12 September 1958, Volume 128, Number 3324 SCIENCE

CURRENT PROBLEMS IN RESEARCH

Growth and Properties of "Whiskers"

Further research is needed to show why crystal filaments are many times as strong as large crystals.

S. S. Brenner

The one outstanding characteristic of most single crystals is their weakness. Refining earlier estimates, Mackenzie (*1*) arrived at the conclusion that the shear strength of a crystal should at least be 3 percent of its shear modulus (μ). In practice, crystals usually deform plastically when stressed less than 10^{-4} μ.

In 1952 Galt and Herring (*2*) demonstrated that at least some crystals possess the strength predicted by theory. These crystals were tiny filaments of tin (Fig. 1), about 2 microns in diameter and a few millimeters in length, that had been discovered several years earlier (*3*) and descriptively termed "whiskers." Although filamentary crystals have been the subject of numerous philosophical and scientific discussions during the last 200 years, this was the first time that it was recognized that they possess unusual properties. A large number of publications have appeared since 1952 dealing both with the properties and growth of whiskers. The results of most of these investigations have been interpreted in terms of the dislocation theory, which has been so widely applied in metallurgy and solid-state physics. Since whisker research has already made a significant contribution in the field of crystal growth and strength of solids, and since whiskers will undoubtedly be of continuing interest for a number of years, it is felt that a review of our knowledge of their growth and properties is appropriate at this time. Hardy (*4*) has described extensively the early work concerned with the filamentary growth of crystals, and hence greater emphasis will be placed in the following pages on the more recent work.

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Growth of Whiskers

Most of the early discussions on the filamentary habit of crystal growth were concerned with the naturally occurring growth of silver and copper filaments (*Haarsilber* and *Haarkupfer*) on silver and copper ores containing sulfur. These filaments, which sometimes are as long as 15 centimeters, were at one time considered to represent a transition from vegetable to mineral. During the latter part of the 18th century it was demonstrated that they can be produced synthetically by reducing or oxidizing silver and copper sulfide. The experimental results and theoretical interpretations of the growth of these filaments during the last 200 years have been reviewed by Hardy (*4*). The latest interpretation of their growth is that due to Kohlschütter (*5*) and Wagner (*6*), who postulated that the growth of the silver whiskers is caused by the difficulty of nucleating silver particles in silver sulfide when the sulfur is removed. The silver ions and electrons migrate freely in the Ag_2S until they meet a silver nucleus on which they condense. If this nucleus is on the surface, it can be pushed out into the form of a whisker as reduced silver is added at its base.

Several other techniques of whisker growth have been discovered or developed in recent times. Generally, the driving force for the growth of the crystals has either been a decrease in internal or applied stress (recrystallization process) or a decrease in supersaturation (condensation, precipitation, electrodeposition, and so on).

Stress-Induced Whisker Growth

The tin whiskers tested by Galt and Herring were found to grow spontaneously from tin-plated steel at a rate of about 10^{-8} centimeters per second. Compton, Mendizza, and Arnold have made an extensive study of their growth (*7*). By applying pressure to the electroplated coating, Fisher, Darken, and Carrol (*8*) were able to accelerate the growth rate as much as 10,000 times. The growth rate is proportional to the applied pressure; this indicates that the driving force for the growth is the relaxation of the strain within the metal. Franks (*9*) has postulated that whiskers will develop on the free surface of any compressed or internally strained metal if general extrusion is inhibited and if the temperature is sufficiently high for diffusion to be reasonably rapid.

Several mechanisms for the growth of whiskers from the solid phase have been postulated (*9–11*). They all essentially involve the motion of dislocation loops out of the substrate. The initial loop, breaking through the surface, leaves a closed step 1 atomic unit high on the surface, and each successive loop increases the step height by one more atomic unit. The mechanisms differ in the details of the generation of the loops and their motion towards the surface.

