Deformation and Annealing Sub-Structures of Niobium and their Relation to the Mechanical Properties and Precipitation Phenomena.

A. Berghezan and A. Fourdeux

Union Carbide European Research Associates, S.A.
95 Rue Gatti de Gamond, Bruxelles 18, Belgium.

Part I : Deformation Sub-Structure of Niobium and its Relation to Mechanical Properties.

Introduction

During the last decade, several deformation theories of metals have been developed, most of them based exclusively on theoretical models of the dislocation structure of deformed metals. Of particular interest are those related to the b.c.c. metals as they represent a very important class of materials such as iron, steel and refractory metals. Among these theories, that of Cottrell was received with particular enthusiasm since it appeared to be of rather general applicability.

Cottrell's theory tries mainly to explain the σ_o and k parameters of the Petch (1) empirical equations which relate the brittle fracture stress and the lower yield point to the grain diameter by the following simple equations :

$$\sigma_t = \sigma_o + k_f \cdot d^{-\frac{1}{2}}$$

$$\sigma_y = \sigma_o + k_y \cdot d^{-\frac{1}{2}}$$

Another important fact, found by Heslop and Petch (2), is the large increase in the yield stress when the deformation temperature is decreased. Fig. 1 shows graphically the important experimental factors found by Petch.

Since the σ_o and k parameters are not interpreted in the Petch relation, Cottrell (3) tried to give them a physical meaning. In his concept σ_o should be considered as the shear stress resisting the movement of dislocations along the slip planes after they have been unpinned from the impurity atmosphere, whereas k is the product of the shear stress (σ_D) needed to unpin a dislocation from its atmosphere and the distance (l) which separates the first dislocation in a pile-up against a grain boundary barrier from the source at which the dislocations of the pile-ups were nucleated. In the Cottrell notation, the Petch relation becomes

$$\sigma_y = \sigma_i + k_y \cdot d^{-\frac{1}{2}} \quad \text{where } k_y = \sigma_D \cdot l^{\frac{1}{2}}$$

This theory thus assumes a definite dislocation model (Fig. 2) of the deformation process in which three factors are given an important physical meaning : the lattice friction stresses (σ_i), the pile-up of dislocations against specific barriers (grain boundaries) and the dislocation sources situated inside the grains.

The Cottrell theory developed only for iron and steel has also been found adequate for the refractory metals both of group V (V, Nb, Ta) and VI (Cr, Mo, W) of the periodic table (4-11). It was therefore thought that this theory might be considered as valid for the deformation of all the b. c. c. metals. However, further work on refractory metals, principally by Johnson's group (12) (Johnson and Wronski (13)), questioned its extension to the refractory metals, although this doubt was not shared by all workers and the applicability to iron and steel was never called into question.

A number of further theories have been developed based on other hypothetical dislocation mechanisms, but all suffered from the fact that their exact verification was extremely difficult, if not impossible, so long as the behavior of the dislocations must be inferred from indirect measurements. With the advent of transmission electron microscopy, however, the situation changed almost overnight because at last a tool was available whereby the deformation process could directly be observed at an atomic scale. The primary purpose of the present work is to report the contributions of this technique to the experimental evaluation of the principal theories that have been proposed and to study at first hand the interaction between the dislocations and impurities remaining in the metal during the deformation and precipitation annealing. The present study, however, is in the nature of a progress report since the results are so far confined to niobium deformed only at room temperature.

Experimental Techniques.

Niobium which had been prepared by electron beam melting was used in all experiments and had the following analysis : 210 ppm carbon, 100 ppm oxygen and 90 ppm nitrogen. The ingots which were initially of 10 mm diameter were first cold rolled to a thickness of 0.1 mm and then annealed in vacuum at various temperatures and for various times to permit recrystallization and grain growth.

It was found necessary to perform two series of deformations ; one inside and the other outside the electron microscope. The final dislocation pattern observed in the latter series can frequently be understood only when the various steps in producing this pattern are seen in the microscope itself. The deformations outside the microscope started with the 0.1 mm sheets which were stretched in a Chevenard micro-tensile machine up to precisely predetermined points on the stress-strain curve and the samples so prepared were electrolytically thinned for viewing in the electron microscope ; the samples stretched in the instrument were first electrolytically thinned.

The majority of the samples used to investigate the initial, recrystallized material were treated at 1100°C for periods up to 15 hours and produced metal with grain sizes in the range between 5 and 10 μ diameter.

These samples are characterized by the complete absence of sub-boundary networks and an extremely small dislocation density within the grains ; the grain boundaries appear to have achieved at least quasi-stable

positions since the interboundary angles at intersections approximate 120° (See Fig. 3). In Fig. 4 the stress-strain curve of these samples is shown, where it is seen that the elastic limit is decidedly low but there is an extremely large elongation. The most striking feature, however, is the extraordinarily small rate of work hardening - it may in fact even be zero. In this respect niobium definitely differs from iron and the members of group VI where the work hardening rate is appreciably larger.

Examination of Samples Deformed Outside the Electron Microscope

The early stages of the deformation are characterized by a very great heterogeneity. So long as the total deformation remains below about 3.5% there is an enormous difference in the behavior of different grains ; some show large dislocation concentrations while others seem to have been totally unaffected ; a fact which is undoubtedly to be attributed to the different orientations of the grains. This is seen clearly in Figs. 5, 6, 7 and 8 which represent different fields in a sample elongated by 1.9%. Two different types of dislocation may be seen : long dislocation lines and dislocation loops. These differ considerably in aspect and distribution. The lines are sometimes straight and well-oriented but more often they are irregular ; curved with frequent cusps or straighter with numerous jogs. The loops appear to be of two different sorts : small, almost round rings and large elongated loops. It is believed that they are formed by two different mechanisms, as will be mentioned in some more detail later.

The rôle of grain boundaries in the deformation process is worthy of special note since, on occasion, they are seen to serve as preferred sources of dislocations (Fig. 9) or as acceptors of mobile dislocations and at all times they form very effective barriers, but against which the dislocations do not form pile-ups (Fig. 10). This last is of particular significance in b. c. c. metals because precipitate particles, as will be seen in a moment, cannot serve this function. When acting in their guise as acceptors, the grain boundaries readily accommodate the newly arriving dislocations thereby modifying their structure far more drastically than would correspond to the change of dislocation density within the grains.

On the portion of the stress-strain curve between about 2% and 3.5% elongation the deformation remains very heterogeneous from grain to grain but there is a considerable increase in dislocation density particularly of the two kinds of dislocation loops mentioned above. These appear to increase more rapidly than do the mobile dislocations. This may be seen in Fig. 11 which is reasonably typical of this stage although it should be emphasized again that there is a wide variation from grain to grain again probably depending on orientation.

In Fig. 12 a high angle grain boundary is seen. In the starting material these boundaries do not show normally any structure because their dislocation network is too fine to be resolved, but the fresh dislocations arriving at the boundaries during the deformation make changes in the initial uniform contrast and the new dislocations can readily be resolved and studied.

Thus it appears reasonable to assume that the dislocations seen here are new ones that have been accepted by the boundary. However, it is not yet certain whether these new arrivals lie actually in the plane of the boundary or in closely neighboring planes ; the latter is the more probable.

One other important point is illustrated by this figure (Fig. 12) : the grain boundaries are at first not "rigid" and only serve to stop the dislocations ; but they are rather "plastic" in that they accommodate the new arrivals into their structure thereby growing and producing kinks, etc. and rearranging their structures. As this process continues, however, the boundaries become more and more rigid and find it increasingly difficult to accommodate the further dislocations.

The interaction of mobile dislocations with precipitate particles is illustrated in Fig. 13 and 14. Here it should be cautioned that the apparent size of the precipitate particles is exaggerated by the low magnification used ; at higher magnification they appear as small dots along the dislocation line on which they nucleated during recrystallization annealing but perpendicularly oriented to it. It is clear from these figures that precipitates, as already mentioned, are very ineffective barriers to the movement of dislocations in these metals ; only a few dislocations and some rings have been pinned. One other frequently observed phenomenon is seen in Fig. 13 : the dislocation lines often separate regions of considerable contrast on the plate. This, as shown by some calculations of Amelinckx (14), is due to the fact that each dislocation line forms an elementary polygonization wall and the minute difference in orientation so produced is sufficient to increase the contrast as observed.

We now proceed to the next stage of the deformation process, between 4 and 5% elongation. The heterogeneity from grain to grain drops markedly, no grain being found now without fresh dislocations in it. In the grains of higher dislocation density there is a very perceptible tendency toward grouping ; the nodular tangles of dislocations are seen in Fig. 15 and 16. The onset of this grouping is probably to be explained by interaction of the mobile dislocations with more sessile prismatic loops. At any rate, in many regions, the grouping seems clearly associated with a higher loop density. Fig. 17 shows further examples of interaction with precipitate particles. Once again one is astonished at the ineffectiveness of these particles in producing pile up ; only a bit of debris and some rings are actually immobilized in this way. Other interesting interactions are seen at A, B, and C in Fig. 17 : at these points two $\frac{a}{2}$ [111] dislocations have combined to form a segment of a [100] dislocation. On annealing these fragments then increase their length and form hexagonal networks of twist boundaries ; a process favored by higher temperature (15).

On increasing the deformation to 5.5% elongation the dislocation density is found to be still on the increase but at a distinctly lower rate. The tangles which were forming earlier now transform into long skeins of tangled

dislocations which rapidly extend until they join up to produce some very confused cells (Fig. 18). Isolated tangled skeins still persist, however, up to 7-8% elongation (Fig. 19). At this stage the individual dislocations are generally still resolved.

The contours of the skeins within the crystal grains appear to be determined by the regions of higher ring or loop density as is particularly well seen in Fig. 20 where the location of the skeins appears to coincide with the presence of larger numbers of loops. Nevertheless, despite the growth of the tangled network of skeins there is a still greater increase in dislocation density within the grain boundaries. As seen in Fig. 21 the individual dislocations in these boundaries can no longer be resolved and the whole boundary begins to take on a spotty appearance. Again, the presence of precipitate particles does not seem significantly to alter the dislocation array in their immediate neighborhoods.

As the deformation is still further increased the skeins gather in more dislocations and form rather well-defined networks (Fig. 22) The grain boundaries, however, still keep ahead and now form regions of almost uniform black contrast (Fig. 23). Another significant feature now emerges : when the developing network of skeins intersects a grain boundary the angle of intersection is invariably close to 90° ; this angle is characteristic of the junctions of polygonization walls with high angle grain boundaries (16).

Continuing along the stress-strain curve as the point of rupture is approached the dislocation walls become much better defined and assume a striking geometric regularity ; the dislocation density in the contracted walls has grown to a point where the individuals can no longer be resolved. Fig. 24 and Fig. 25 show this characteristic situation before and after rupture and the highly regular cells are clearly evident. The growth of dislocation density in the walls has, of course, largely depleted the remaining crystals and increased the disorientation between adjacent cells. The length of an edge of the square cells is of the order of 0.5 μ while the longer dimension of the rectangular cells may reach 1 μ or even more. It is evident, then, that the deformation process has led to a decided subdivision of many of the original crystallites into a much smaller, geometrically regular network of square and rectangular cells of astonishingly uniform size. This agrees well with earlier observations of Wood (17), Hirsch (18) and others (19),(20) who found a similar phenomenon in iron, aluminum and aluminum alloys. Nevertheless, it must be remarked that this process of subdivision is not completely uniform throughout the structure. Some of the cells which got started late in the deformation process never catch up and, at the point of rupture, it is still possible to find crystallites - such as the one shown in Fig. 26 - which are still in a rather primitive state so far as building a cell structure is concerned.

Finally, in Fig. 27, an extremely interesting effect is seen. Particles of precipitate are here throwing out dislocation loops by a prismatic punching mechanism thereby giving rise to a very characteristic

pattern. In a sample with a considerable number of precipitate particles this could be a significant source of the relatively sessile dislocation loops (21). This may also contribute to dispersion hardening.

Discussion of Results on Samples Deformed Outside the Microscope.

We have seen that the deformation process in niobium is characterized by an initial rapid increase in the number of mobile dislocations and, what is especially significant, an even larger increase in the density of the far less mobile prismatic loops and rings. This stage is followed by a progressive grouping of the mobile dislocations into nodular tangles, then into skeins and finally into well-defined and highly regular walls. It appears that the distribution of these walls is principally determined by the arrangement of the loops, a process which may be visualized as follows : In the earliest stages of the deformation the mobile dislocations can cross-slip very easily in the b.c.c. structure and hence readily by-pass the loops. However, as the density of such loops increases the mobile dislocations find it progressively more difficult to cross-slip over their whole lengths and consequently only a portion of the dislocation can engage in this sport. The partial slipping produces jogs which reduce mobility and inaugurates the early beginnings of grouping. At the same time some climb is to be expected and this, together with the cross-slip, bring the dislocations out of their original slip plane and produce the irregular tangles in place of pile-ups. These tangles, as we have seen, are the forerunners of the well-organized walls to be formed later, but the progress toward this final state is rendered difficult by the limited climb. Consequently the rearrangement of the tangles into the regular orientation of the walls proceeds relatively slowly as compared to the development of the grain boundaries already present. Still, the fact that when finally formed the walls make the same angles (near 90°) with the high angle grain boundaries and that they produce a disorientation somewhat less sharp but of the same order as that of the polygonization walls forces us to consider even the initial tangles as incipient polygonization walls.

This view finds additional support in some recent work by Keh (22), (23) on iron at low and at high temperatures. He observed that at low temperatures there was little tendency toward grouping of the dislocations but at higher temperatures a dislocation structure was achieved which was nearly as regular as the polygonization walls. This strengthens the argument in our case that the tangled skeins are in fact the first step in polygonization.

Still further confirmation is found in recent observations by Morgand (24) on Armco and zone refined iron. The tangled dislocation structures were found to be far more regular in the purer material showing that increased purity has in some respects the same influence as raising the temperature. It appears, therefore, that in Morgand's experiments the refined metal underwent a more advanced dynamical recovery than the Armco iron ; and here again we must conclude that the tangled dislocation groups are to be considered as the primitive ancestors of sub-boundaries but with dislocation structures still far from their equilibrium positions.

A further deduction from our studies is the significant rôle played by the initial grain boundaries in the progress of the deformation process. These structures show contradictory behavior in that they not only nucleate the majority of the mobile dislocations but they also accept and, consequently, terminate the motion of, considerable numbers of these dislocations. As we have seen, however, they are at first plastic and accommodate the majority of the newcomers which reach them into their structures with considerable ease. In so doing the boundaries extend and become somewhat ragged, but as the density of accommodated dislocations increases they become more rigid and this fact seems to have a profound influence in decreasing the nucleation of new dislocations ; a process which substantially ceases in the course of the deformation process. This can be seen in the relative unavailability of new dislocations from this point on. During the rest of the deformation the walls improve their ordering and contract considerably but hardly add any new dislocations. In view of the fact that extensive pile-ups of dislocations behind barriers has not been observed in our studies and since it is generally accepted that in those metals showing pile-ups it is the back field stresses produced by these dislocation pile-ups which rob them of sufficient plasticity further to withstand rupture, it is reasonable to assume that the process just described is, at least in niobium, the one which prepares this material for the final debacle. If this were so, it would give an interpretation of the observed extremely low rate of work hardening ; a phenomenon which is probably characteristic of the influence of the extensive dislocation pile-ups ; we shall return to this point.

Observations during Stretching within the Electron Microscope.

We now pass on to the results of experiments performed within the electron microscope which nicely complement the work described thus far. Here we can actually follow the movement of the individual dislocation and, because of the tracks which are fortunately left behind, such movement can even be seen in the photographs.

The most striking observation in watching the movement of dislocations in stressed niobium is the fact that they follow extremely sinuous paths. This is even true at the very beginning of the deformation and is illustrated in Fig. 28 and 29 where the moving dislocations appear to deviate from their slip planes with no appreciable hindrance. In fact straight paths, in direct contrast to the situation in f. c. c. metals, are very rare because nearly all dislocations have more or less screw character and consequently easily change from one slip plane to another. This gives the overall impression that the dislocations do not remain on any precise slip plane. However, if the motion be carefully analysed, it will be found that each segment of the path in fact lies in a (110) slip plane and pursues precisely a $[\,111\,]$ direction. No doubt this difference in behavior as compared to f. c. c. metals is to be explained by the greater number of available active slip planes making smaller angles with one another. In Fig. 29 we also see the first emergence of dislocation loops which only appear in regions where slip has already occurred. In Fig. 30 we see that the slip seems to be more pronounced

near the grain boundaries and in Fig. 31 we observe that it becomes more and more prolific inside the grains as the deformation progresses.

The rôle of grain boundaries in nucleating dislocations is apparent in Fig. 32 where it is seen that a single boundary can send out dislocations in both lateral directions. Here again one sees the relatively high density of dislocation loops in the region which has experienced slip while outside such regions they are completely absent. This underlines that even within a crystallite there is considerable heterogeneity from one place to another in the effects produced. In Fig. 33 we again see the grain boundaries in the guise of dislocation acceptors and we note once more the absence of pile-up. Finally, an indication of the markedly different behavior of different grains is apparent in this figure.

In Figs. 34 and 35 we are able to contrast the relatively sessile prismatic loops and rings already described with the mobile dislocations ; whereas the latter have passed completely through the photograph, the former have shown no perceptible movement. There is some reason to believe that the rings and the distended loops may be formed by separate mechanisms. In the former case, the small rings are apparently produced by condensation of vacancies since, when watching the sample being stressed in the microscope, they seem suddenly to appear with no apparent preparation for their coming. The rings are found from the very beginning of the process even in regions where cross-slip has been very limited and this suggests that the point defects may have been produced by dislocations of indeterminate axis according to the mechanism of Kuhlmann, Wilsdorf and Wilsdorf (25). This conviction is strengthened by the frequent appearance of dislocation lines with sharp cusps - seen clearly at the arrows in Fig. 36 and also in Fig. 32 - which must be expected if the Kuhlmann, Wilsdorf and Wilsdorf mechanism were operative.

