomicrographs of a prism plane and the interferogram on the same face. Even though growth features and growth steps are absent, it is clear from the interferogram that the surface is not very smooth. On etching the prism face in $H_2SO_4$ at 120°C the pit density is found to be very low. No low-angle grain boundaries are observed in these crystals. Generally rows of pits running parallel to the c-direction are observed at the centre of faces, and sometimes three or four rows parallel to the same direction are observed towards the tip of the crystal. The pit density is higher towards the tip. On many prism faces a line is seen running parallel to the c-direction along the entire length of the surface. Fig.V.8 is such a plane. On etching, a row of pits is seen running parallel to it and very close to it. Fig.V.9 is the etched surface. The dislocation line remains as it was. Towards the tip of the crystal many more rows parallel to the previous one appear which indicates that the dislocation density is relatively high towards the tip. It is a minimum towards the base.

In a few cases, growth elevations, such as seen from Fig.V.10 had been observed towards the tip of

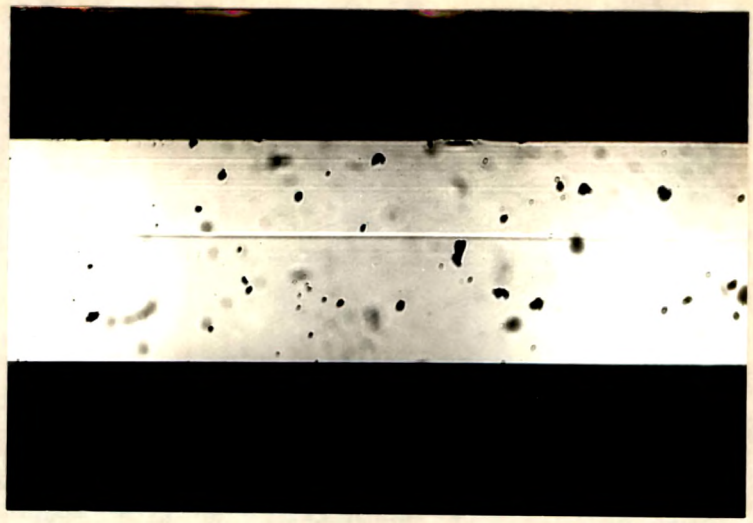


Fig.V-8 X135

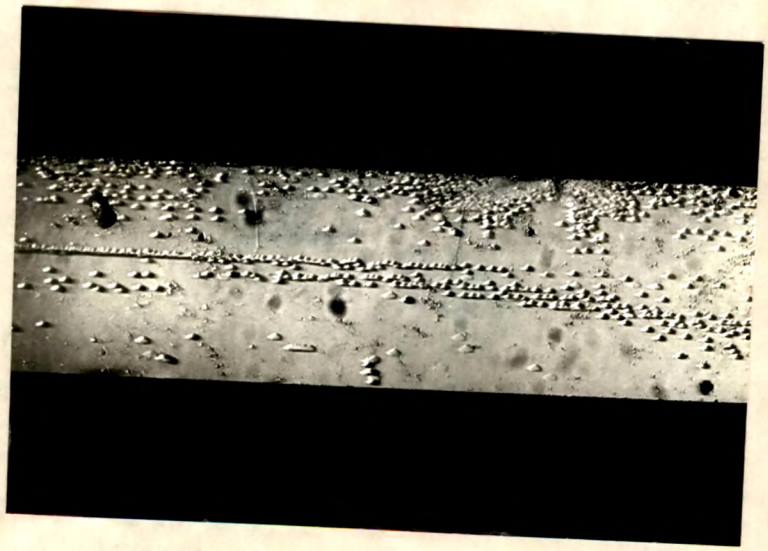