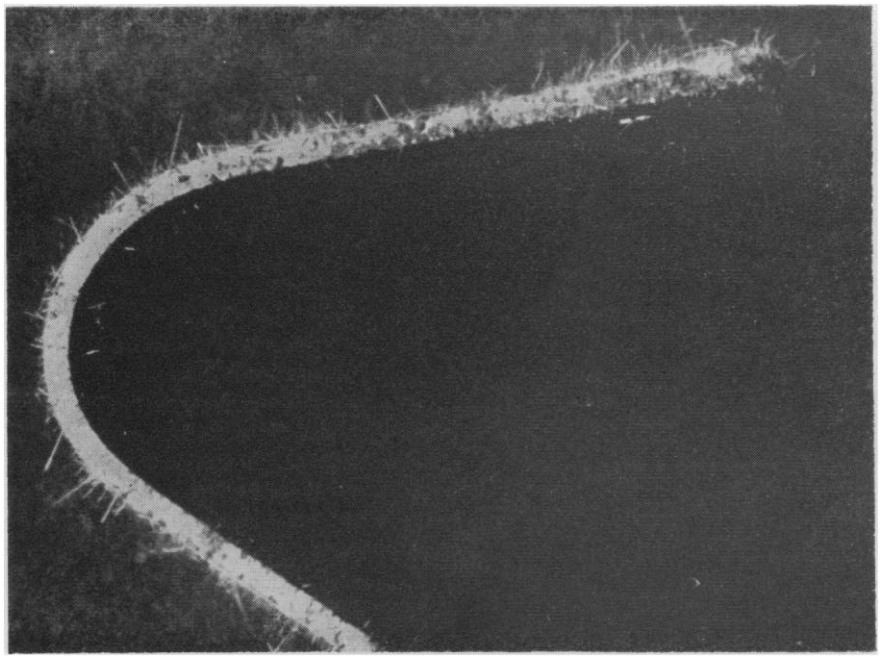


Fig. 1. Whiskers on tin-plated steel. [Compton, Mendizza, and Arnold]

However, they all imply that the whiskers, after growth, either contain no dislocations or at least only a single axial one.

Growth from a Supersaturated Medium; Vapor Deposition

Crystal growth from a supersaturated medium, especially a vapor, has frequently been investigated, both theoretically and experimentally (*12, 13*). It has been recognized that at small supersaturations a molecule or atom from the vapor phase can condense only at a ledge or step on the surfaces of the growing crystal. The classical theory of crystal growth considers a crystal to be structurally perfect and assumes that each time a step on the crystal sweeps over the surface, a new one has to be nucleated on the freshly completed crystal layer (Fig. 2). Since the creation of a step on the surface increases the surface energy of the crystal, a critical supersaturation is required for continued growth. In practice, however, it was found (*13*) that crystals grow at supersaturations which are immeasurably small. Frank, therefore, concluded (*14*) that real crystals are not perfect but contain screw dislocations (Fig. 3) which developed during the early stages of their growth and which provide the crystals with permanent growth steps. As material condenses, the step due to the dislocation winds itself into the form of a spiral because of the greater angular velocity of the step near its emergence. The observation of growth spirals on numerous crystals (*15*) (Fig. 4) provided evidence that Frank's dislocation mechanism of crystal growth is applicable in many cases.

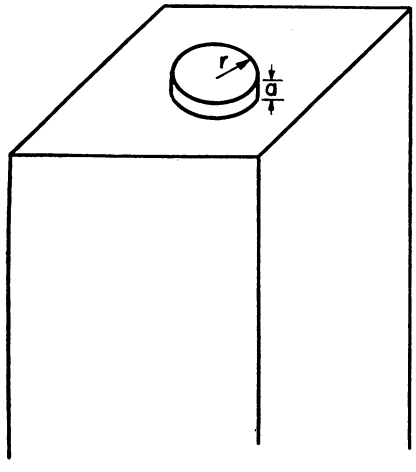


Fig. 2. Nucleation of new crystal layer. Surface energy of crystal increases by $2\pi r a \gamma$ where γ = surface energy.

Volmer and Esterman (*16*) in 1925 found that under certain conditions crystals can grow faster in some directions than in others. They observed that sometimes mercury condenses in the form of thin platelets, with growth occurring many times faster at the crystal edges than at the basal faces. Sears (*17*) extended the work of Volmer and Esterman and found not only platelets but also whiskers. He reported that the shape of the condensed crystals depends on the supersaturation, with three-dimensional massive crystals growing at the highest supersaturations and one-dimensional whiskers at the lowest.

Applying Frank's dislocation theory of crystal growth, Sears (*18*) postulated that the anisotropic growth rate of mercury crystals is due to the absence of dislocations in certain crystal directions. With respect to the whisker habit he proposed that the crystal contains a single dislocation along the center of the crystal, with the lateral crystal surfaces bounded by surfaces which are atomically smooth. The criterion for whisker growth according to this hypothesis is that (i) the whisker embryo contains screw dislocations parallel to only one crystal direction and (ii) during growth the supersaturation of the vapor is less than that required for the nucleation of crystal layers on the lateral surfaces of the crystal. Sears (*19*) has demonstrated that the second requirement is met for the growth of mercury, silver, zinc, cadmium, and cadmium sulfide whiskers from their pure vapor. The first criterion—that the screw dislocations in whiskers, if there are any, are oriented parallel to the whisker axis—has as yet not been demonstrated.

Whisker Growth by Reduction of Halides

A large number of metals can be grown in the form of whiskers by the reduction of halides at elevated temperatures (*5, 20–22*). The method is simple and reproducible. A boat is filled with the halide—for instance, ferrous bromide—and is pushed into a hot furnace through which hydrogen is flowing. During the period of a few hours, filaments, some several centimeters long

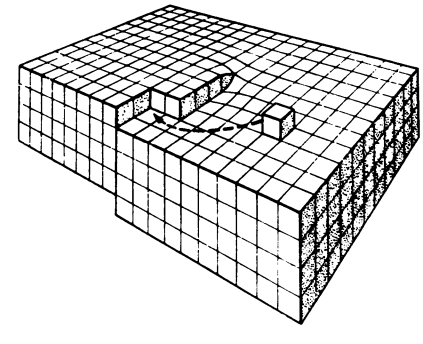


Fig. 3. Screw dislocation intersecting crystal surface, providing crystal with a permanent growth step.

and 1 to 500 microns thick, grow on the sides of the boat. Figure 5 shows some iron whiskers grown by this method.