For the formation of the elongated loops we have no definite suggestions beyond the possibility that they may be produced by one or both of the two mechanisms already proposed : double cross-slip followed by closing up of the dislocation dipole (26), (27), (28), (29) or by the interaction between two mixed dislocations on parallel slip planes (30).

The interaction of mobile dislocations with precipitate particles could be better followed during the studies inside the microscope. The very minor rôle played by such interaction is clearly apparent in Fig. 36 and also in Fig. 37. Here again the effectiveness of cross-slip in enabling the dislocations to escape entrapment is well revealed. Particularly instructive in this connection, however, are the next four figures (# 38-41 inclusive) which show the same field at successive instants. If attention be fixed on the precipitate particles A, B, C and D in these figures, it will immediately become apparent that not more than 3 to 6 dislocations pile up behind each particle and, although a plethora of new dislocations follow the original ones, by a cross-slip zig-zag movement reminescent of the football field, they all circumvent the traffic congestion. Nevertheless, a few

dislocations are pinned.

Fig. 42 is especially instructive because it shows that large precipitate arrays can temporarily slow down dislocation movement. Even here, however, most of the dislocations escape through cross-slip but they are largely deflected from the penumbra of the particle. It is believed that this photograph provides strong support for the cross-slip mechanism for avoiding pile-up.

Still another significant observation is shown in Fig. 43 where a Piobert-Lüders or striction band is shown the edge of which is serving as a source of dislocations - a nucleation possibility already predicted by Johnson (40) in his theory of the deformation of b. c. c. metals. In Fig. 44 the subdivision of such a Lüders band into blocks reminiscent of those already reported in aluminum is seen. It is striking here, however, that these dividing walls, in direct contradistinction to the results for aluminum (31), are not effective dislocation barriers and produce no significant pile-up.

To summarize the conclusions from studies inside the electron microscope it seems well established that the most important single feature of the deformation mechanism is the predominant importance of cross-slip which determines all the remaining characteristic features : absence of dislocation pile-ups, failure of total dislocations to separate into partials, and the weak or transitory trapping of dislocations behind precipitate particles. These facts well explain the extremely low work hardening rate * shown by the stress-strain curve as well as the extreme ductility of b. c. c. metals (when sufficiently free of interstitials) which can easily surpass that of f. c. c. metals. A further deduction from the absence of visible separation of total dislocations suggests that the appearance of large stacking faults in such metals is highly improbable and indicates that those reported in annealed samples (32), (33) are probably due to a local segregation of impurities - in all likelihood introduced through contamination during annealing. All this is further in accord with Crussard's (36) view that the Suzuki effect might produce such stacking faults in b. c. c. metals.

Summary and Conclusions.

Some observations on the impact of the results here reported on the deformation theories which have been advanced to date will now be made. We started our discussion with Cottrell's attempts to provide through a specific dislocation model a general theoretical basis for the purely empirical relations discovered by Petch. In the model chosen for this purpose, dislocation sources within the grains and large dislocation pile-ups against the grain boundaries played key rôles. Unfortunately, our electron microscope results do not support this model. In fact, neither in our work nor in the results of Keh and Morgand on iron can large dislocation pile-ups be detected at the boundaries. Although the

---

* It will be seen later that an additional reduction of the work hardening rate is expected from the dynamical recovery which operates by both cross-slip and climb.

boundaries do, in fact, accept dislocations and accommodate them into their structure, thus serving as a sort of barrier, they also act as the primary, if not the only, source of dislocations during the earlier stages of the deformation and this fact has yet to be introduced into any model used as a basis for a general theory. Furthermore, we have already seen that the boundaries during a considerable portion of the deformation are not "rigid" but rather plastic. The main effect of this fact is a continuous rearrangement in the boundary structure as new dislocations are absorbed, the gradual development of rigidity during the deformation process and the progressive drying up of these boundaries as dislocation sources. Here we see the elements of a theory of "source hardening" which increases with plastic strain and which several theoreticians - for example, N.F. Mott (35) have been seeking. Another point worth stressing is the fact that the grain boundaries, since they completely surround the grains and hence cannot be avoided by cross-slip are really the only effective barriers, but even these, because of their ready and efficient fitting of the acquired dislocations into their structures, do not cause the pile-ups of the sort visualized in the Cottrell theory and actually observed only in certain f.c.c. metals (alloys).

We are thus led to recognize the vital rôle played by grain boundaries in the deformation process and it is certainly in their ambivalent behavior as both sources and sinks of dislocations that the extremely high ductility of pure niobium is to be sought. This indicates that the ductility is dependent on grain size and further suggests that a new interpretation of the Petch parameters should be made on the basis of a more realistic model, since Cottrell formulated his before direct observations of dislocation structure became possible.

No attempt will be made here to reinterpret the Petch relations in a quantitative way - in our view such treatment must await more extensive measurements on other b.c.c. metals over a considerably wider range of temperatures than the single temperature results reported here. Furthermore, significantly more detailed studies of the effect of impurities must be carried out and such studies will at present be rendered extremely difficult by the uncertainty of the analyses in these pure materials and the ever present danger of serious contamination of initially carefully refined material during the necessary heat treatments.

During this discussion the small influence of precipitate particles - especially the smaller ones - in hindering the motion of dislocations in niobium has been pointed out several times. It follows from this fact that precipitates, at least at low concentration, should not greatly affect the mechanical properties of such metals. Actually, the principal precipitates in the niobium used here prove to be carbides and we conclude that this metal should be able to tolerate relatively large quantities of carbon before the mechanical properties begin to be impaired. It must also be recalled that the

precipitate particles themselves can, by prismatic punching during the deformation, nucleate copious quantities of dislocations and this augmented supply will increase with the concentration of precipitate. It appears reasonable, on the basis of our studies, to suggest that the lower observable limit of carbide influence on mechanical behavior of niobium might be of the order of twice the analysis of the present samples - that is, about 500 p.p.m. On the other hand oxygen behaves considerably differently, but its quantitative behavior cannot presently be predicted.

The introduction of the tangled skeins of dislocations and their development during the deformation process into well-defined cell-walls has some extremely puzzling aspects particularly with respect to the actual influence such structures have on mechanical behavior. The presence and similarity of these arrangements in two b.c.c. metals, niobium and iron, as well as in f.c.c. metals requires considerable explanation in view of the considerable difference in mechanical behavior of these two types. The mystery is deepened by the fact that the jog theory of deformation, based on the density of dislocations in the tangles proposed by Hirsch (35), (36) for f.c.c. metals, has been shown by Keh (22) to be applicable also to iron despite the fact that Li (37) has shown that the Hirsch formula cannot hold for b.c.c. metals for completely different reasons. To resolve this difficulty, Li has proposed a new theory applying some ideas concerning the repulsive forces between the mobile dislocations and those in the skeins first put forth by Friedel (38) and Saada (39). However, contrary to these authors, Li does not believe that the mobile dislocations penetrate the array of dislocations in the skeins but rather that the latter move cooperatively. These conflicting points need clarifying.

However, it seems inescapable that neither the presence of the skeins nor their subsequent development into a regular system of cell-walls achieves any detectable work-hardening. It may be that the very concentration of the new dislocations into such regular structures, thereby leaving considerable areas almost free, may serve so to change the average distribution that the mean free path of a mobile dislocation is actually increased. Such a mechanism would, therefore, counteract the opposite tendency of the gradually stiffening grain boundaries in decreasing ductility. Said another way the steady draining off of the mobile dislocations into the tangled, but rather concentrated cell-walls may be a measure of the extent of dynamic recovery which the metal experiences during deformation. This idea needs to be verified by further work but it does seem to fit all the facts known so far. In particular, the parabolic aspect of the stress-strain curve of polycrystalline materials could be explained as the progress of the dynamic recovery in counteracting the stress fields due to the increasing numbers of new dislocations. The same mechanism might apply to stage III of the work hardening curves of f.c.c. single crystals - this stage is produced by the onset of dynamic recovery. Further support is found in the observation by Keh that at low temperatures, where the yield stress is significantly higher, there is no tendency of the dislocations to group and by the observation by Morgand that this grouping, at a given temperature, is greatly favored by high purity. This induces in the stress-strain curve a steady plastic strain which thus appears to be a result of both cross-slip and climb since both should

operate during the dynamical recovery.

Finally, it is known that some extremely pure metals may begin to recrystallize during deformation at room temperature. In iron and niobium there is no question of this because of their high melting points but it does appear to us that a corresponding rôle in holding down the rate of work hardening might be assumed by the ordering inherent in the dynamical recovery and this, together with the concomitant effects of cross-slip, could perfectly well, in our view, explain the near zero work hardening rate observed in pure niobium.

Part II : Annealing Sub-Structures of Niobium and Preferential Precipitation on Dislocations.

A. Polygonization in Niobium.

The most striking feature of the structure evolution in deformed niobium is the tendency to form stable polygonization boundaries of tilt, twist and intermediate character. Figs. 45, 46 and 47 show, respectively, examples of each of these types. Actually, polygonization is seen to be a very easy process in niobium which implies the possibility of large amounts of climb and hence of high concentrations of vacancies which do not anneal out up to the polygonization temperature. The mechanism by which this concentration is maintained may be shown to be associated with the presence of dislocation rings formed in large quantities during the room temperature deformation as may be seen in Fig.49 where the density is of the order of $5 \times 10^{14}/cm^3$. These rings, which are of 70 to 100 Å diameter and hence only resolved at high magnifications, appear to be formed by condensation of vacancies during the deformation ; a process already shown (41) to occur in zinc. In that case, however, the dislocation rings surround stacking faults which is not true in b.c.c. metals.

If the samples are annealed at 750°C following deformation the rings are seen (Fig.50) to expand significantly to 300 to 600 Å diameter either by capture of existing free vacancies or by the disappearance of some of the smaller rings, since their density simultaneously decreases to 0.5 to $2 \times 10^{14}/cm^2$. This evolution of the rings does not appear to be accompanied by any particular rearrangement of the mobile dislocations.

If the samples are annealed at a higher temperature (~ 900°C) the dislocation rings disappear completely by contraction while the mobile dislocations rearrange themselves into polygonization walls (Fig.51). Since these two phenomena appear simultaneously it is reasonable to assume that they are connected. Since the contraction of the rings, in turn, doubtless occurs with reemission of the vacancies, it is further reasonable to assume that in the course of this contraction the metal receives a flux of vacancies

which, as a result of the greatly facilitated climb, triggers the polygonization process. Support for this interpretation is provided by the phenomena observed at the intermediate temperature of 825°C ; here in some regions only polygonization is observed in others only expanded rings, but the two never occur together.

The high incidence of twist boundaries is an extremely interesting feature of these structures. According to the geometrical dislocation model such a boundary should possess a losange-shaped pattern with sides parallel to $[2\bar{1}1]$ and $[\bar{2}11]$. This model, however, is not stable since at points of intersection the dislocations react according to the equation

$$\frac{a}{2}[111] + \frac{a}{2}[1\bar{1}\bar{1}] \longrightarrow a[100]$$

to form a [100] segment, thereby transforming the losange into a hexagonal network. Such a reaction may be seen to happen each time a single dislocation reaches a pure tilt boundary and this produces a zig-zag pattern (see arrows) in the regular parallel array of dislocation lines in the tilt boundary (Fig. 48). It follows that the interaction of two or more dislocations converts locally a tilt into a twist boundary (Fig. 52) and accounts for the prevalence of twist boundaries in niobium ; this should be equally true of other b.c.c. metals.

A further interesting observation is concerned with the interaction of grain boundary junctions during annealing as seen in Fig. 53 where a pure tilt boundary interacts with a pure twist boundary. It is clearly seen that, at the intersection, the dislocation concentration increases and the mesh size of the resulting network correspondingly decreases. As multiple junctions are formed this process is repeated and the structure becomes progressively more complicated (Fig. 54) and more fine-meshed until it can no longer be resolved in the electron microscope. The final result is boundaries of higher angle of disorientation the structures of which are deducible from this mechanism of repeated junctions.

B. Precipitation Studies.

It is well known from many optical microscope studies (42), (43), (44) that the precipitation of a second phase takes place preferentially along dislocation lines, particularly low angle grain boundaries. This is shown in Fig. 55 in an aluminum alloy (42) and transmission electron microscopy has generally confirmed this conclusion (45), (46), (47). In Fig. 56 the decoration of a single dislocation in niobium is shown while Fig. 57 shows a tilt boundary where each dislocation is individually decorated. In Fig. 58 a new phenomenon of considerable interest is seen ; this is a twist boundary where only certain dislocations are decorated with precipitate. These are all parallel and have a Bürgers vector of the $\frac{a}{2}[111]$ type ; the undecorated dislocations are also parallel but differently oriented having a Bürgers vector [100]. Figs. 59 and 60 show that at small supersaturations the precipitation begins, not on the dislocations in boundary networks, but rather at isolated

dislocations. This shows that these isolated dislocations have a larger field of attraction than those which are grouped into boundaries or, said another way, the free energy per dislocation is a function of their separation and this naturally influences the nucleation rate. It may be concluded that, when the impurity content is low, precipitation on individual dislocations will be preferred. Further important conclusions are that the amount of precipitation seems to be related to the dislocation density and no precipitation is found in areas free of dislocations. Proof of these statements may be found in Figs. 61, 62, 63 and 64 the last two of which show samples first annealed at a high temperature (>1200°C) to dissolve the majority of impurities. On cooling they show no precipitation. One of these was then deformed 2%, the other 5% at room temperature and both were annealed 15 hours at 1000°C. The dislocations of both samples are now decorated but the samples 5% deformed have a higher dislocation density and, as is readily seen, a greater amount of precipitation. Since the total impurity content is the same in both samples, it is clear that the amount of precipitation is determined by the precipitation sites available.

In another experiment six identical samples were solution-treated at 1500°C and cooled to room temperature. Thereupon three of the samples were stretched to rupture and all six were reannealed in the precipitation range ; i.e. 15 hours at 1000°C. The undeformed samples showed neither dislocations nor precipitation (Fig. 63) while the ruptured samples showed copious decoration of the numerous dislocations present (Fig. 64). It is concluded that, at least at the supersaturation level of these samples, precipitation occurs only on dislocations. In the case of more contaminated samples having very high supersaturations there may be some precipitation between the dislocations (Figs. 65 and 66) but it always starts preferentially on them.

As the degree of saturation depends on the temperature, these phenomena should be influenced also by the annealing precipitation temperature.

In Fig. 67 the penetration of oxygen into a niobium sample during annealing in a poor vacuum is shown. There is apparently preferential penetration of oxygen along grain boundaries and, in some cases, along individual dislocations as shown by the precipitate laid down. The precipitate particles, which have not actually been identified, are presumed to be oxide.

In some samples, where the precipitation was carried out in a better vacuum (2×10^{-7} to 10^{-8} mm Hg) or where the samples were protected by a niobium foil, the precipitate particles have actually been identified after extraction on a carbon replica. This technique permits identification of the origin (grain boundaries or interior of the grains) of the particles. Fig. 68 shows precipitate particles from an individual dislocation line which were found, by electron diffraction, to have the hexagonal structure characteristic of Nb_2N or Nb_2C. Fig. 69 shows precipitates extracted from high angle grain boundaries which have the cubic structure of NbC or NbN. The lattice

parameters of the carbides and nitrides are so similar that positive identification is impossible although these are more probably carbides because of the high carbon content of the samples.

A curiosity extracted in these experiments are the rosettes shown in Fig. 70 where the dislocation line is at the center of the rosette. It is possible that growth in this form causes a minimum of lattice strain.

The authors are particularly grateful to Dr. R.H. Gillette, Director of our Laboratory, for the constant advice, helpful discussions and the help in the editing of the manuscript.

REFERENCES.

1. N.J. PETCH - J. Iron Steel Inst. 174 (1953) p. 25.

2. J. HESLOP and N.J. PETCH - Phil. Mag. 1 (1956) p. 866.

3. A.H. COTTRELL - Trans. A.I.M.E. - 212 (1958) p. 192.

4. M.A.ADAMS, A.C. ROBERTS and R.E.SMALLMAN, Acta Met. 8 (1960)p.238.

5. A.A. JOHNSON - Acta Met. 8 (1960) p. 737.

6. A.T. CHURCHMAN - J. Inst. Metals 88 (1960) p. 221.

7. R.C. KOO - J. Less Common Metals 4 (1962) p. 138.

8. M.A. ADAMS and A. IANNUCCI - Private communication.

9. M.J. MARCINKOWSKI and H.A. LIPSITT - Acta Met. 10 (1962) p. 95.

10. H.J. BECHTOLD, Trans. ASM 46 (1954) 1449.

11. H.J. BECHTOLD and P.G. SHEWMON - Trans. ASM 46 (1954) 972.

12. A.A. JOHNSON - Phil. Mag. 5 (1960) p. 413.

13. A.S. WRONSKI and A.A. JOHNSON - Phil. Mag. 7 (1962) p. 213 ;
A. WRONSKI - Thesis 1961 (Imperial College).

14. S. AMELINCKX - Private communication.

15. A. BERGHEZAN and A. FOURDEUX - 4ème. Colloque de Métallurgie (Saclay (1960) - Propriétés des joints de grains (Presses Univ. de France, 108, Bd. St. Germain (1961) p. 127 and Compt. Rend. 252 (1961) p. 1462.

16. A. BERGHEZAN - Thesis 1952 - Pub. Scient. et Techn. Ministère de l'Air, 2, Av. de la Porte d'Issy, Paris (1953).

17. W.A. WOOD and W.A. RACHINGER, J. Inst. Met. Mars 1949, p. 371.

18. P. GAY, P.B. HIRSCH and J.H. KELLER, Acta Cryst. 7 (1954) p. 41.

19. A. BERGHEZAN and J. HERENGUEL - Comptes Rendus 240 (1955) p. 1343.

20. A. BERGHEZAN - Métaux, Corrosion, Industrie 359-360 (Juillet-Août 1955, p. 1).

21. A. FOURDEUX and A. BERGHEZAN - Comptes Rendus 252 (1961) p. 1462.

22. A.S. KEH - Proc. A.I.M.E. Symposium on "Direct Observation of Imperfections in Crystals" - Interscience (1962) p. 213.