Fig.V-9 X135

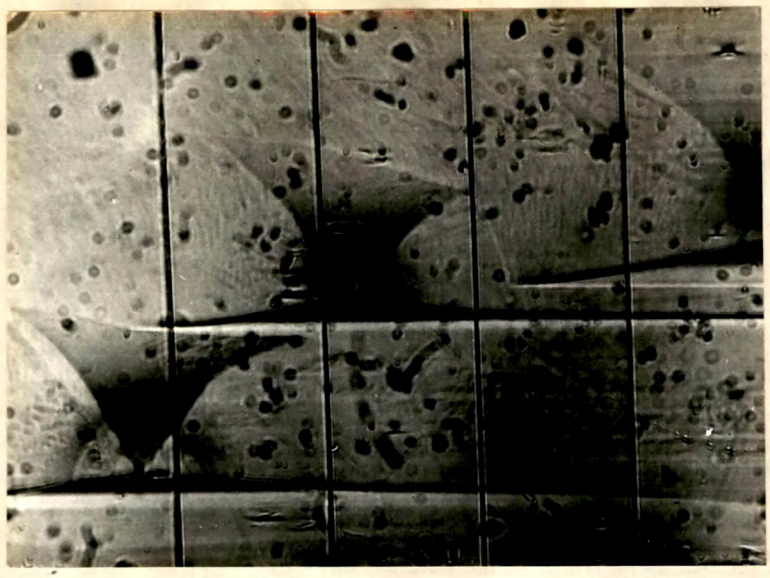


Fig.V-10 X135

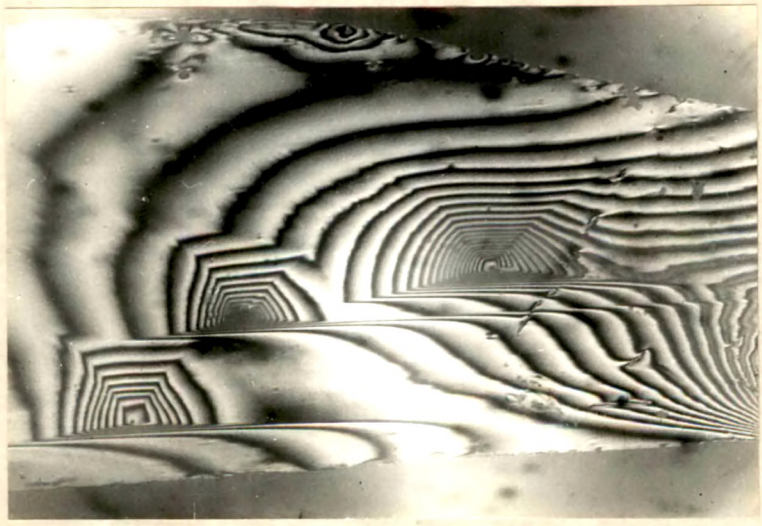


Fig.V-11 X135

the crystal. Fig.V.11 is an interferogram on the same region and Fig.V.12 is an interferogram on an individual feature. Figs.V.13,14,15 & 16 are the various features observed on the as-grown faces. They are somewhat triangular in shape. The triangular feature in Fig.V.16 on the edge of a step shows no misorientation eventhough it is situated at two different levels. Therefore these features may be the depositions on those surfaces after the cessation of the growth of the parent crystal.

Three kinds of dome faces have been obtained; (1) Completely developed faces, (2) With the hollow channel ending at the centre of the face and (3) Partially developed faces on the sides of the hollow channel. No growth spirals or growth hillocks could be found on these faces. In the case of completely developed faces slip lines and some inclusions are seen. Fig.V.17 is a dome face with slip lines. On etching such faces sometimes short grain boundaries are also observed. Pits are produced along the slip lines. Fig.V.18 is a dome face of the second type. Marks of layers parallel to the edge of the cavity are seen.