There are two different mechanisms of growth of these whiskers. Some of the whiskers, notably silver obtained from AgCl, grow at their base (*22*), and hence a mechanism such as that proposed by Wagner and Kohlschütter for the growth of whiskers from sulfides must apply here. In contrast, copper and iron whiskers grow at their tip, and a vapor transport mechanism is most probable. However, experimental results (*22*) and thermodynamic considerations (*23*) indicate that growth does not occur by the direct condensation of metal vapor, and it is most likely that the halide molecules are adsorbed on the growing whiskers and preferentially reduced at the tip. At present the reason for the greater rate of reduction at the tip is not clear. Sears (*24*), extending his whisker growth hypothesis, suggested that these whiskers also contain only axial dislocations. If this is the case, the preferential reduction at the tip may be due to the catalytic reduction of the halide at the step associated with the dislocation. Price, Vermilyea, and Webb (*25*) have suggested for the electrolytic growth of whiskers a mechanism which does not rely on any particular dislocation arrangement and which may be applicable to other methods of whisker growth. They propose that while the lateral surfaces of the whiskers become covered with adsorbed impurities and thus become poisoned, the tip may remain clean because of its rapid rate of advancement.

It is well known that adsorbates have an important influence on crystal growth and crystal habit, and undoubtedly impurity adsorption plays a significant role in whisker growth.

Growth of Whiskers by Precipitation

The precipitation of salts in needle-shaped crystals is not uncommon. The *Handbook of Chemistry and Physics* gives many examples of such crystals, both organic and inorganic. In most cases there probably is no real distinction between whiskers and needles except one of size. With whiskers we usually associate diameters of less than 25 microns. Many of the needle crystals go through a whisker stage during the early part of their growth. This was clearly illustrated by Gordon (*26*) for the precipitation of $MgSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 7H_2O$, quinone, resorcinol, and so on. The precipitated crystal is at first in the form of a fine whisker, which thickens as it weaves through the solution.

The growth of alkali-halide whiskers from aqueous solutions has received particular attention (*27–29*). The solutions are supersaturated either by slowly evaporating the water or by changing the temperature. An interesting method shown in Fig. 6 is that attributable to Amelinckx (*29*). A cellophane bag filled with the alkali halide solution is held suspended for a day or two. During this time the solution permeates the cellophane and, as the water evaporates, leaves a crop of whiskers and other crystals on the outside of the bag.

Dislocation mechanisms have also been applied to the growth of whiskers by precipitation. Sears (*30*) has proposed with respect to the growth of $NaClO_3$ whiskers that the solution migrates along the sides of the whiskers by hydrodynamic flow and the solute is precipitated at the dislocation emerging from the tip. Amelinckx reports that whisker growth on cellophane occurs through the addition of material at the base and proposes that the rate of growth depends on how fast the solution can feed the capillary layer separating the cellophane and the whisker base.

The role of impurities in the growth of whiskers has been found to be signifi-

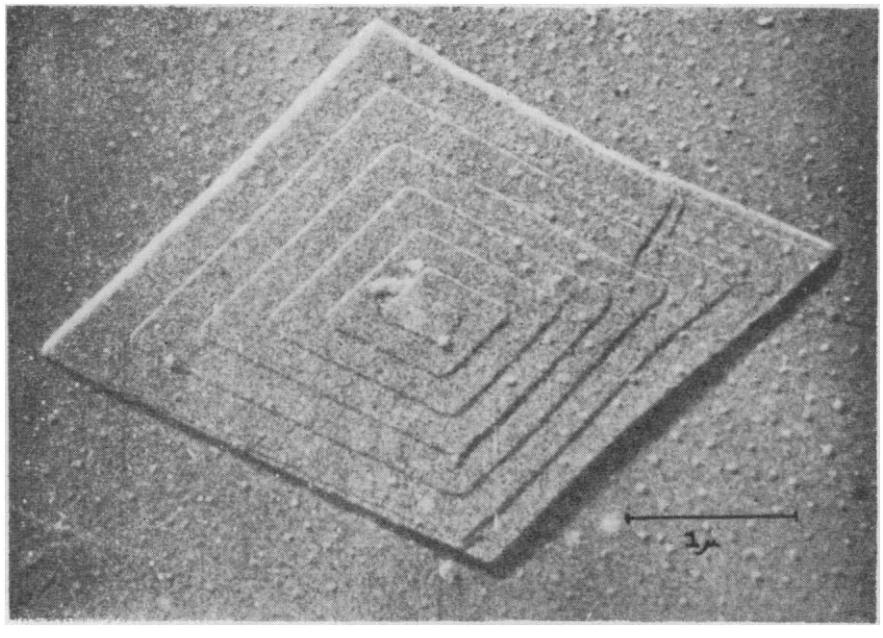


Fig. 4. Growth spiral on paraffin $n - C_{36}H_{74}$. [Verma]