23. A.S. KEH and S. WEISSMAN - in press "Electron Microscopy and Strength of Crystals" by Interscience.

24. P. MORGAND - Compt. Rend. 254 (1962) p. 2578.

25. D. KUHLMANN-WILSDORF and H.G.F. WILSDORF - Acta Met. 10 (1962) p. 584.

26. B.P. PRICE - Phil. Mag. 5 (1960) p. 873 and J. Appl. Phys. 32 (1961).

27. J.T. FOURIE and H.G.F. WILSDORF - J. Appl. Phys. 31 (1960) 2219.

28. J.R. LOW, Jr. and A.M. TURKALO - Acta Met. 10 (1962) p. 215.

29. R. BENSON, G. THOMAS and J. WASHBURN - Direct Observations of Imperfections in Crystals - Edited by J.B. Newkirk and J.H. Wernick - Interscience Publ. (1962) p. 375.

30. A.S. TETELMAN - Dislocation Dipole Formation in Deformed Crystals - [Report - 1962 - of the University of Paris (Physique des Solides) Boîte Postale N° 11, Orsay (S. et O.) France]

31. A. BERGHEZAN and A. FOURDEUX - J. Appl. Phys. Vol.30 (1959) p.1913.

32. A. FOURDEUX and A. BERGHEZAN - J. Inst. Metals 89 -(1960) p. 31.

33. A. FOURDEUX and A. BERGHEZAN - Letter Editor J. Inst. Metals - July (1961) p. 191.

34. C. CRUSSARD - Compt. Rend. 252 (1961) p. 273.

35. N.F. MOTT - Trans. A.I.M.E. 218 (1960) p. 962.

36. J.E. BAILEY and P.B. HIRSCH - Phil. Mag. 5 (1960) p. 485.

37. J.C.M. LI - Discussion on work by Keh, see Ref. 16.

38. J. FRIEDEL - Symp. Internal Stresses and Fatigue of Metals, G.M. Tech. Center Detroit (1959).

39. G. SAADA - Acta Met. 8 (1960) p. 20 ; Acta Met. 8 (1960) p. 841 and Acta Met. 9 (1961) p. 166.

40. A.A. JOHNSON - Phil. Mag. 7 (1962) p. 177.

41. A. BERGHEZAN, A. FOURDEUX and S. AMELINCKX - Acta Met. 9 (1961) p. 464.

42. P. LACOMBE and A. BERGHEZAN, C.R. Ac. Sci., Paris 226 (1948) p. 2152 ; 229 (1949) p. 365 and Alluminio 4 (1949) p. 1.

43. R. CASTAING and A. GUINIER - C.R. Ac. Sci. Paris 228 (1949) p. 2033.

44. H. WILSDORF and D. KUHLMANN-WILSDORF, Rept. Conf. Defects Crystalline Solids - Bristol (1954) p. 175.

45. D. Mc LEAN and K.F. HALE - Electron Microscopy Conference - Exeter (England) 1959.

46. G. THOMAS, Phil. Mag. 4 [41] (1959), p. 606.

47. A. BERGHEZAN and A. FOURDEUX - 4ème. Colloque de Métallurgie (June 1960 - Saclay - France) - "Propriétés des Joints de Grains" - Edition : Institut des Sciences et Techniques Nucléaires - Presses Universitaires de France, 108, Bd. Saint-Germain, Paris (1961).

Figure 1

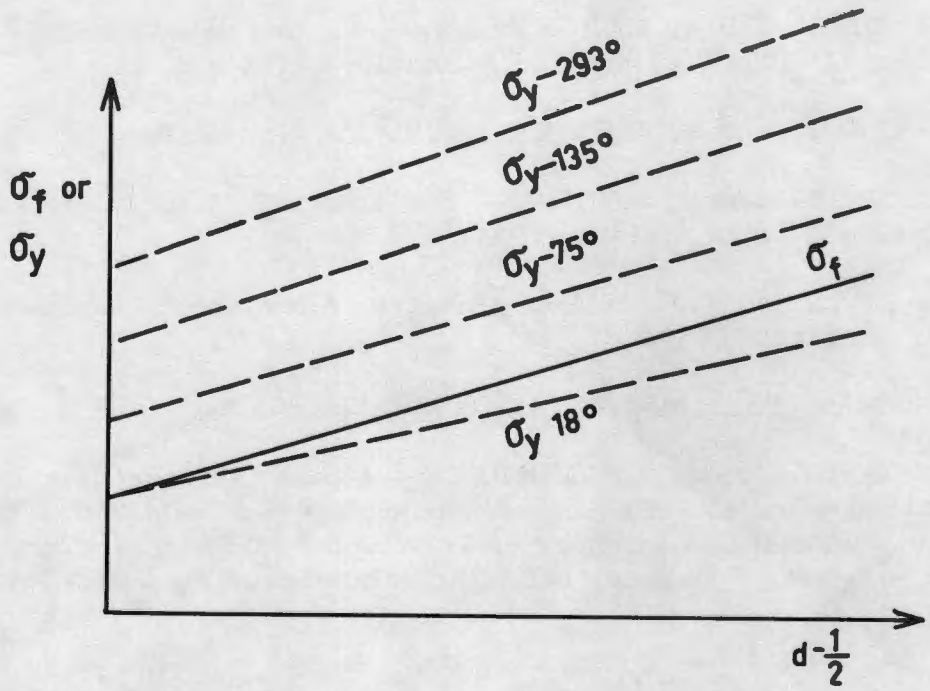


Figure 2

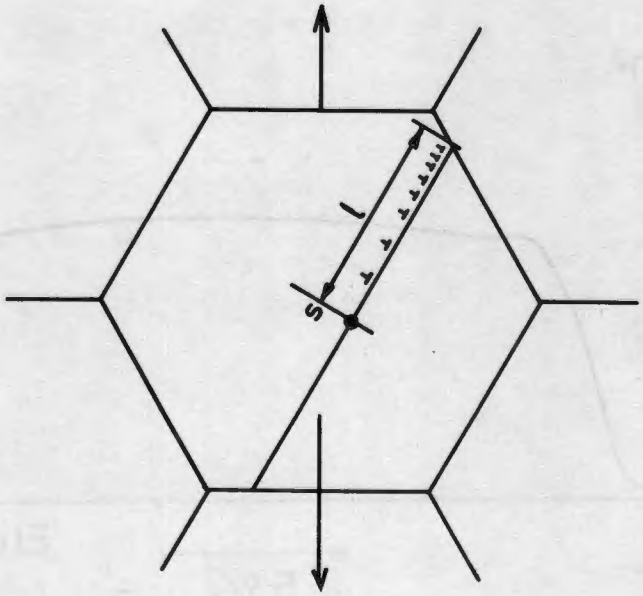


Figure 3

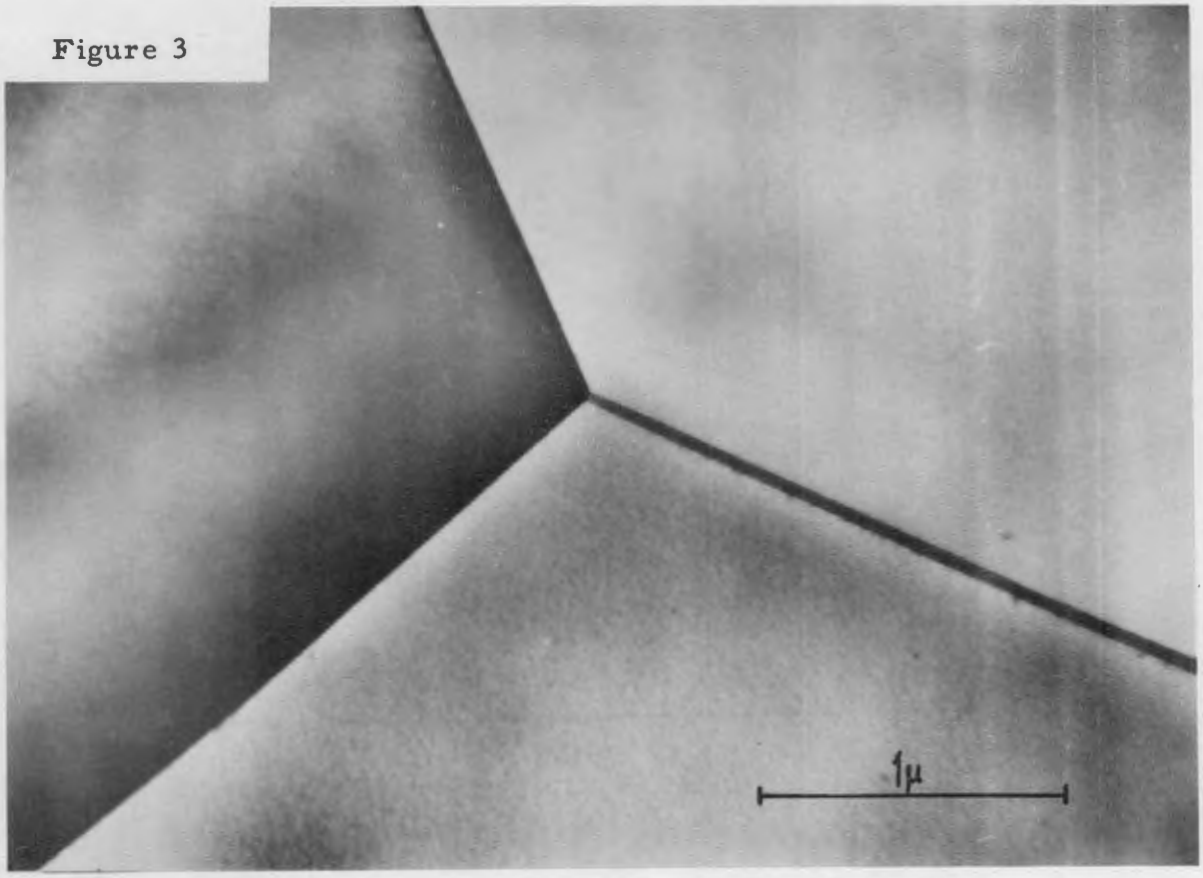


Figure 4

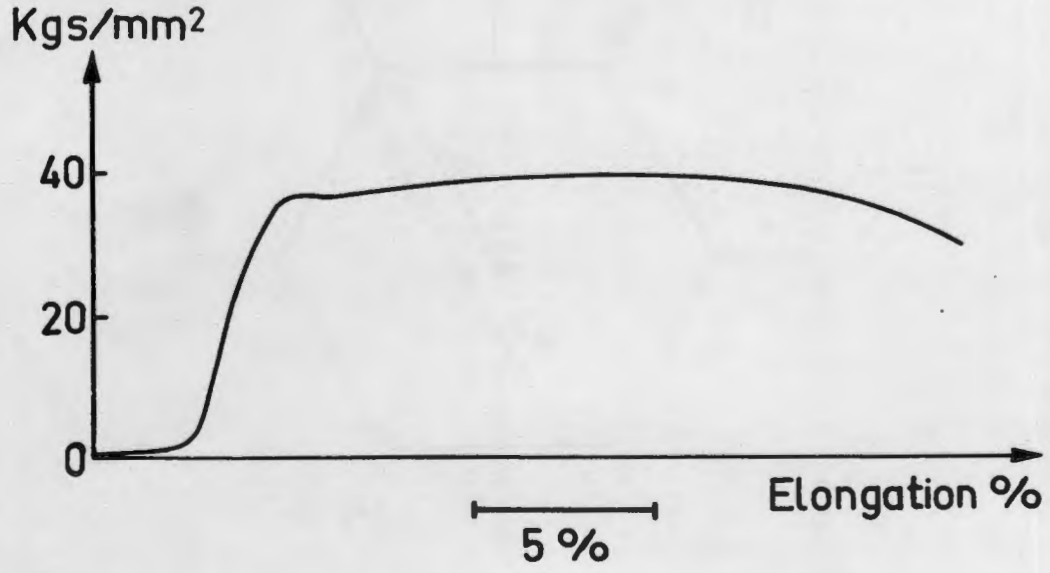


Figure 5

Figure 6

Figure 7

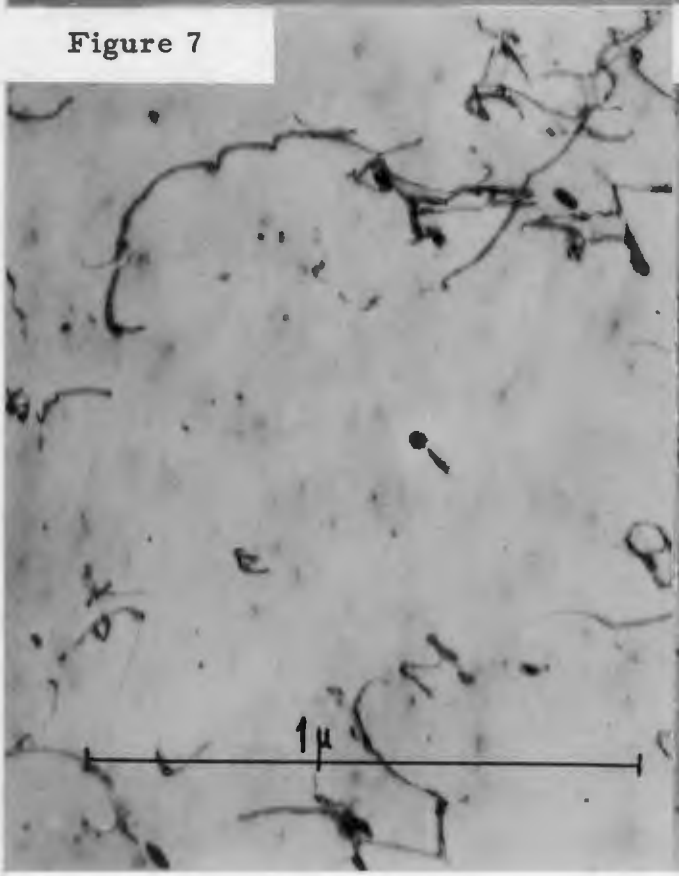
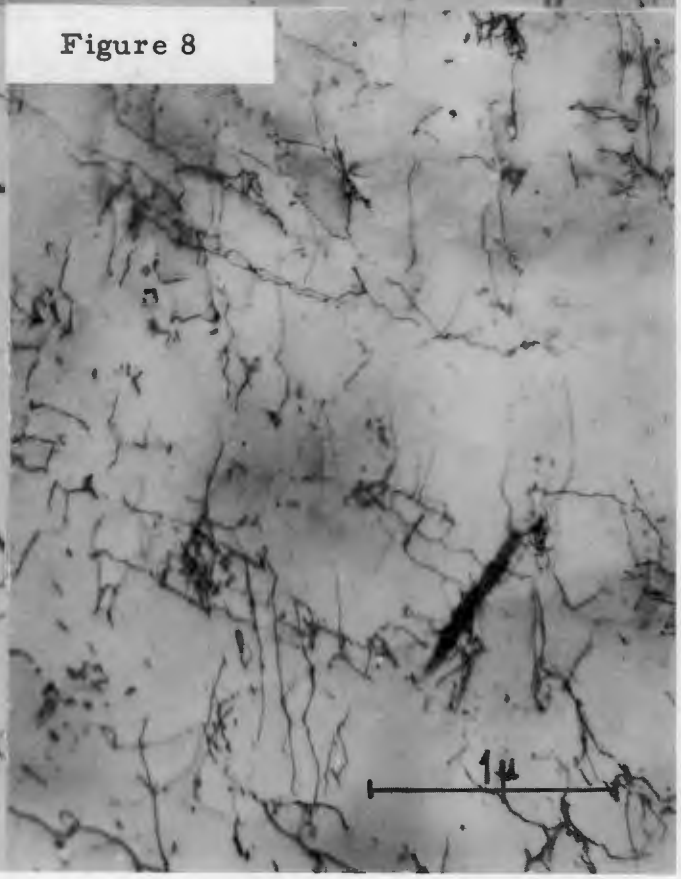