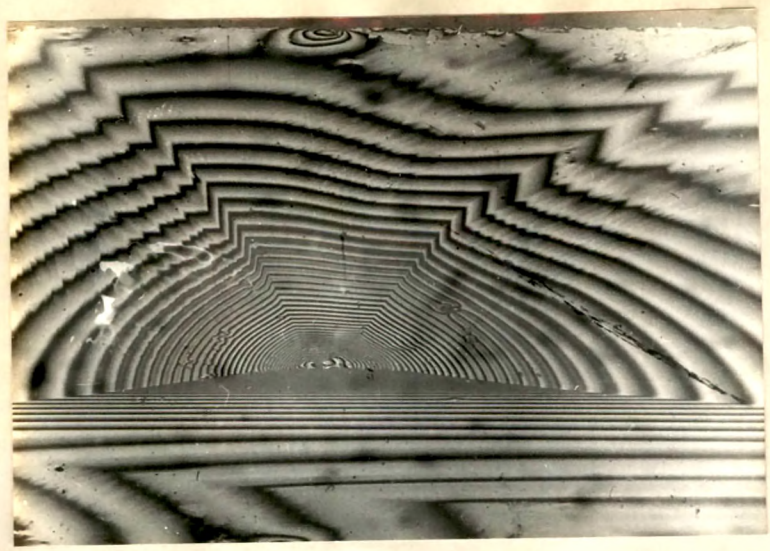


Fig.V-12 X360

Fig.V-13 X240

Fig.V-14 X240

Fig.V-15 X240

Fig.V-16 X460

Fig.V-17 X170

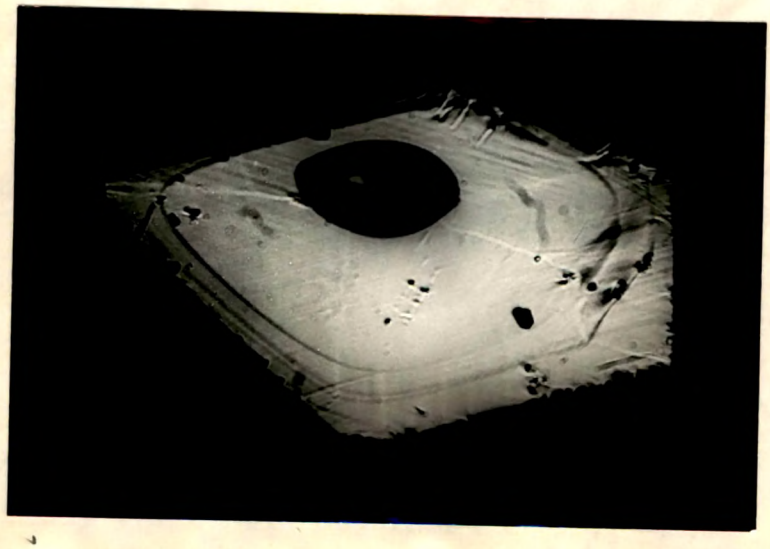


Fig.V-18 X220

These may be the marks left by the advancing steps from inside the hollow channel which might have intersected this face after the cessation of linear growth. Fig.V.19 is a photomicrograph of a partially developed dome face. The same sort of layer marks as in the previous case are seen on this face also. Some dome faces, especially the fully developed ones contained twin planes also. The intersection of a twin plane is seen in Fig.V.20.

In hollow crystals the tip of the whiskers ended irregularly i.e. all the prism faces did not terminate at the same height. The edges nearer to the source are longer than the other sides. In a few cases the face away from the source did not develop. It is found that this happens when the crystals grow from the tube walls at an angle more than 45°. The crystals are longer and well developed when the inclination is smaller. However, the conditions required to obtain this could not be assessed.

The hollow crystals with partially developed prism faces had been used to study the features inside the hollow channels. Fig.V.21 shows the features inside

Fig.V-19 X170

Fig.V-20 X170

a hollow channel. The triangular features are elevations. Such features have been observed only in a few crystals. In most cases, the hollow channels contained macroscopic steps, as shown in Figs.V.22 and 23. Here each step contains striations parallel to the c-axis. The step height increases towards the tip, which shows that the macroscopic steps are formed due to bunching of monatomic layers. Fig.V.24 is a photomicrograph of the steps as viewed normal to the dome face where the hollow channel ends. The profile shows that the planes of the macroscopic steps are the same as that of the dome face.