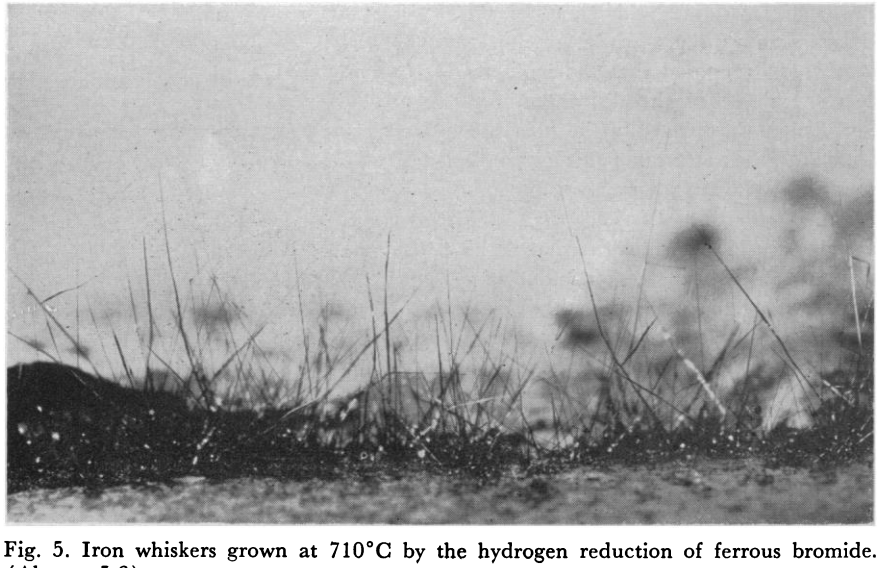
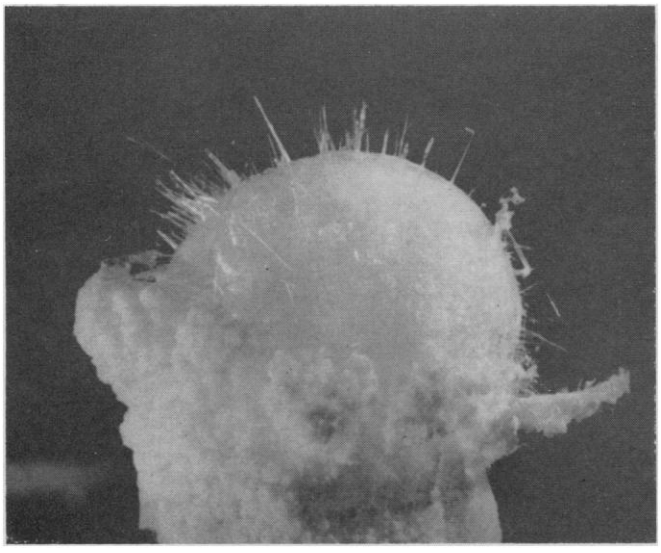


Fig. 5. Iron whiskers grown at 710°C by the hydrogen reduction of ferrous bromide. (About × 5.6)



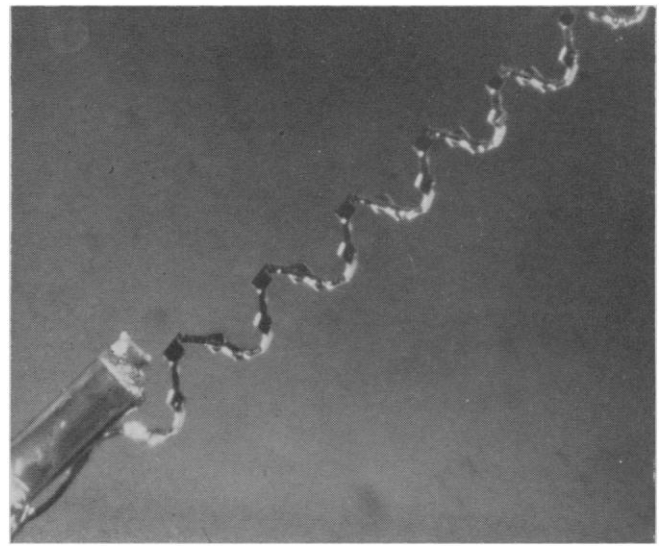


Fig. 6 (Left). Growth of NaCl whiskers on cellophane bag. (About × 1.5). Fig. 7 (Right). Helical copper whisker.

cant. Addition of polyvinyl alcohol or sucrose (*31*) increases the number and length of NaCl whiskers, while addition of a few parts per million of iron salts influences the growth of LiF whiskers (*32*).