Figure 8



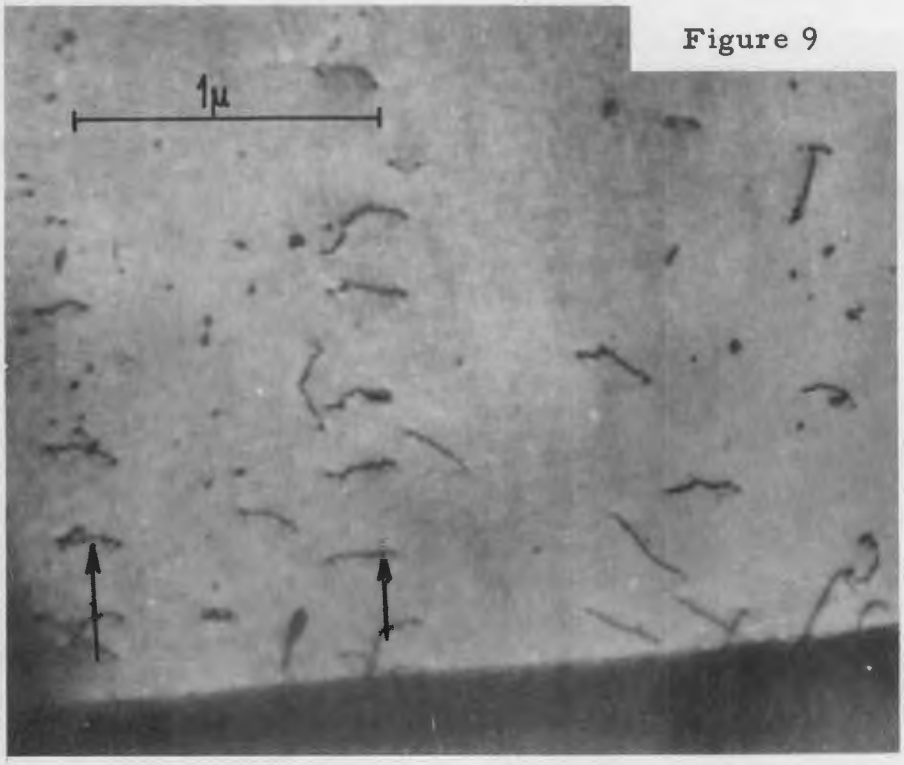


Figure 9

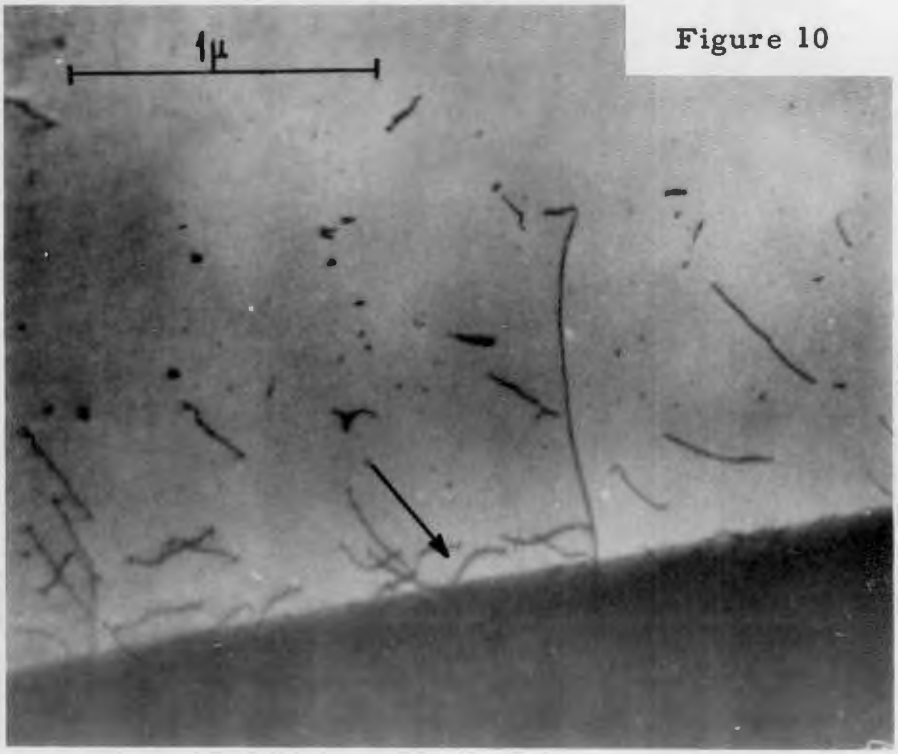


Figure 10

Figure 11

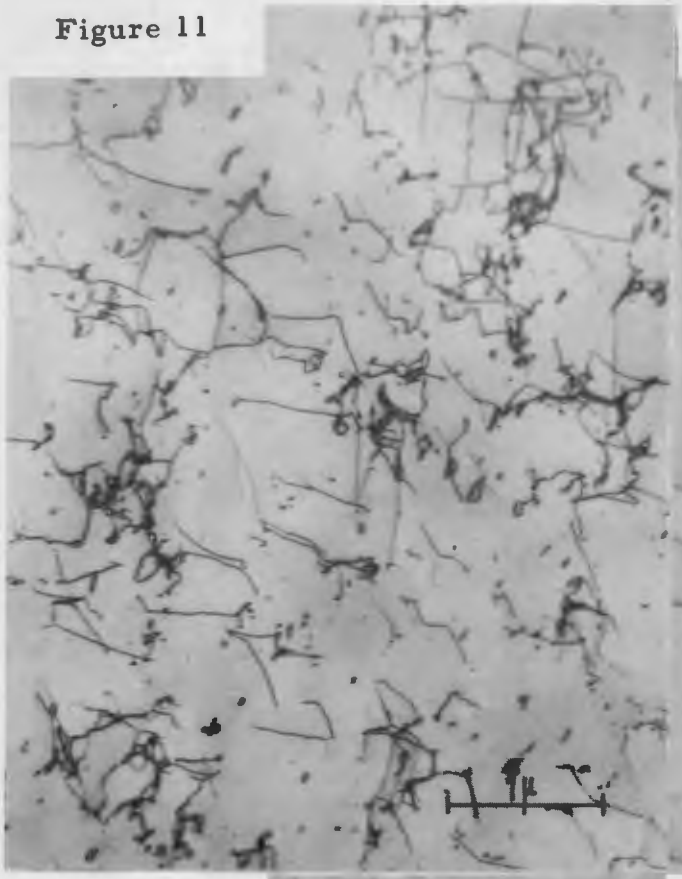


Figure 12

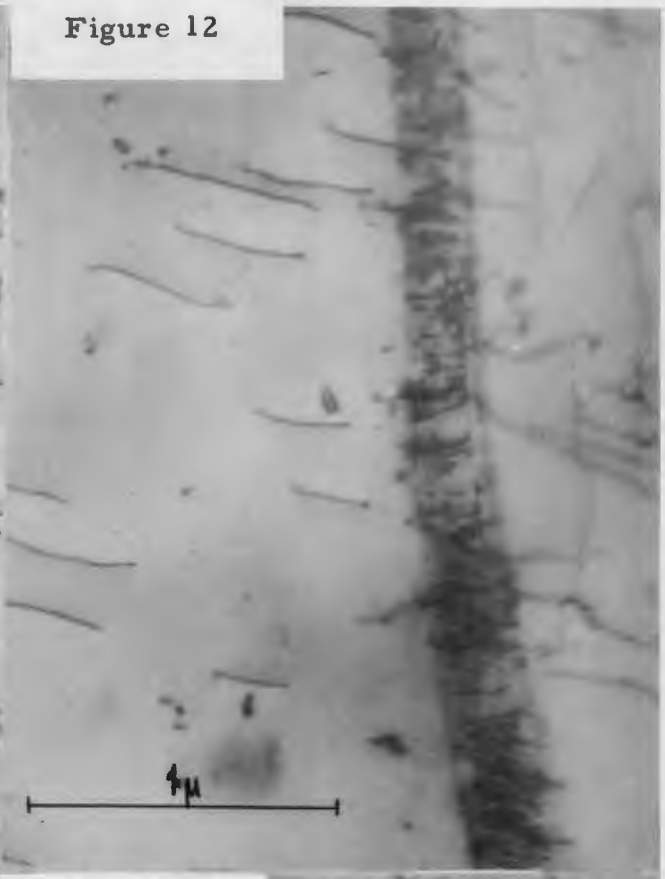


Figure 13

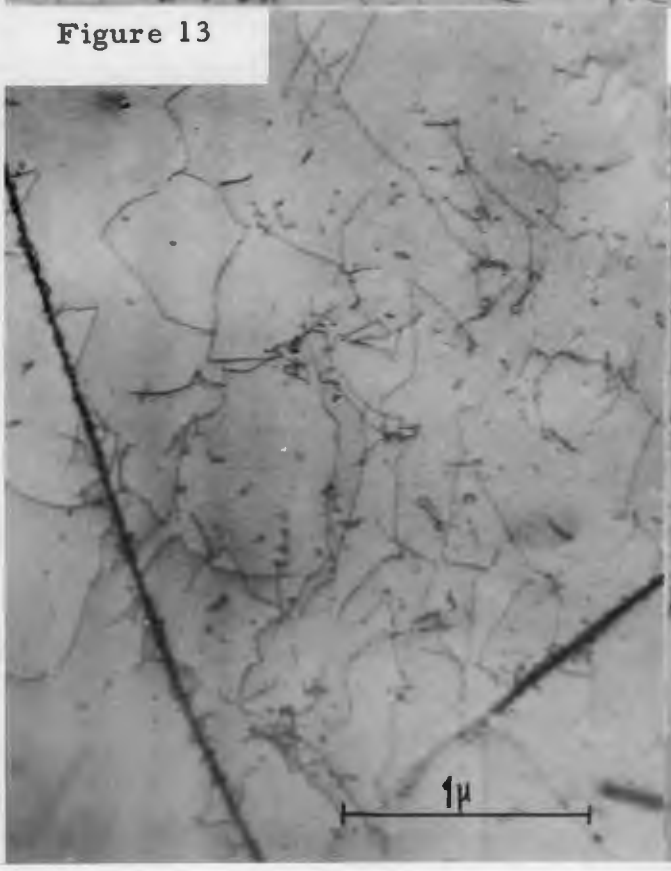


Figure 14

Figure 15

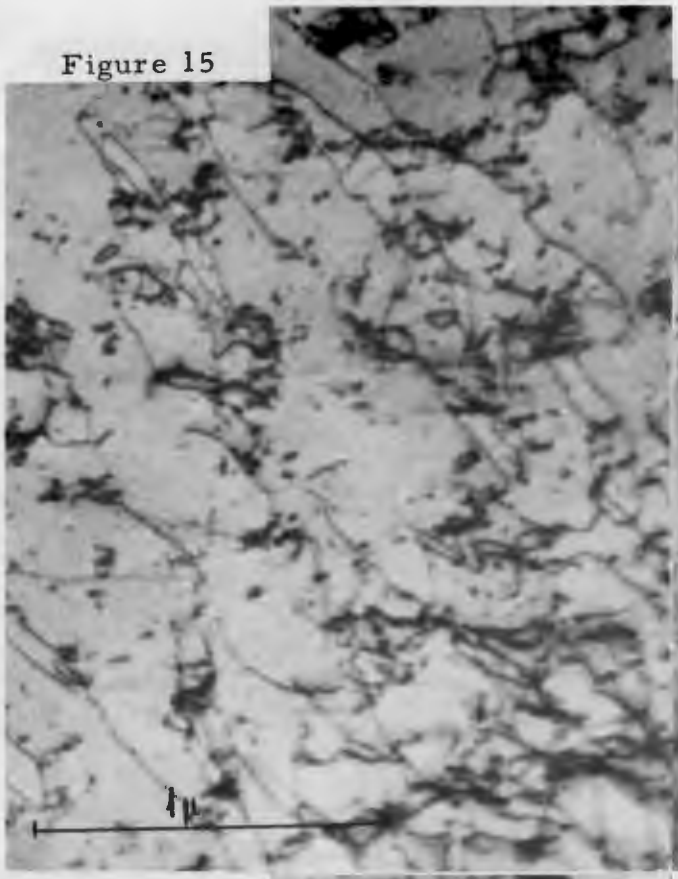


Figure 16

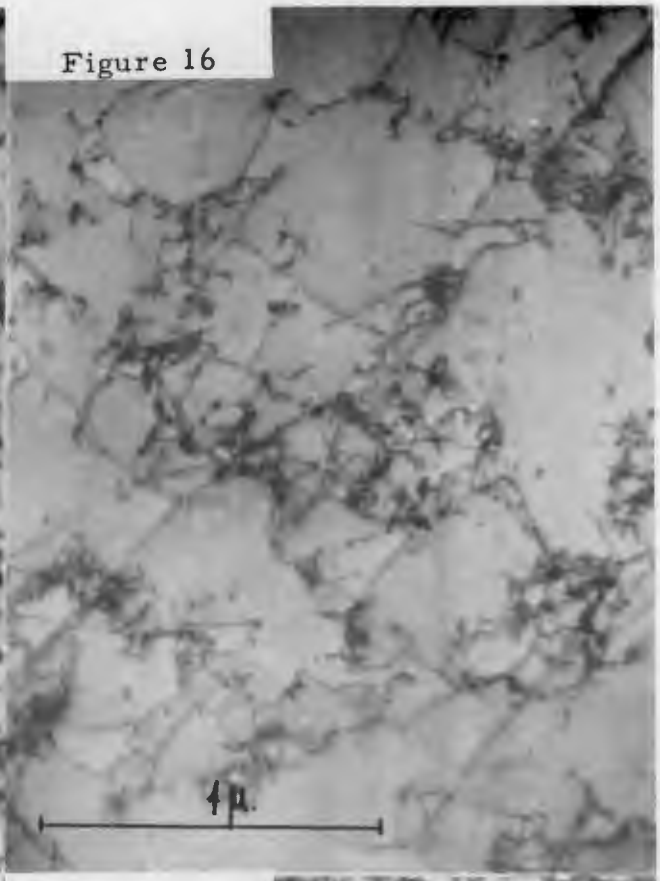


Figure 17

Figure 18

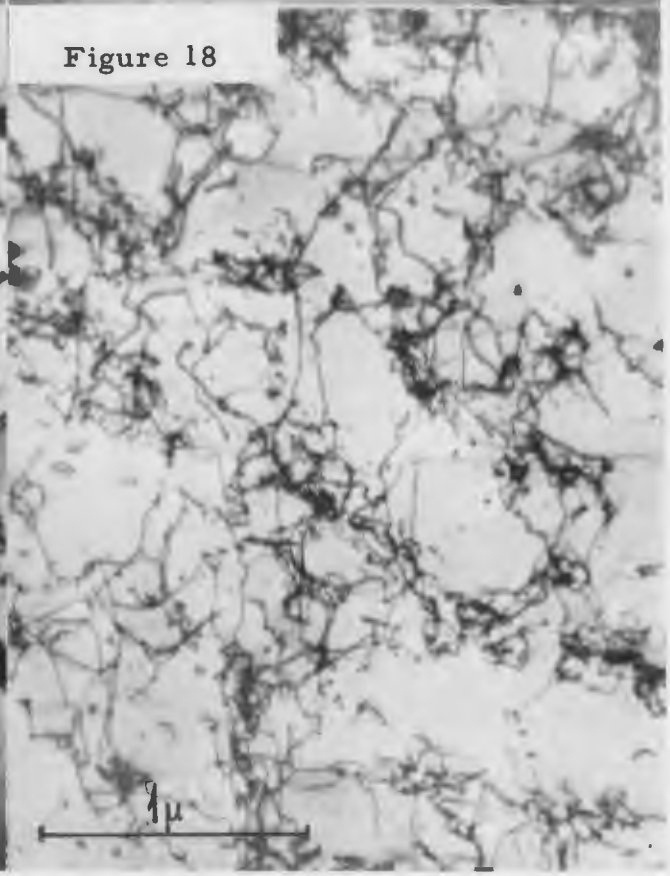


Figure 19

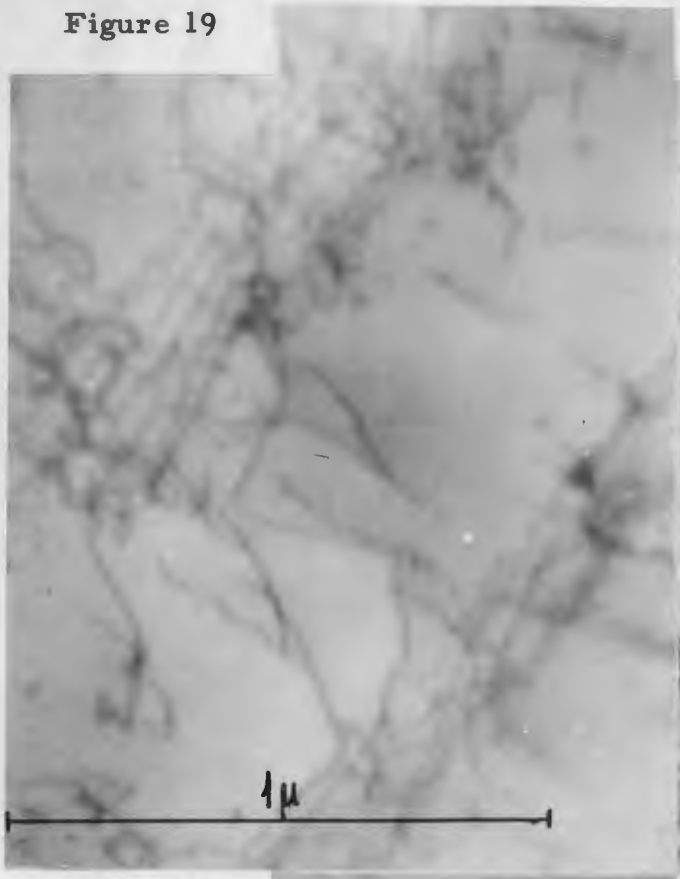