From the observations made above, it seems that growth takes place by the adsorption of atoms at the tip of the whiskers. Once the linear growth stops, the crystal thickens by addition of material on the side faces. The steps inside the hollow channel also advance slowly.

As no hemispherical termination is observed on the whisker tips, the growth of these crystals by a VLS mechanism is ruled out. The dislocation density,

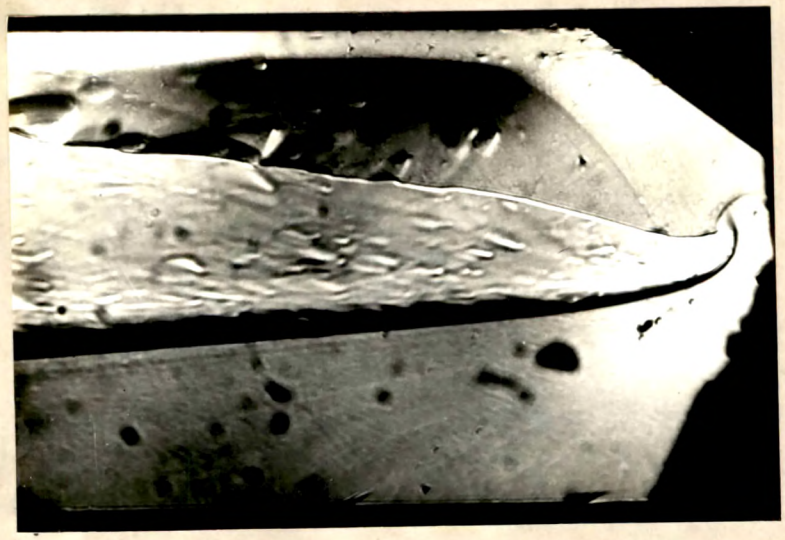


Fig.V-21 X450

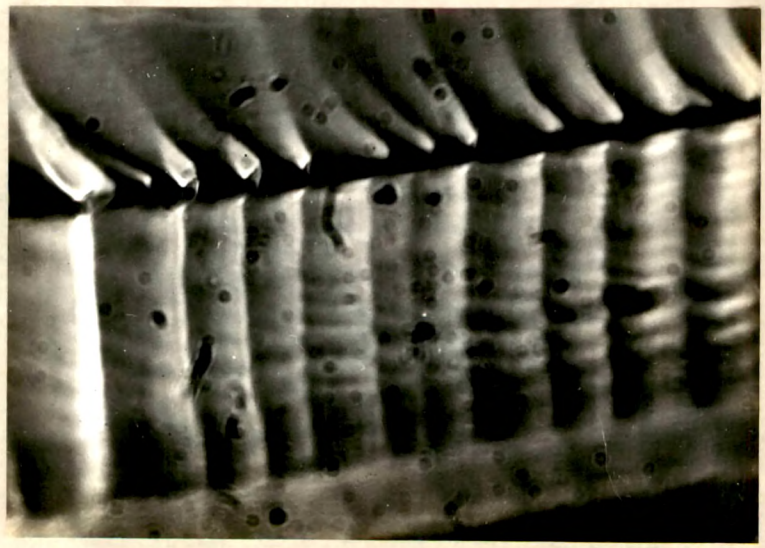


Fig.V-22 X460

Fig.V-23 X460

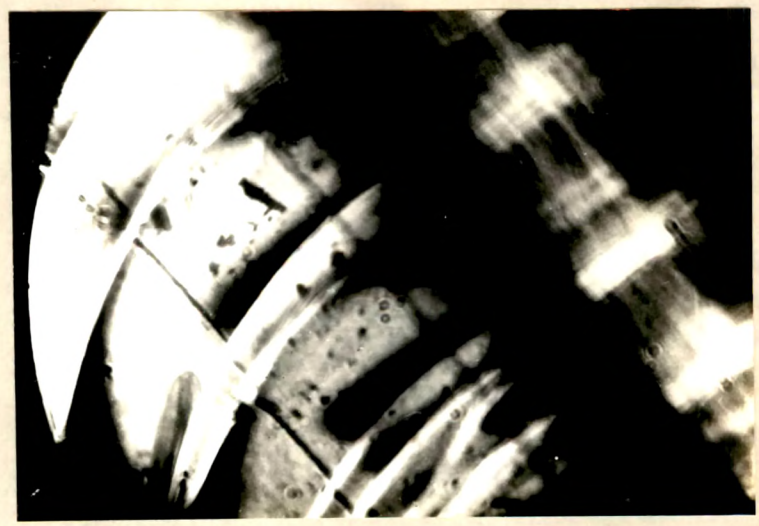


Fig.V-24 X540

though much less than the melt-grown crystals, is higher than that expected for crystals grown by VLS mechanism.

The rows of dislocation pits parallel to the crystal axis suggest that one or more screw dislocations parallel to the c-direction are active in the growth process of the crystal. Moreover the funnel shaped channels observed in these crystals cannot be explained by any other mechanisms. Frank and later Sears have proposed that a complex screw dislocation with a large Burgers vector will have a hollow core.

Another mechanism has been suggested by Mason[25] for the growth of hollow crystals. If the crystal is practically stationary relative to the surrounding vapour, layers will usually be nucleated near the edge of the crystal where the local supersaturation is highest. And then it will spread slowly towards the centre of the surface, where the supersaturation will be less. This gradient of supersaturation together with the onset of bunching allows new growth layers to form before the earlier ones have completed their travel towards the centre. This leads to

preferential thickening at the periphery, more pronounced starvation at the face-centre and thus to the development of hollow prisms.

The macroscopic steps observed inside the hollow channels may be due to bunching. But the mechanism by which the hollow crystals are produced may not be the one described above, since, in such a case all the crystals produced in a single tube must be hollow which is not so in the present case. Moreover, if the layers are just originating at the edge only due to a gradient of supersaturation, the growth rate will be very slow and as a result it may leave only a shallow depression at the tip of the crystal. Whereas if the edge nucleation is due to a complex screw dislocation the edge will grow very fast leaving the centre much behind and thus leading to the development of hollow crystals.