Shape, Orientation, and Purity of Whiskers

While most of the whiskers are straight, an amazing variety of shapes frequently occurs in the same batch. Polygonal spirals (*33*), kinks (*34*), twists (*21*), helices (*21*), and many other shapes have frequently been observed. Of considerable interest are the helical whiskers, an example of which is shown in Fig. 7. Little effort has been made to determine the mechanism of growth of these complex shapes. Twinning (*33*) has been associated with some of the kinks in tin whiskers, while Amelinckx *et al.* (*11*) proposed that the kinks reflect the shape of the dislocation network below the surface of the substrate. Sears (*30*) has associated the low-angle bends in $NaClO_3$ with impurity precipitation. Webb and Forgeng (*35*) and Amelinckx (*36*) have suggested that the shape of the helical whisker is due to a precession of the axial growth dislocation. However, since it has not been firmly established that a single axial dislocation is responsible for the growth of even the simplest whiskers, it is somewhat premature to discuss its possible precession.

While many whiskers have simple polygonal or round cross sections (*37*), others are complex in shape. Star-shaped (*38*) and hollow (*35*) cross sections have been reported. An outstanding feature of many whiskers, especially of those that are strong, is the optical perfection of their surfaces. The surfaces of some are smooth at magnifications as high as 40,000.

Most whiskers, including those which are kinked (*39*) and helical (*22*), are single crystals. The axis of the whisker is frequently parallel to a major crystallographic direction. Some whiskers, such as silver from silver sulfide, are polycrystalline with a preferred orientation (*40*).

The purity of whiskers is not exceptionally high. The average impurity content as determined by chemical analyses is about 3×10^{-5} for copper whiskers grown from CuI and 10^{-4} for iron whiskers grown from $FeBr_2$. The lowest residual resistivity measurements obtained thus far indicate about 10^{-4} impurities for zinc (*41*) and copper (*42*).

Mechanical Behavior of Whiskers

The strengths of a large number of whiskers prepared by a variety of methods have been measured, either by means of bend tests or tensile tests. The maximum values are summarized in Table 1. In all cases the maximum elastic strain at the yield point was at least 0.01. In comparison, annealed single crystals usually yield at elastic strains of less than 10^{-4}. The ultimate tensile strengths

Table 1. Strength of whiskers.

Material	Max. elastic strain (%)	Method of testing	Method of growth	Reference
Fe	4.9	Tension	Halide reduction	(*43*)
Cu	2.8	Tension	Halide reduction	(*43*)
Ag	4.0	Tension	Halide reduction	(*43*)
Ni	1.8	Tension	Halide reduction	(*43*)
Si	2.0	Tension	Halide reduction	(*44, 65*)
Zn	2.0	Tension	Vapor condensation	(*66*)
NaCl	2.6	Tension	Precipitation	(*27*)
SiO_2	5.2	Tension	Vapor condensation	(*47*)
Al_2O_3	3.0	Tension	Vapor condensation	(*47*)
MoO_3	1.0	Tension	Vapor condensation	(*47*)
C	2.0	Tension	Vapor condensation	(*67*)
Sn	2 to 3	Bending	Growth from solid	(*2*)
Ge	1.8	Bending	Halide reduction	(*44*)
ZnO	1.5	Bending		(*44*)
ZnS	1.5	Bending	Vapor condensation	(*68*)
LiF	3	Bending	Cleavage	(*69*)
$MgSO_4 \cdot 7H_2O$, hydroquinone, etc.	> 2		Precipitation	(*26*)

of bulk materials compare more favorably with the strength of whiskers, but a work-hardened metal is in a "metastable" condition while the whiskers are annealed.

Not every whisker of a particular substance is as strong as indicated in the table. Efficiency in producing strong whiskers differs with the material and the method of growth. For instance, the value for NaCl given in the table is the highest from about 100 tests, while that for iron is the highest value obtained from about 75 tests. There appears to be some effect of growth conditions on efficiency in producing strong whiskers. Whiskers grown by precipitation from solution or the reduction of halides show a much larger scatter in strength than the whiskers grown under "cleaner" conditions, such as deposition in vacuum or inert atmosphere. Deliberate additions of impurities to solutions have significantly altered the maximum value and scatter of NaCl whiskers (*31*). In spite of the large scatter in strength there is a trend towards lower strengths as the diameter of the precipitation whiskers (*27*) and halide reduction whiskers (*43*) increases (Fig. 8). When the diameters become larger than 25 microns, the strengths approach those of bulk crystals.

The results on strength versus diameter suggest that the whiskers contain weak points which are distributed either on the surface or in the interior of the crystals. As the size of the whisker increases, the number and perhaps degree of weakness of the weak spots may increase, thus giving rise to the decrease in strength. Such weak points are undoubtedly common to all crystals but, in bulk crystals, are overshadowed by other defects which activate plastic deformation at lower stresses.

The number of weak points of a given degree of weakness is small. If a whisker is fractured several times and one of the remaining halves is tested each time, the final strength is often considerably higher than the initial (*43*). For instance, the strength of a copper whisker 4.3 millimeters long increased tenfold when the whisker was successively fractured three times. The final test section was 2.6 millimeters long.