Figure 20

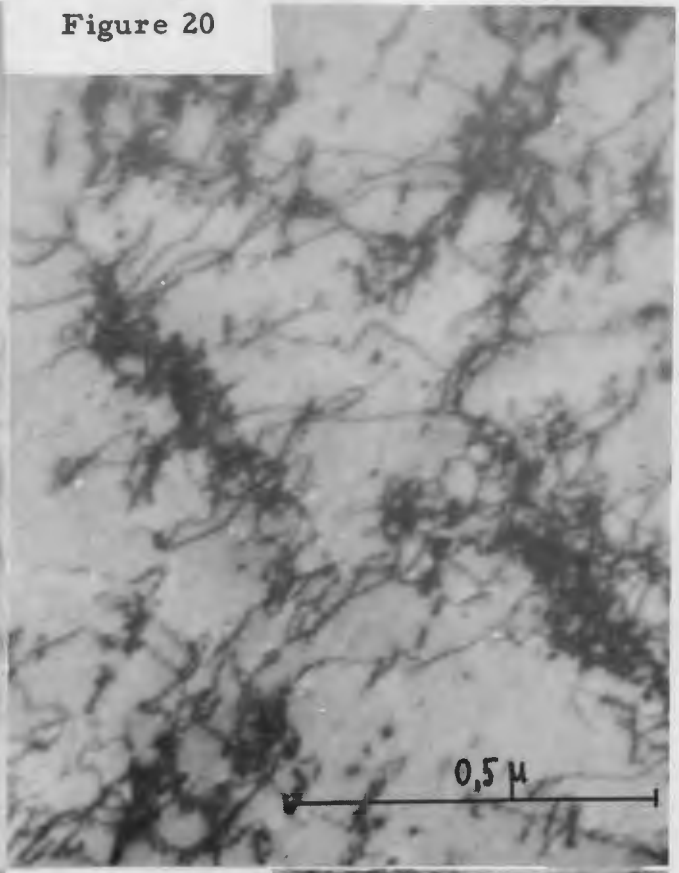


Figure 21

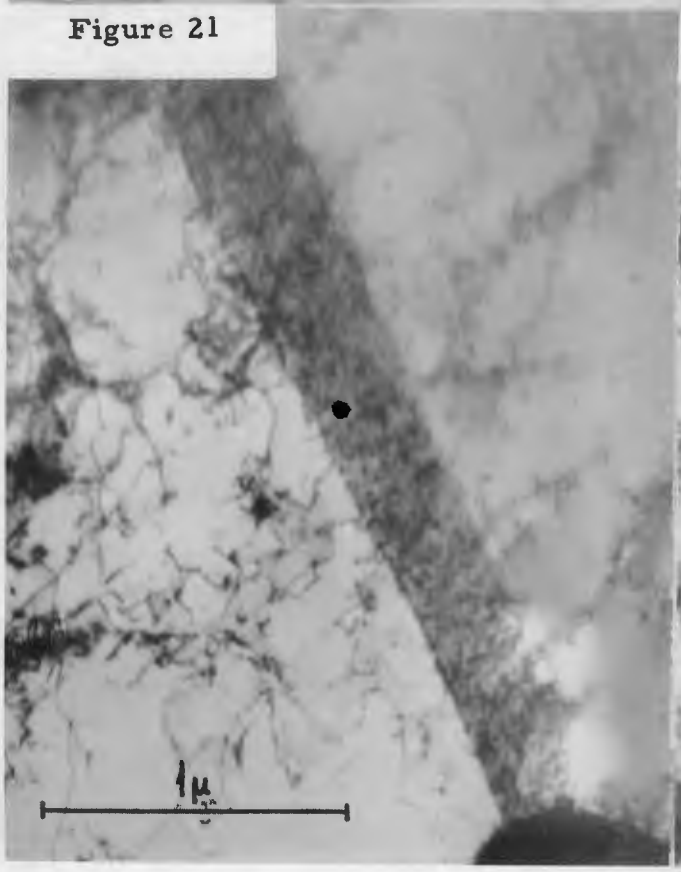


Figure 22

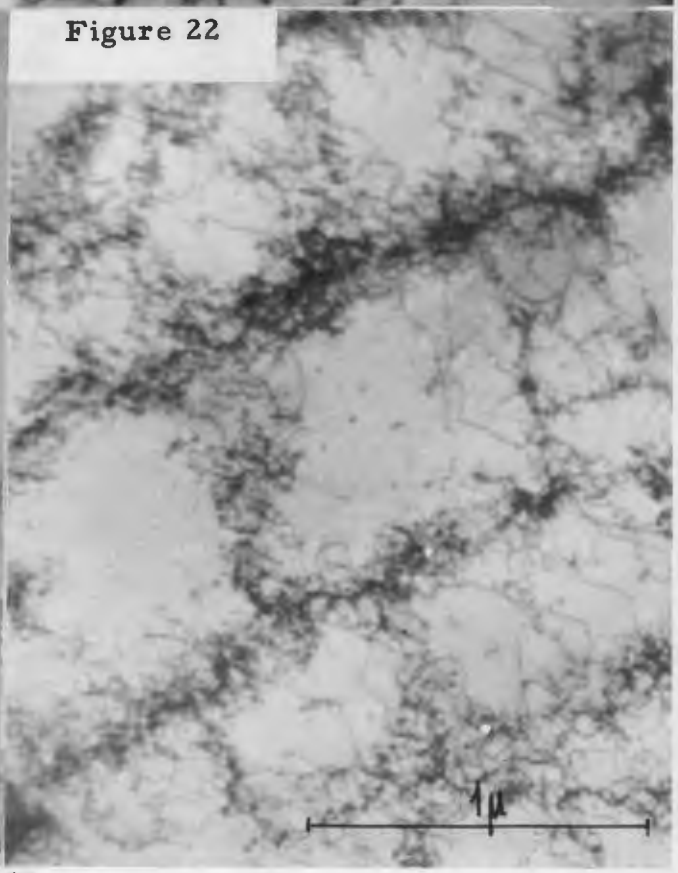


Figure 23

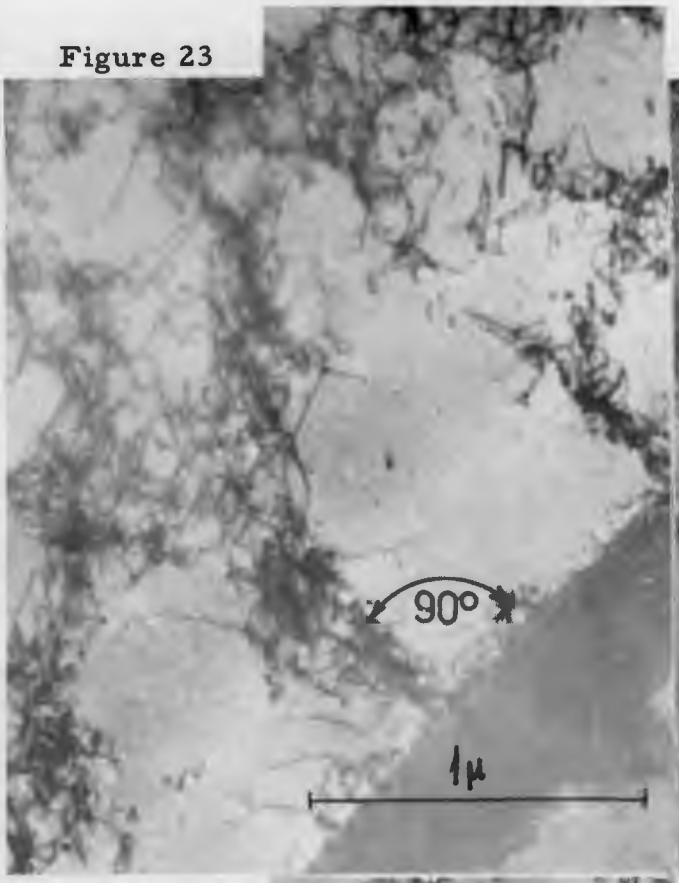


Figure 24

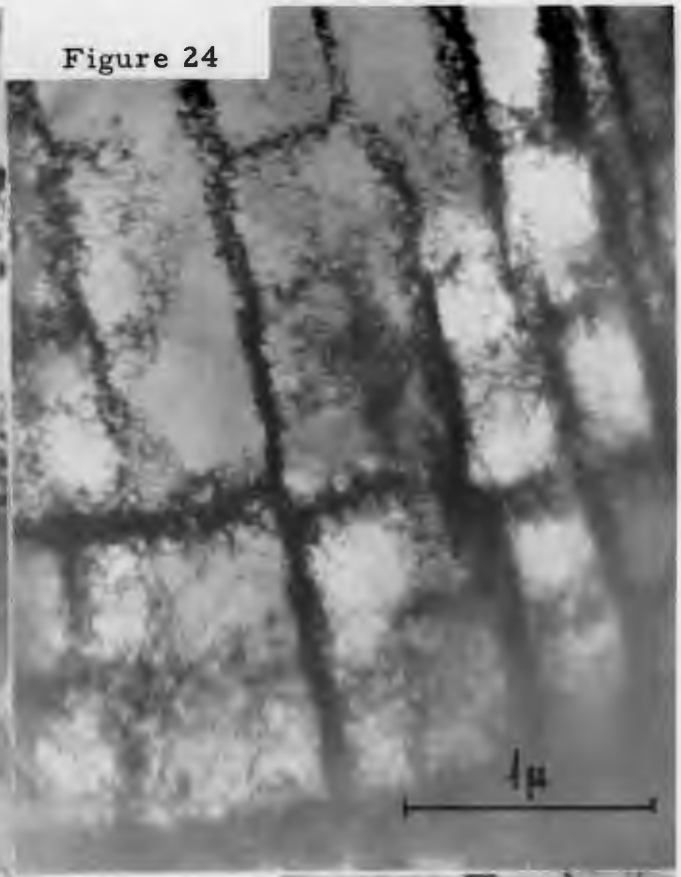


Figure 25

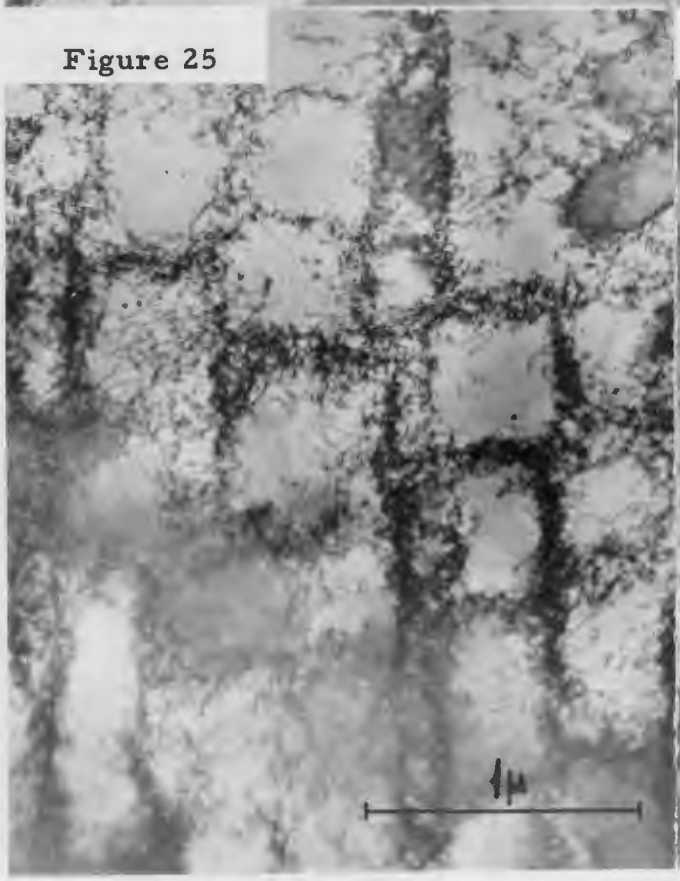


Figure 26

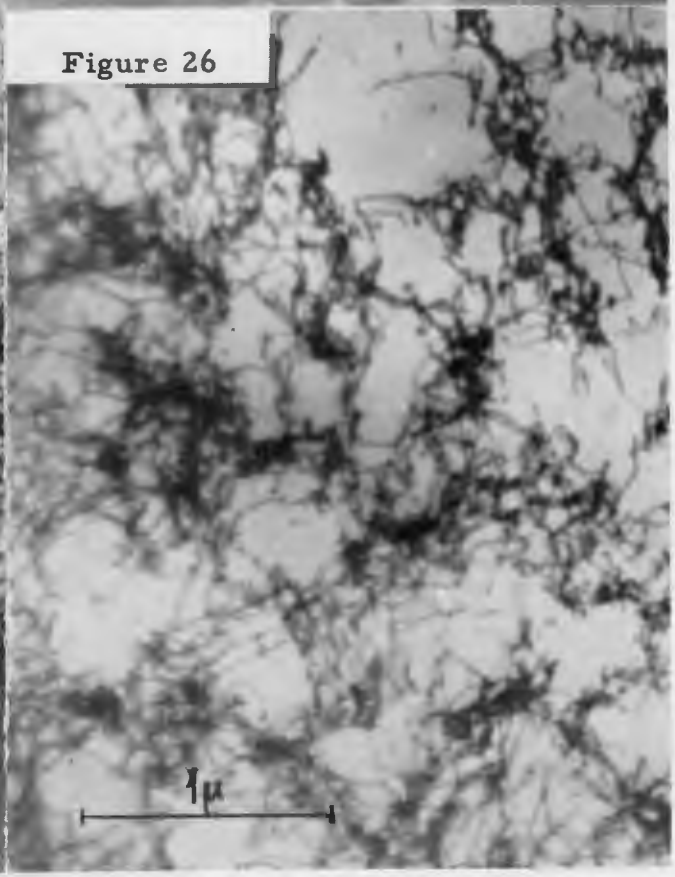


Figure 27

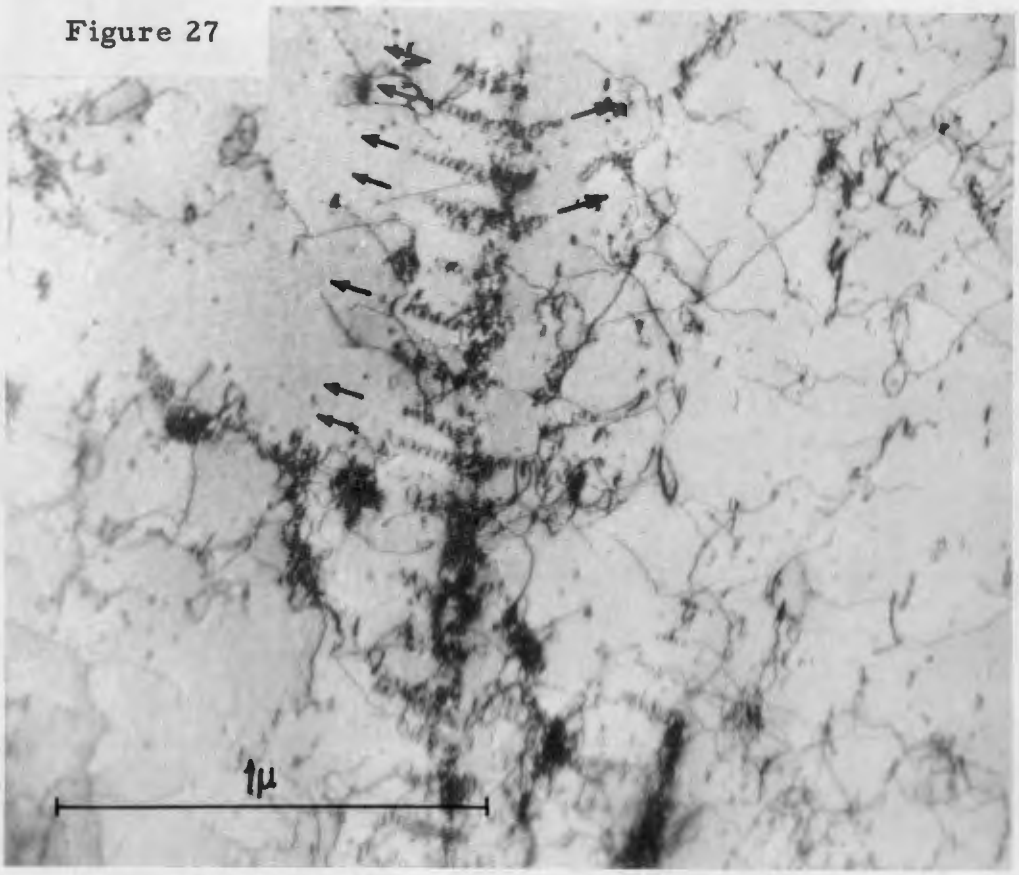


Figure 28

Figure 29

Figure 30

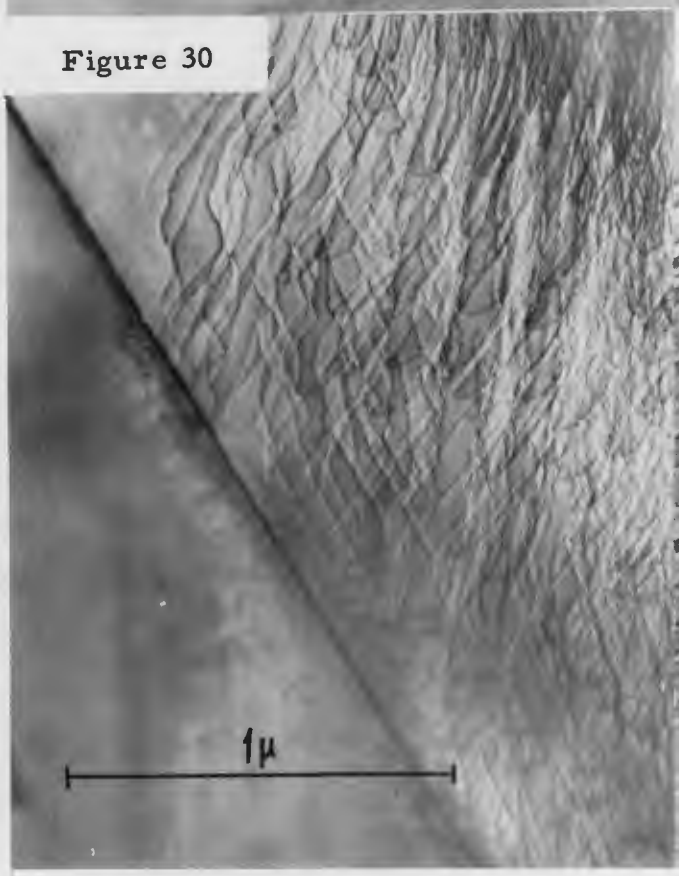