In the present case the crystals may be nucleating due to the impurities present. In most cases it is found that a thin solid stalk or a small globule appears on the walls of the container and

suddenly a hexagonal crystal, much thicker than the original stalk starts growing from it. It may be that due to impurity adsorption or thermal stresses large spiral dislocations will originate. Once the complex dislocation appears the centre becomes depressed and local supersaturation at the edges will be higher than that at the centre. Because of the supersaturation gradient on the tip, the edge starts growing faster. The growth rate slows down towards the centre. Once the depression becomes deep, the availability or arrival of atoms at the centre decreases. This leaves a deep funnel shaped hollow in the centre of the crystal. Once the linear growth stops the side faces continue to grow and the crystal thickens. It could not be ascertained at which point the linear growth stops and the thickening commences.

In a few cases twin lines could be observed on the dome face as in Fig.V.20. This led the author to conclude that the twin mechanism also plays a part in the growth of some crystals. In such cases the crystals were solid prisms and the dome faces were well developed.

CONCLUSIONS:

(1) It is possible to grow hexagonal Te crystals of high quality, from the vapour phase in a pyrex tube sealed under vacuum.

(2) Provided the other conditions are steady, the rate of cooling and consequently the supersaturation ratio play an important role on deciding the habit of crystals.

(3) Impurity plays an important role in the nucleation of the crystals. With metal of very high purity and a slow rate of cooling it may be possible to get fairly big crystals of Te.

(4) The tellurium whiskers grow by screw-dislocation mechanism and in a few cases by twin mechanism. No VLS mechanism is active in the present case of the Te crystal growth.

(5) It is not possible in the present mode of crystal growth to control the nucleation centres or to assess the local supersaturation near the growing crystals.

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