Yielding of Whiskers

When the elastic limit of the whisker is exceeded, either fracture occurs or plastic deformation is nucleated in a localized region. When the elastic limit is exceeded in a whisker strained by bending the whisker kinks; if the kinked whisker is now annealed at a high temperature, it frequently unkinks and recovers its original shape (*27, 44, 45*). In a tensile test the localized plastic region is usually recognizable by the presence of slip line. When a small force is applied, the slipped region travels along the whisker, eventually reaching the extremities of the crystal. Many of the whiskers, including NaCl and LiF, deform plastically as much as 35 percent or more. The flow stress of the stronger whiskers is usually only a small fraction of the yield stress (Fig. 9). Ratios of yield stress to flow stress as high as 90 to 1 (*46*) have been measured. It is of interest to observe that once defects are introduced by means of plastic deformation, the whiskers behave more nearly like bulk crystals. Recovery of the initial high yield stress by annealing at moderate temperatures (*47*) has not been observed except in silicon whiskers (*44*), where the yield stress was partially recovered.

Strength and Perfection

Although whiskers have exhibited the potential strength of perfect crystals, it has not been established whether they are structurally perfect. Structural perfection implies here only the absence of extended defects—in particular, dislocations—and does not include point defects such as vacancies, interstitial atoms, impurities, and electronic defects.

Annealed bulk crystals normally contain from 10^4 to 10^8 dislocations per square centimeter (*48*). These dislocations interact with each other and arrange themselves into networks and boundaries. A crystal deforms plastically by the motion of dislocations, an elongation of about 2×10^{-8} centimeter occurring each time a dislocation leaves the crystal. To account for the large total deformation during plastic flow it has been necessary to postulate that new dislocations are constantly created within the crystal. One dislocation source postulated by Frank and Reed (*49*) supposes that a dislocation segment pinned at two ends repeatedly gives off dislocation loops in somewhat the manner that soap bubbles are formed from a soap-filled loop. The pressure, or stress, required to operate the source is inversely proportional to the length of the pinned dislocation segment. Yield stress data indicate that dislocation sources operating at the yield point of massive crystals must be of the order of 3 to 30 microns in length. Mott (*50*) has suggested that the dislocation sources correspond to the links of a three-dimensional dislocation network. If the width of a crystal is now reduced to less than the average length of these links, it becomes unlikely that it will encompass a dislocation network, and hence the probability of the crystal containing dislocation sources is small.

This leads us to the question of whether whiskers are strong simply because they are small or whether high strength is peculiar to whiskers. Sears's whisker-growth theory assumed a single axial dislocation, which implied high strength since the single dislocation is unlikely to provide the crystal with a dislocation source. There is indirect evidence that Al_2O_3 (*35*) whiskers and Hg

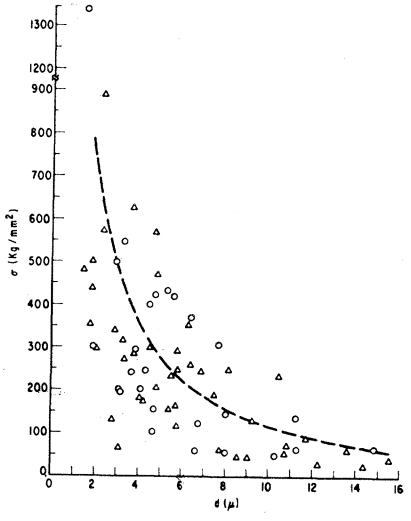


Fig. 8. The strength of iron whiskers as a function of size.

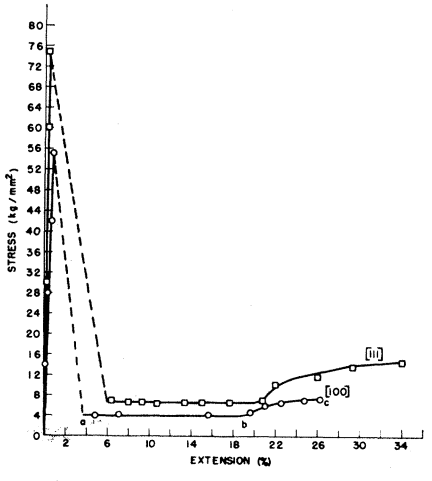


Fig. 9. Stress-strain curve of copper whiskers. After yielding, whiskers deform plastically (*a* to *c*) at much lower stresses.