Figure 31

Figure 32

Figure 33

Figure 34

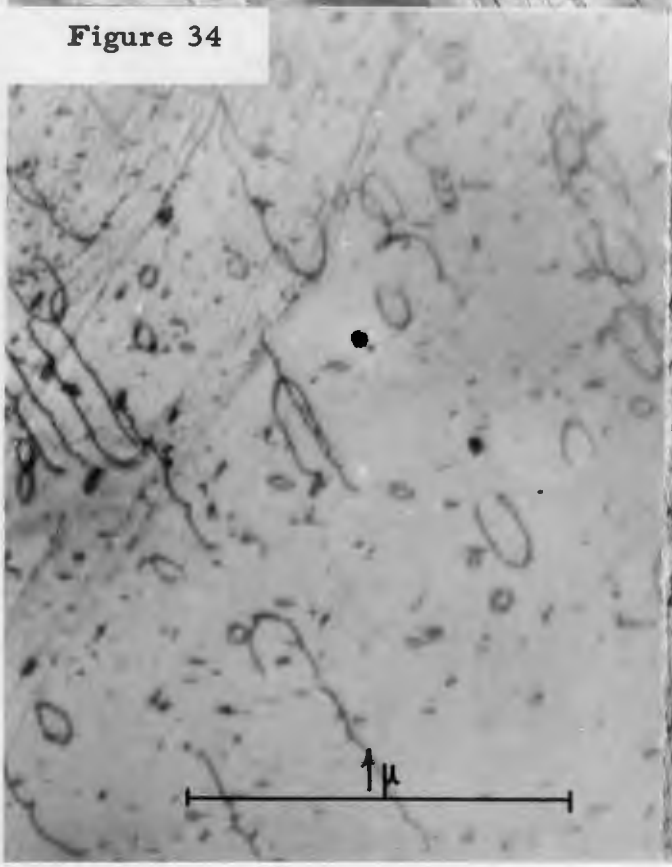


Figure 35

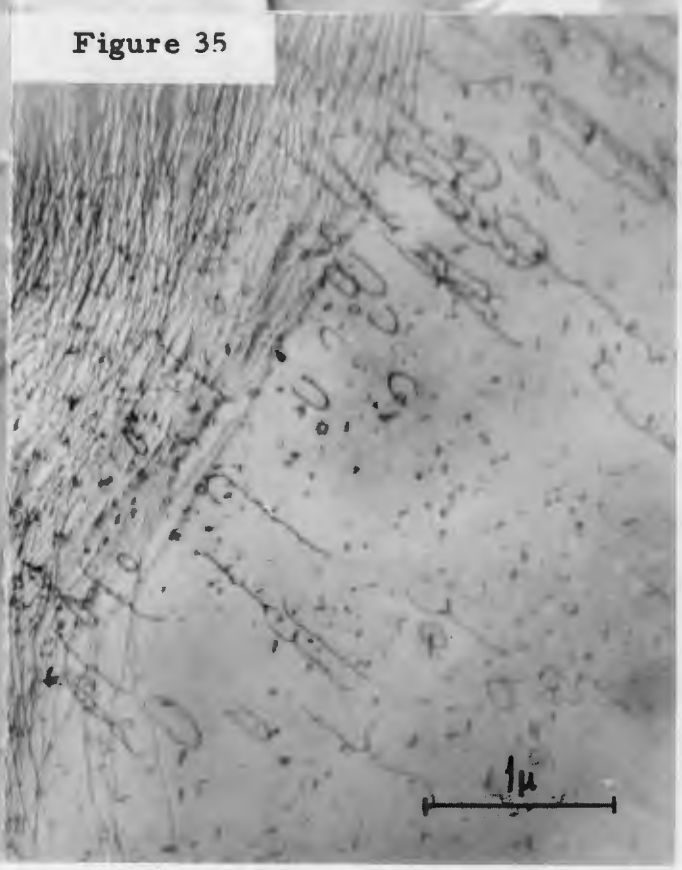


Figure 36

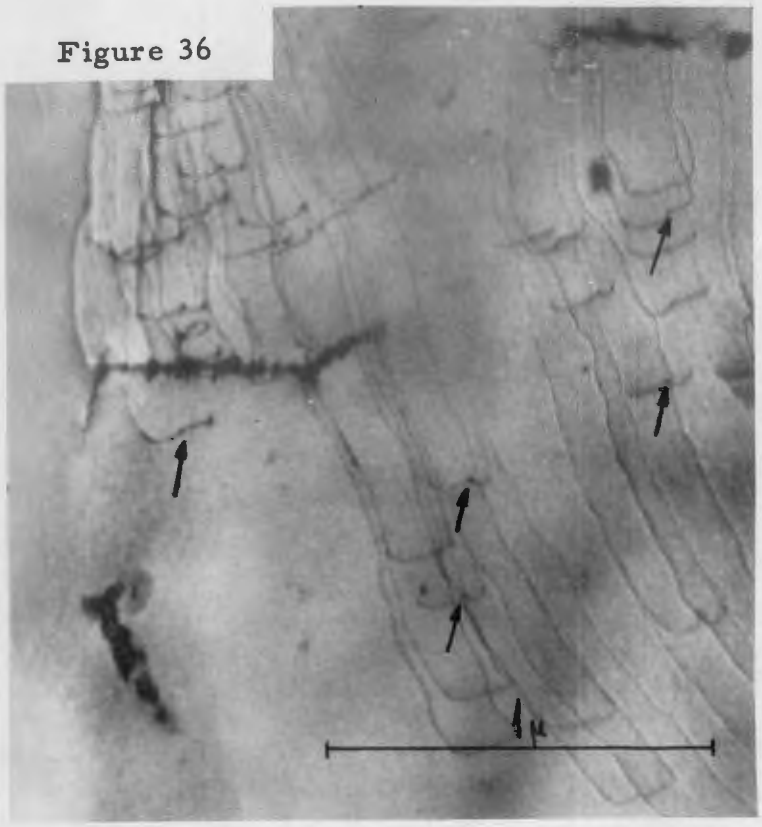


Figure 37

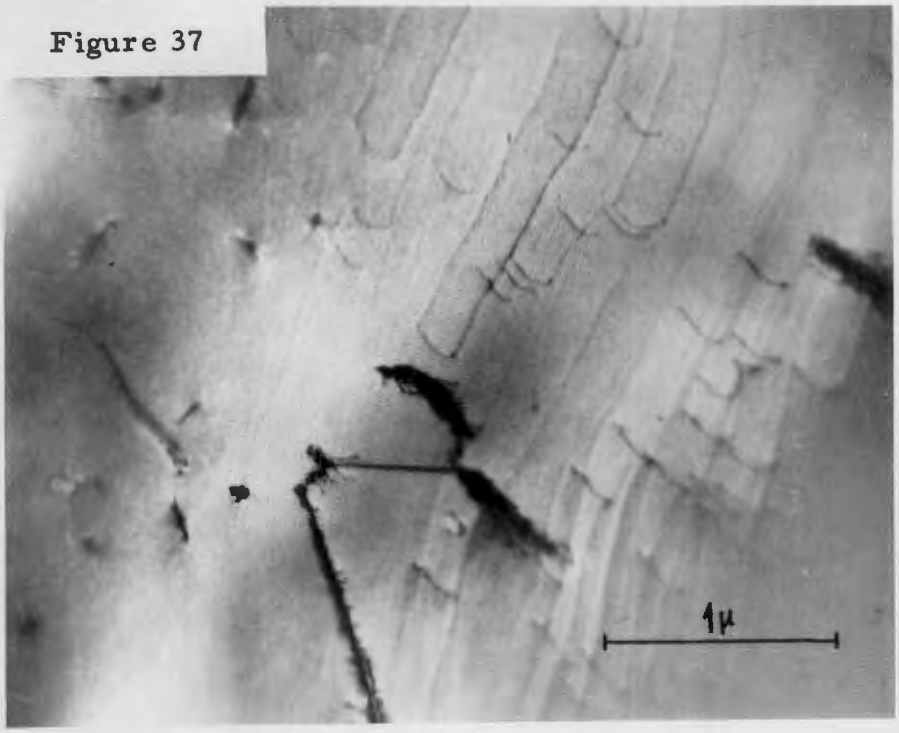


Figure 38

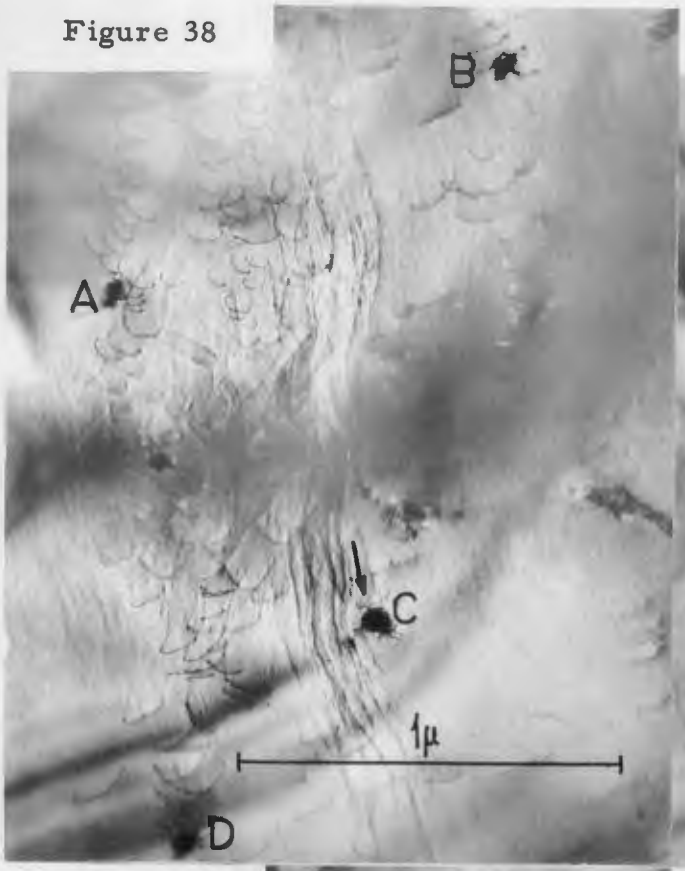


Figure 39

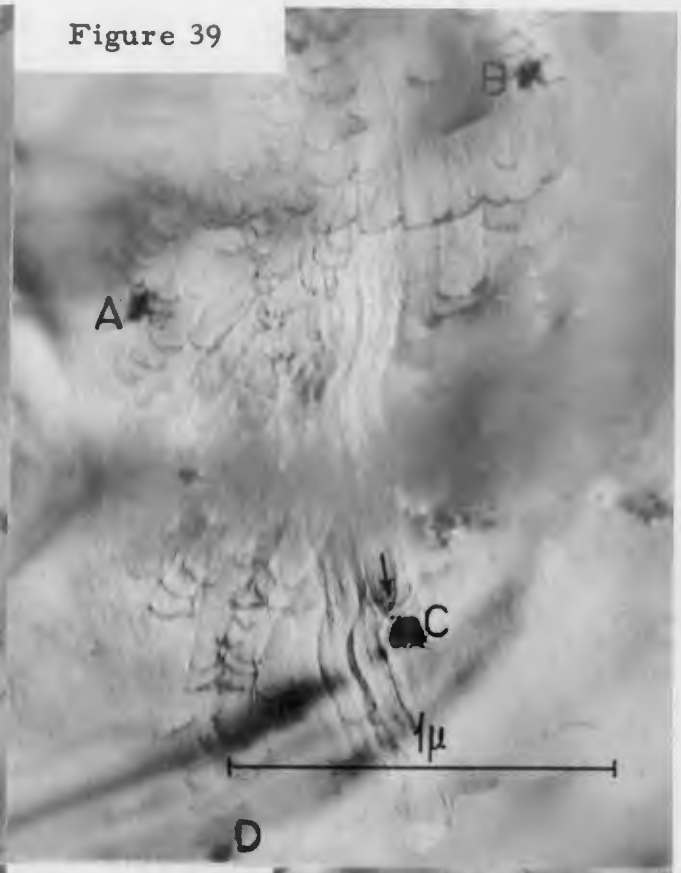


Figure 40

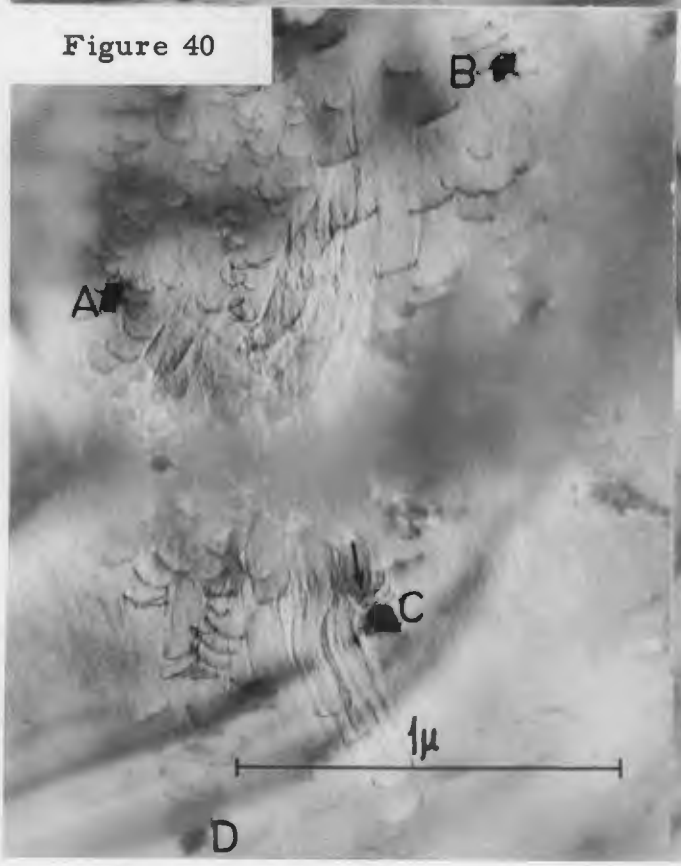


Figure 41

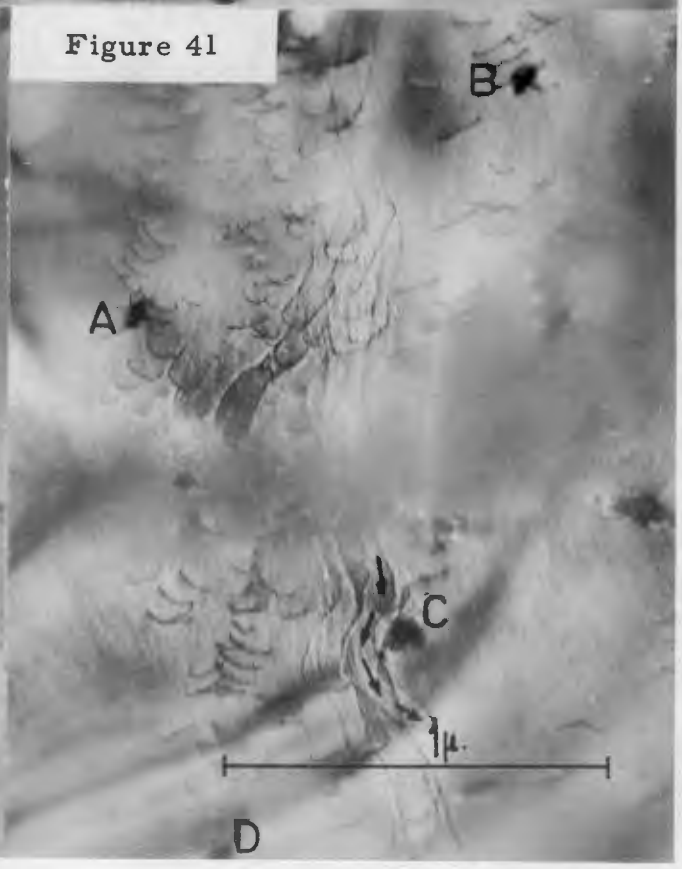


Figure 42

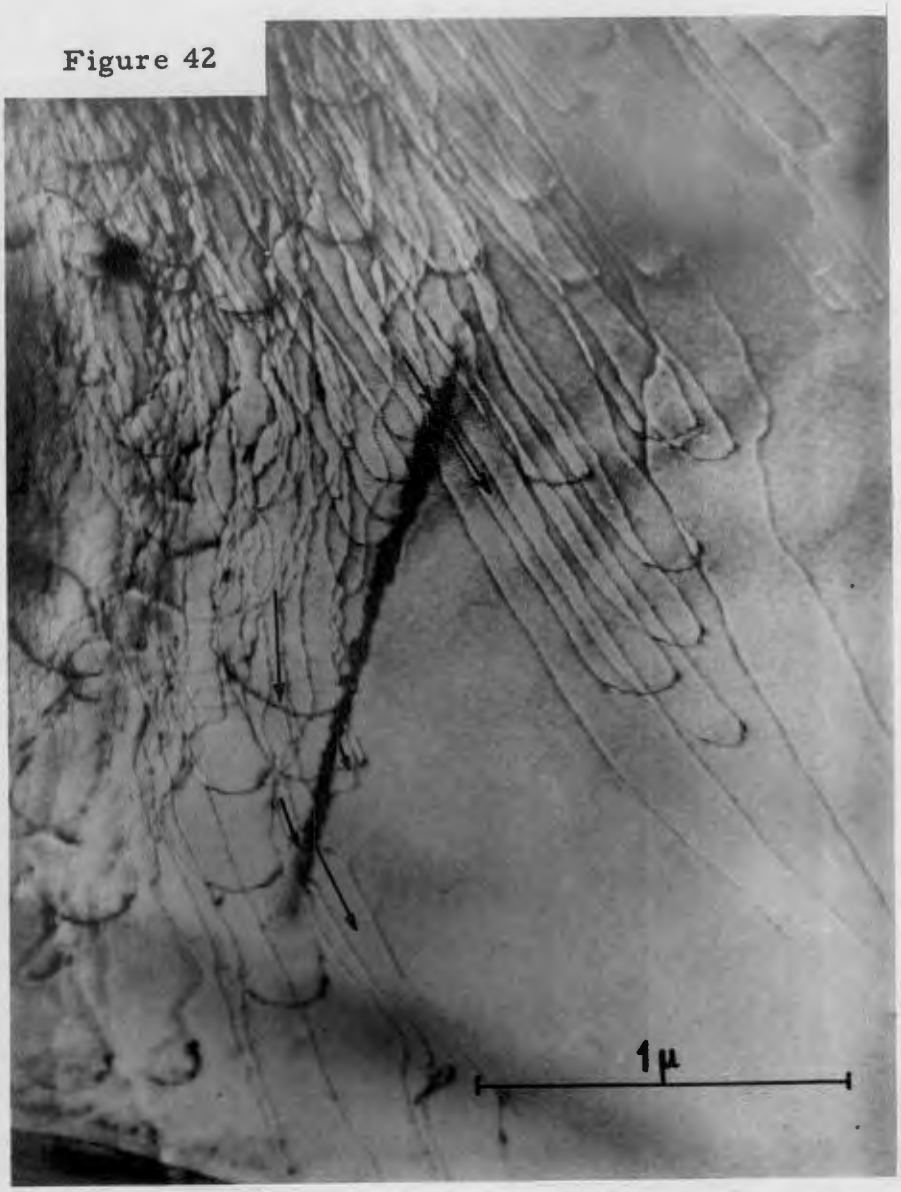