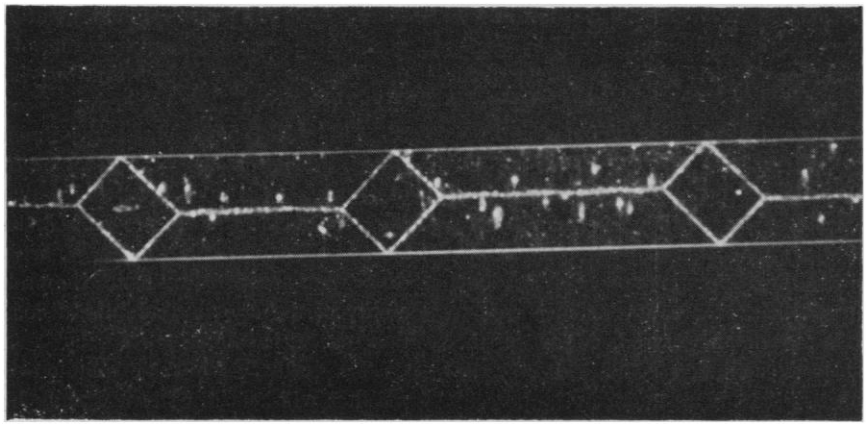


Fig. 10. Domain walls in iron whisker decorated by the Bitter method. (× 20) [Graham and DeBlois]

whiskers (*51*) may contain only single axial dislocations. On the other hand, there is no evidence for single dislocations in Fe, Cu, Ni, Zn, and Mn (*52*). Gorsuch (*53*) concluded from his x-ray diffraction experiments that iron whiskers have a high degree of perfection, but he was unable to estimate the dislocation content. Smith and Randle (*54*) recently found that tin whiskers 2 to 11 microns in diameter contain some imperfections but fewer than bulk crystals.

From the growth forms and mechanical behavior of zinc whiskers, Coleman and Cabrera (*55*) concluded that zinc and cadmium whiskers are not exceptionally perfect and that they contain many dislocations. Pearson, Read, and Feldman (*44*) concluded from their work on silicon whiskers that high strength does not necessarily imply absence of dislocations. It must be remembered, however, that silicon is brittle and that fracture is not preceded by dislocation motion at temperatures below 600°C.

There is evidence that size per se can increase the strength of crystals. For instance, the critical shear stress of Cd crystals increases 14-fold if their diameters are reduced by etching to 25 microns (*56*). Smaller effects have been observed with NaCl crystals reduced to 200-micron diameter (*57*). More recently Pearson, Read, and Feldman (*44*) have demonstrated that the strength of 50-micron silicon rods is sixfold the strength of bulk crystals from which they were cut. Taylor (*58*) reports that the tensile strength of wires in the micron range (prepared in capillary tubes) is considerably higher than that of thicker wires.

Whether the dimensional effects are responsible for the total increase in the strength of whiskers can at present not be ascertained from the experimental results. To reach a more definite conclusion it would be desirable to direct research along two avenues: (i) to determine the dislocation content of strong whiskers by some direct means, and (ii) to prepare crystals comparable in size to whiskers from crystals of known perfection. The latter approach presents the difficulty of producing surfaces equivalent to those of whiskers. Indirect evidence has shown that surface imperfections can lower the strength of whiskers considerably (*43*).

Significance of Whisker Research

The greatest significance of whisker research is that it has demonstrated that crystals of strength equal to the strength predicted by theory can be obtained. Gaining an understanding of the cause of their strength will increase our knowledge concerning the mechanical behavior of solids. In addition, an understanding of the mechanism of their growth will be of considerable importance in the field of crystal growth.

Aside from these considerations, whiskers have proven useful in studies that require crystals with (i) high elastic strength, (ii) surface perfection, or (iii) small dimensions. For instance, it has been possible to observe large deviations from Hooke's law in iron and zinc. Seeger (*59*) has made use of the data on iron to compute second-order elastic coefficients.

Important contributions have been made in the field of magnetism through the use of iron whiskers. The whiskers have a simple orientation and lend themselves readily to the study of domain wall patterns (*60*) (Fig. 10), from which a number of interesting observations have been made. Because of their surface perfection, coercive forces of close to the estimated theoretical limit of 530 oersteds have been obtained (*61*). In bulk crystals, domain wall nucleation occurs at much lower fields at imperfections on the surface. By applying these high coercive forces, domain wall velocities in excess of 50 kilometers per second were measured, whereas earlier measurements had been limited to velocities of less than 0.3 kilometers per second.

Whiskers have become useful in studies of corrosion and electrolysis. Green and Woolf (*62*) report a decreased rate of corrosion of silver whiskers in 8*N* nitric acid, while the rate of oxidation of iron whiskers at 500°C (*42*) is sometimes only 2 percent of the corrosion rate of polycrystalline iron. Vermilyea (*63*) found that the overvoltage for deposition on thin copper whiskers is sometimes ten times larger than the overvoltage that is required for deposition on bulk copper.

Whiskers are useful in studies where size effects are important, such as electrical resistivity at low temperatures. Lutes (*64*), using tin whiskers, showed that size has an important effect on superconductivity.

Conclusion

Crystals in the form of thin filaments or whiskers have strengths which are sometimes between 100 and 1000 times greater than those of large crystals. At present it is not known whether their strength is due to their small size, their surface perfection, a unique structural perfection, or a combination of these factors. Small crystals prepared from large imperfect crystals have shown an increase in strength, but whether strengths equivalent to the strength of whiskers can be obtained by decreasing the size of such crystals still further is at present uncertain. A knowledge of the cause of whisker strength is of importance both for technological and scientific reasons. Most mechanisms of whisker growth that have been proposed assume a unique dislocation density and orientation in the whiskers. If this assumption is invalid, the present hypothesis will have to be modified. Technologically it is of importance to know the cause of the whisker strength, for only if the strength is due to a unique perfection of either the surface or the interior is there some hope of realizing the high strengths in bulk crystals.