Figure 43

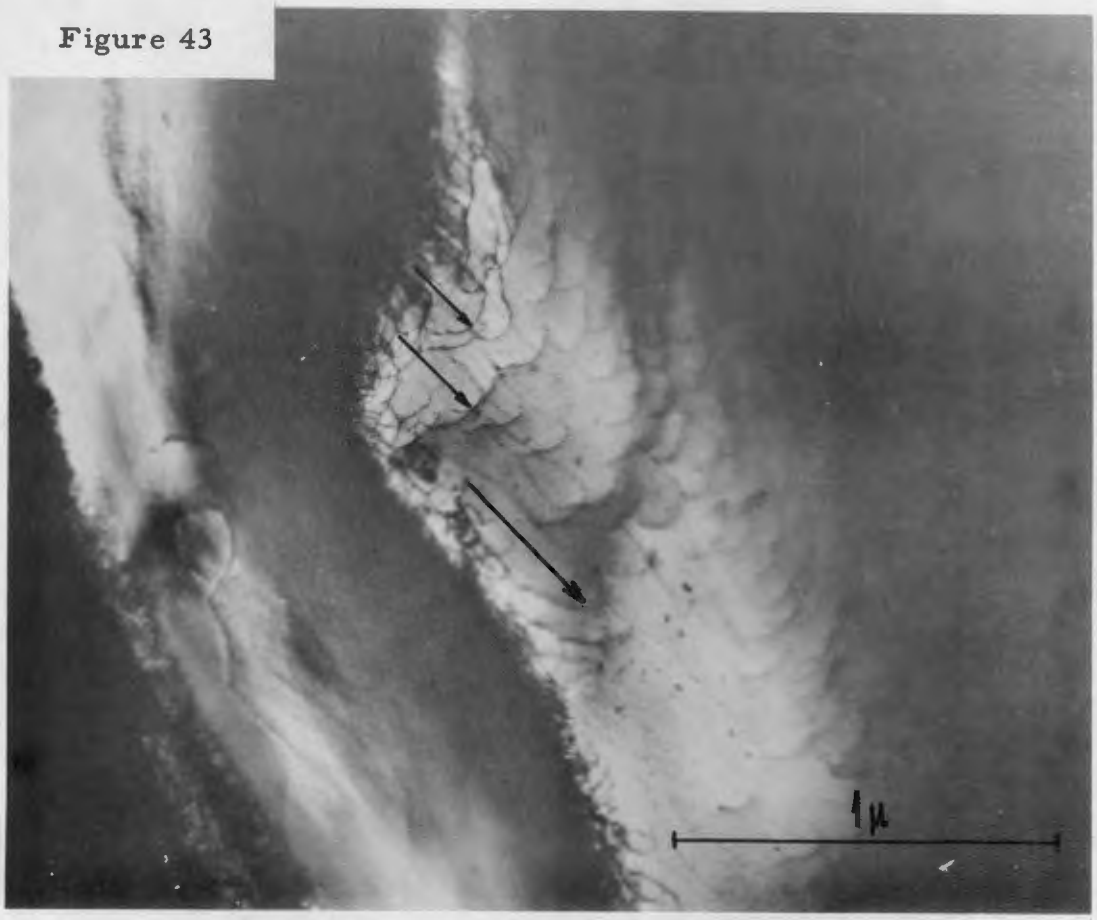


Figure 44

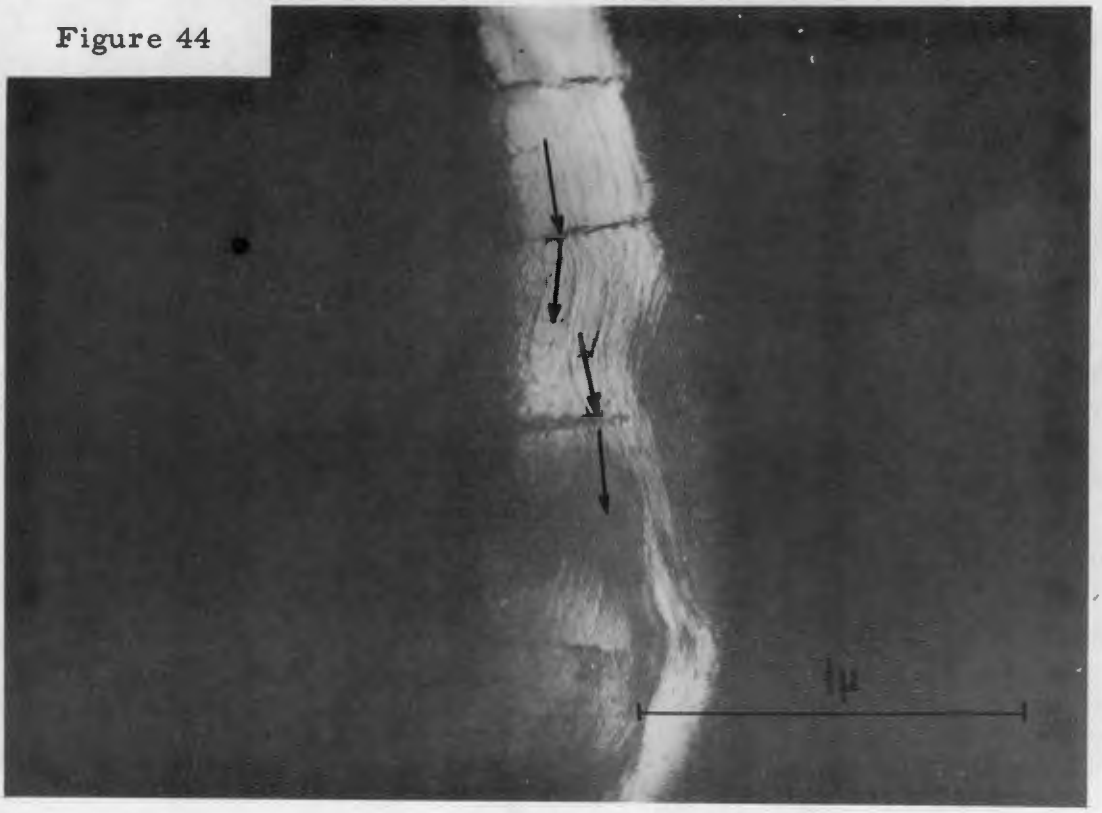


Figure 45

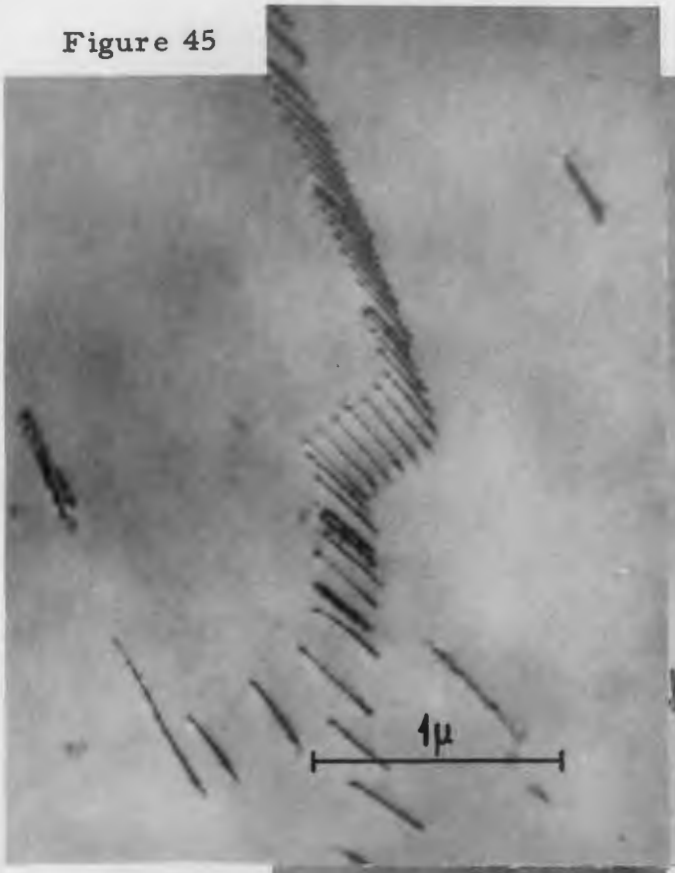


Figure 46

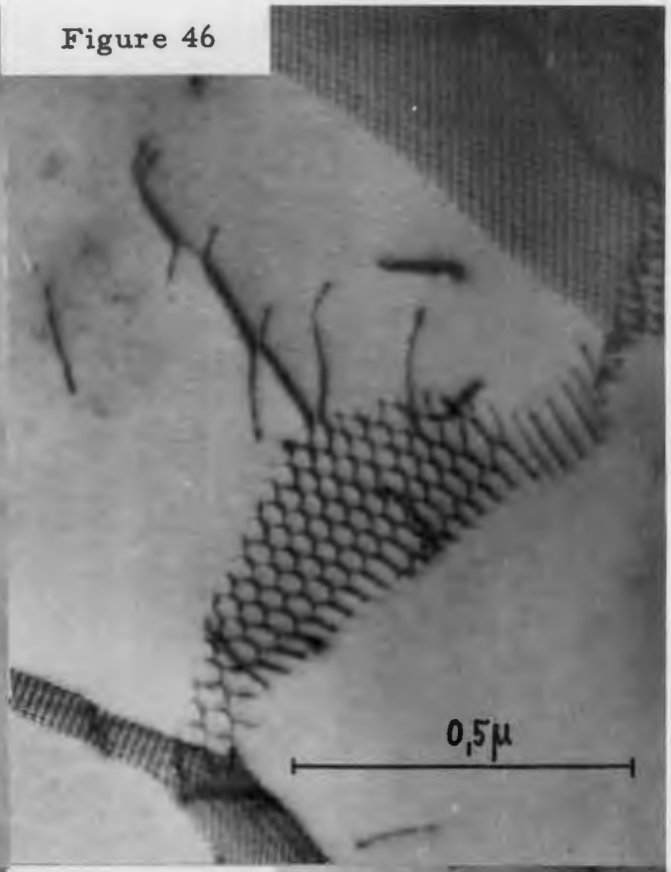


Figure 47

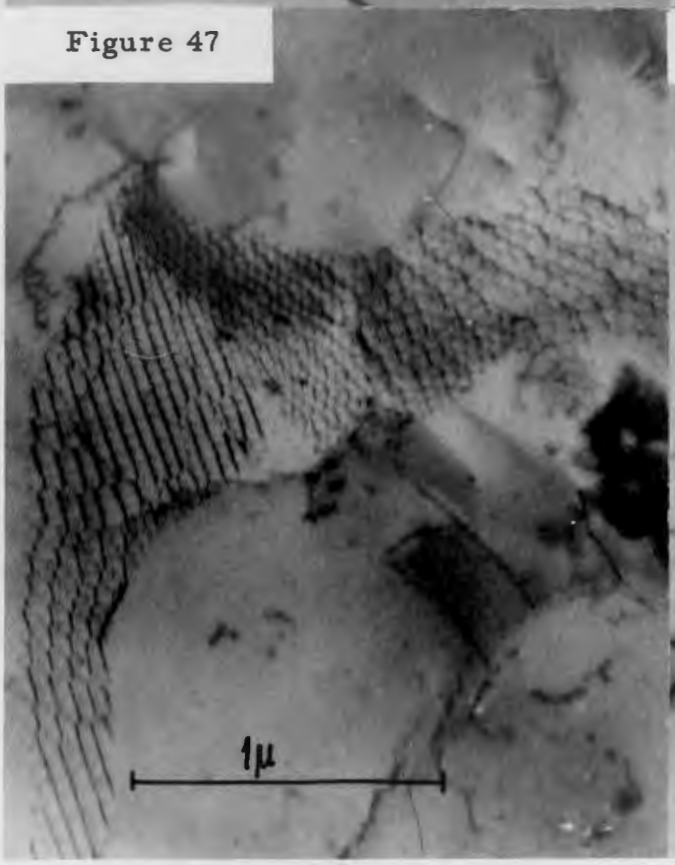


Figure 48

Figure 49

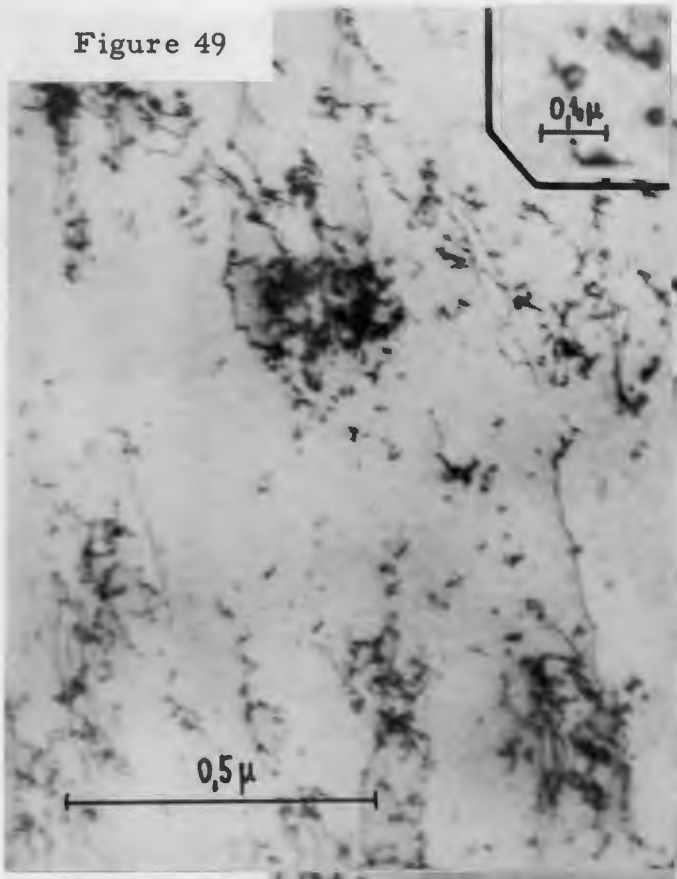


Figure 50

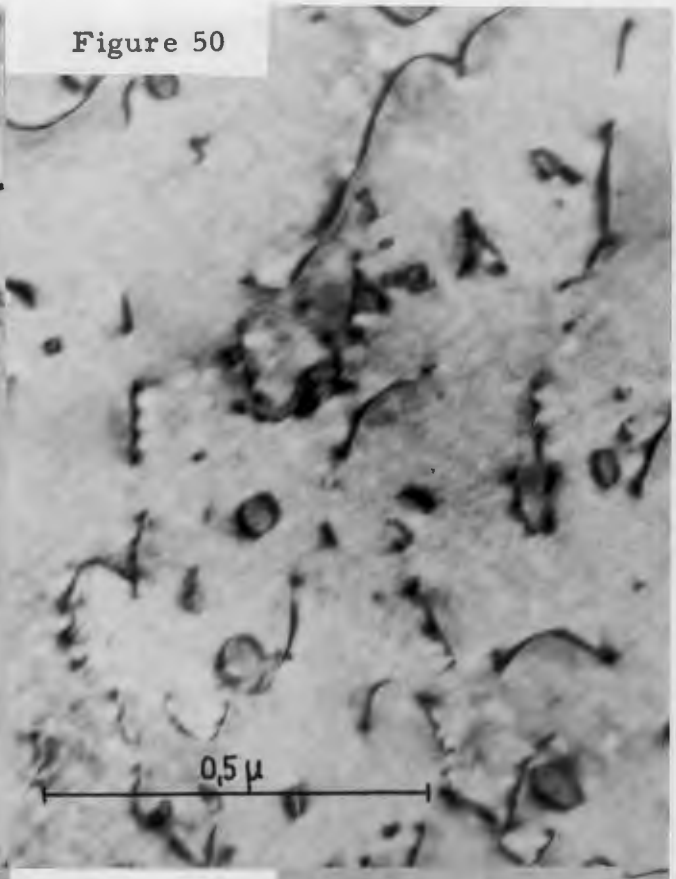


Figure 51

Figure 52

Figure 53

Figure 54

Figure 55

Figure 56

Figure 57

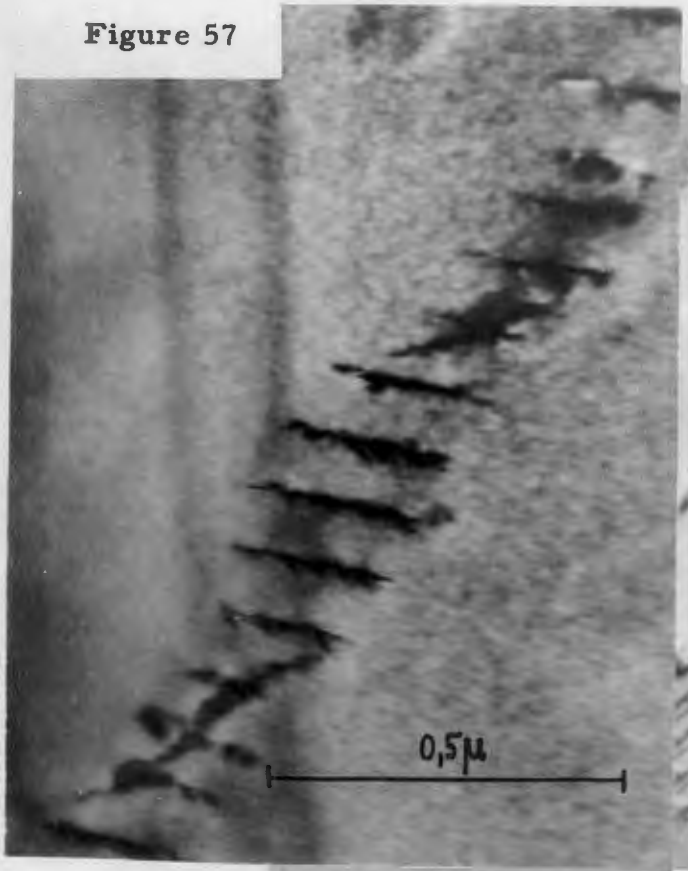


Figure 58

Figure 59

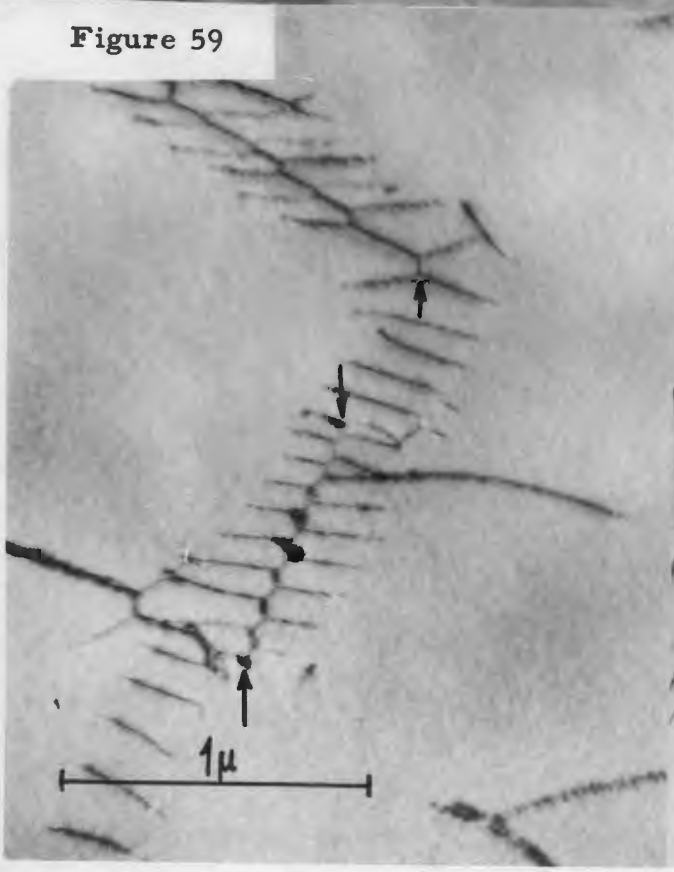


Figure 60

Figure 61

Figure 62

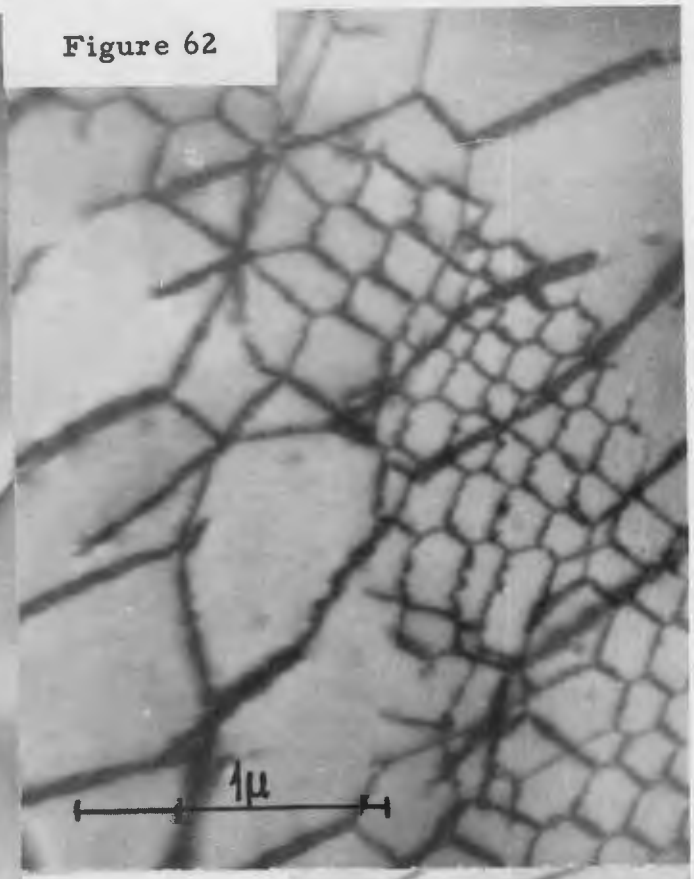


Figure 63

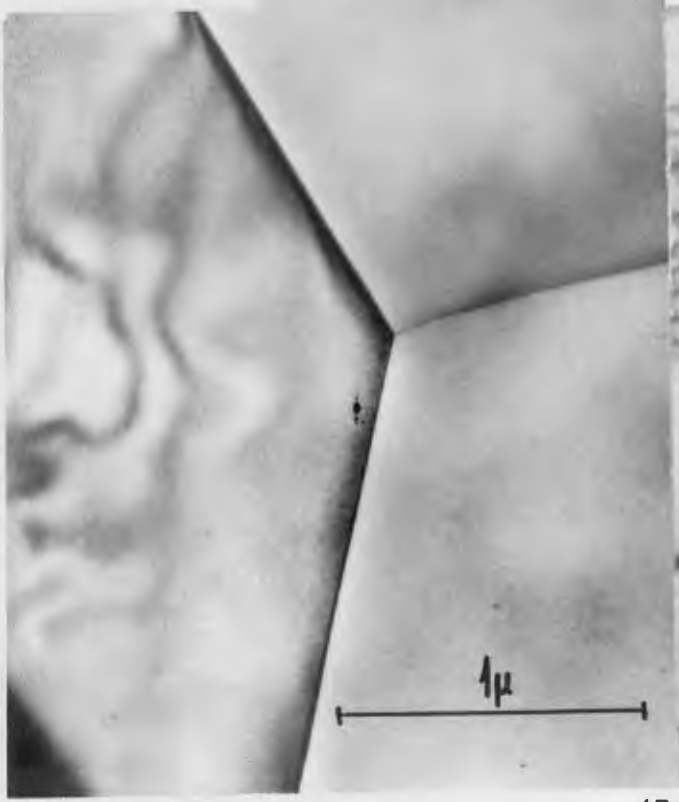
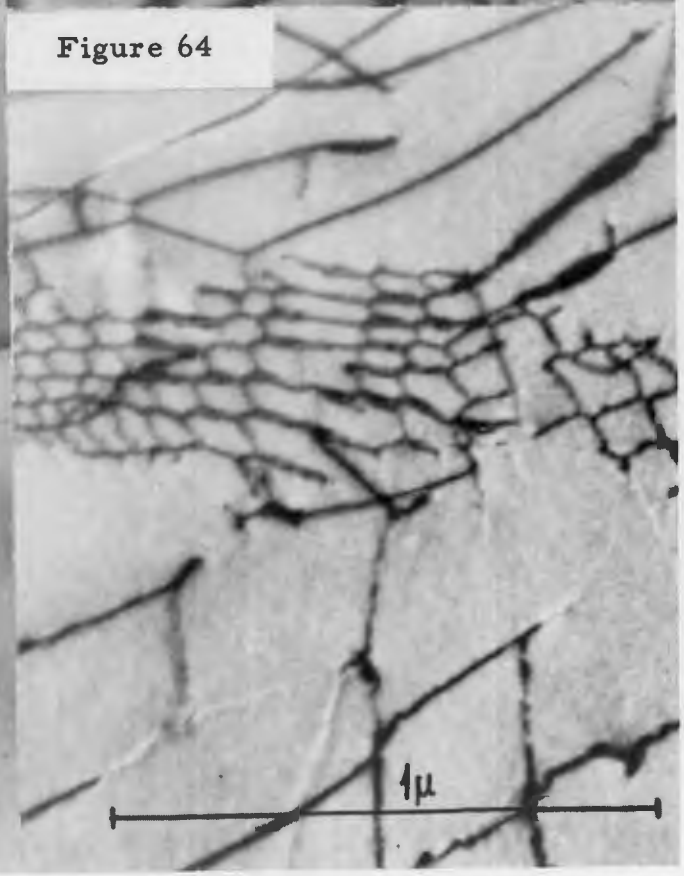


Figure 64



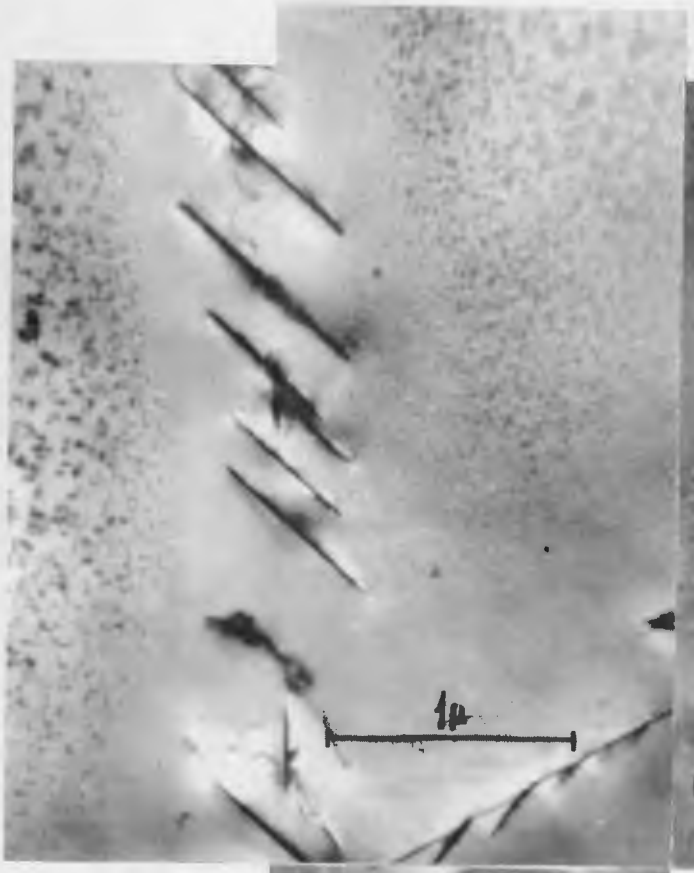


Figure 66

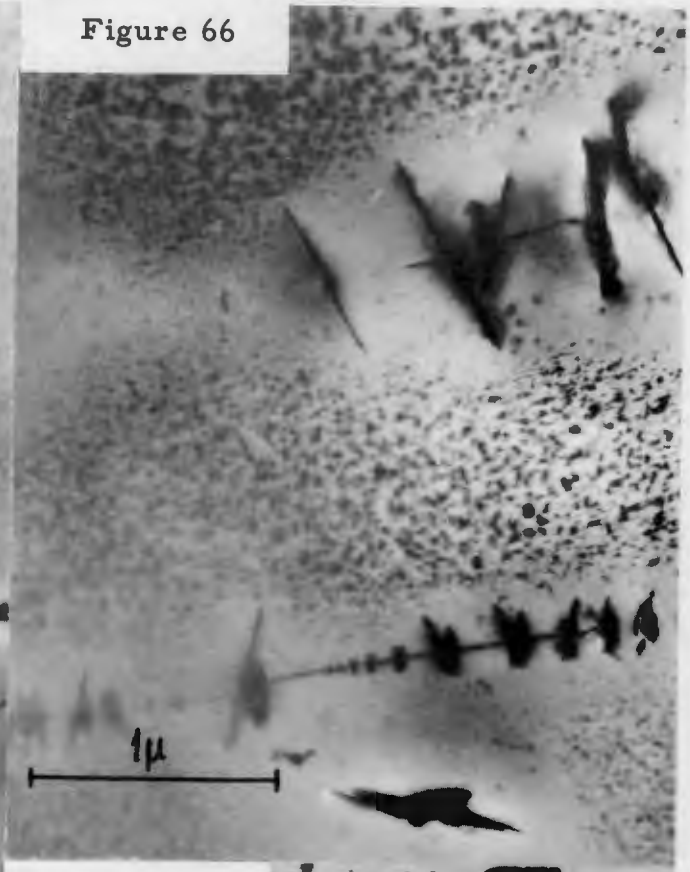


Figure 67

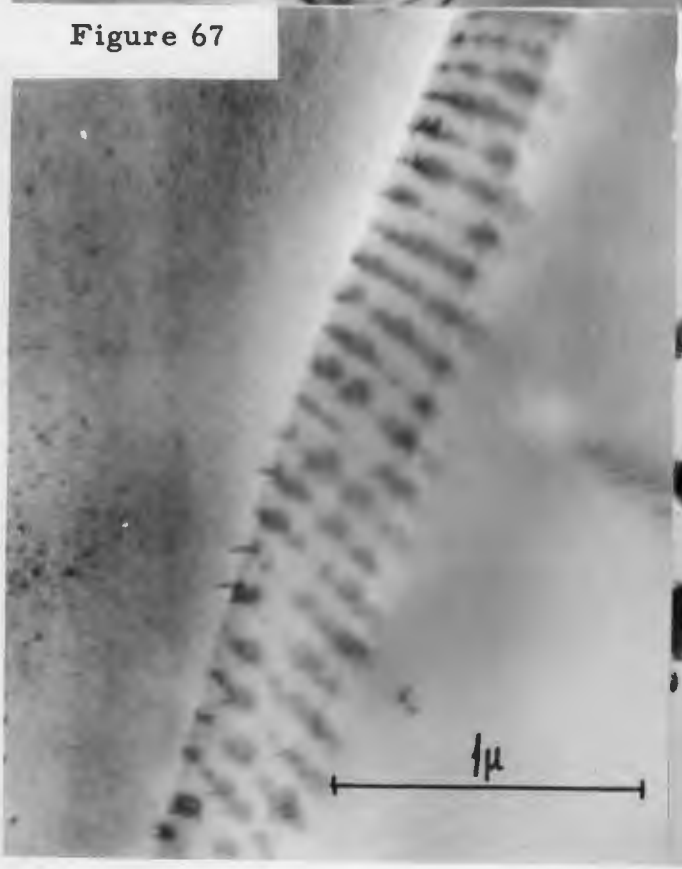


Figure 68

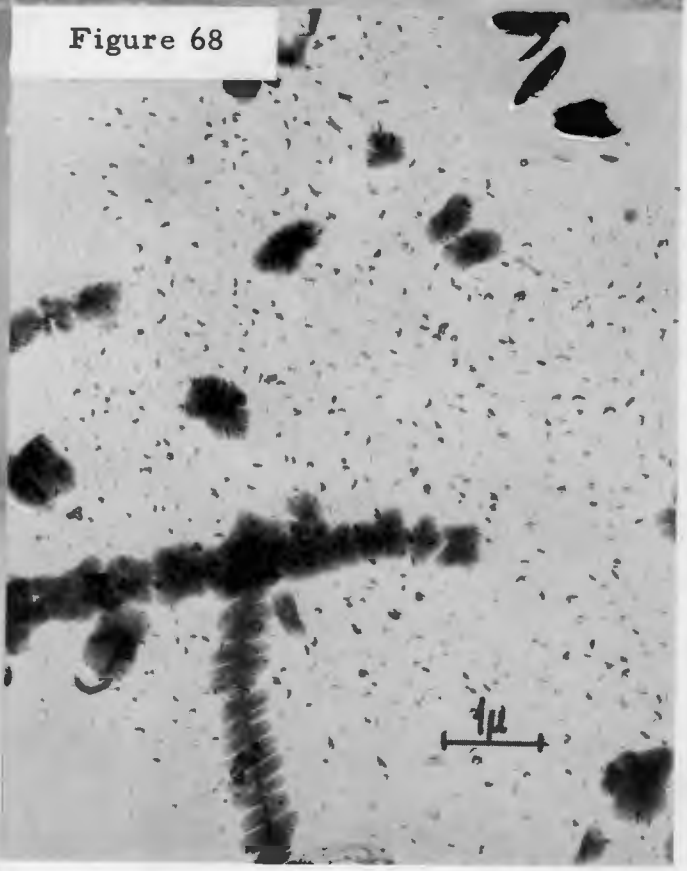


Figure 69

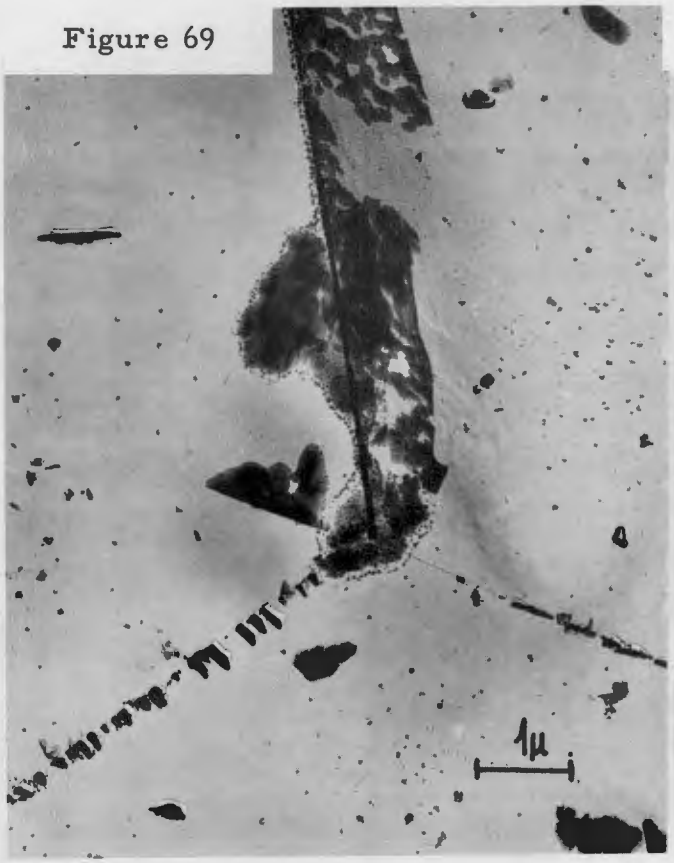


Figure 70