In the meantime, whiskers are proving to be useful tools in many areas of research. As the methods of their growth become more widely known and experience is gained in their handling, their use will become increasingly more widespread.

References and Notes

1. J. K. Mackenzie, thesis, University of Bristol, 1949.
2. C. Herring and J. K. Galt, *Phys. Rev.* **85**, 1060 (1952).
3. H. L. Cobb, *Monthly Rev. Am. Electroplaters' Soc.* 33, 28 (1946).
4. H. K. Hardy, *Prog. in Metal Phys.* 6, 45 (1956).
5. H. W. Kohlschütter, *Z. Elektrochem.* 38, 345 (1932).
6. C. Wagner, *Trans. Am. Inst. Mining, Met., Petrol. Engrs.* 194, 214 (1952).
7. K. G. Compton, A. Mendizza, S. M. Arnold, *Corrosion* 7, 327 (1951).
8. R. M. Fisher, L. S. Darken, K. G. Carrol, *Acta Met.* 2, 368 (1954).
9. J. Franks, *ibid.* 6, 103 (1958).
10. J. D. Eshelby, *Phys. Rev.* 91, 755 (1953); F. C. Frank, *Phil. Mag.* 44, 845 (1953); R. R. Hasiguti, *Acta Met.* 3, 200 (1955).
11. S. Amelinckx, W. Bontinck, W. Dekeyser, F. Seitz, *Phil. Mag.* 2, 1 (1957).
12. "Crystal Growth," *Discussions Faraday Soc. No. 5* (1949).
13. W. Burton, N. Cabrera, F. C. Frank, *Phil. Trans. Roy. Soc. London* 243, 299 (1951).
14. F. C. Frank, *Discussions Faraday Soc. No. 5* (1949), p. 67.
15. A. R. Verma, *Crystal Growth and Dislocations* (Academic Press, New York, 1953).
16. M. Volmer and I. Esterman, *Z. Physik* 7, 13 (1921).
17. G. W. Sears, *Acta Met.* 1, 458 (1953).
18. ———, *ibid.* 3, 361 (1955).
19. ———, *ibid.* 3, 367 (1955).
20. E. R. Everett and J. A. Amick, *J. Appl. Phys.* 25, 1204 (1954).
21. S. S. Brenner, *Acta Met.* 4, 62 (1956).
22. ———, thesis, Rensselaer Polytechnic Institute, 1957.
23. H. W. Wiedersich, *Westinghouse Research Labs. Research Rept. No. 60-8-01-08R1*; P. D. Gorsuch, *General Electric Research Lab. Rept. No. 57-RL-1840* (1955).
24. G. W. Sears, A. Gatti, R. L. Fullman, *Acta Met.* 2, 727 (1954).
25. P. B. Price, D. A. Vermilyea, M. B. Webb, unpublished.
26. J. E. Gordon, *Nature*, 179, 1270 (1957).
27. Z. Gyulai, *Z. Physik* 138, 317 (1954).
28. G. O. Matthai and G. Syrbe, *Z. Naturforsch* 12a, 174 (1957).
29. S. Amelinckx, *Physica* 24 (1958).
30. G. W. Sears, *J. Chem. Phys.* 26, 1549 (1957).
31. C. C. Evans, paper presented at the Cambridge Conference on Strength of Whiskers and Thin Films, 1958.
32. G. W. Sears, work in progress.
33. P. W. Levy and O. F. Kammerer, *J. Appl. Phys.* 26, 1182 (1955).
34. G. S. Baker, *Acta Met.* 5, 353 (1957); R. G. Treuting and S. M. Arnold, *ibid.* 5, 598 (1957).
35. W. W. Webb and W. E. Forgeng, *J. Appl. Phys.* 28, 1449 (1957).
36. S. Amelinckx, in preparation.
37. S. S. Brenner and C. R. Morelock, *Rev. Sci. Instr.* 28, 652 (1957).
38. J. Franks, *Nature* 177, 984 (1956).
39. E. E. Thomas, *Acta Met.* 4, 94 (1956).
40. R. Schenck, R. Fricke, G. Brinkman, *Z. physik. Chem. (Leipzig)* 139, 32 (1928).
41. H. H. Hobbs and E. P. Stilwell, in preparation.
42. T. H. Blewitt, R. R. Coltman, J. K. Redman, *J. Appl. Phys.* 28, 651 (1957); C. R. Morelock, work in progress.
43. S. S. Brenner, *J. Appl. Phys.* 27, 1484 (1956).
44. G. L. Pearson, W. T. Read, W. L. Feldman, *Acta Met.* 5, 181 (1957).
45. S. S. Brenner and C. R. Morelock, *ibid.* 4, 89 (1956).
46. S. S. Brenner, *J. Appl. Phys.* 28, 1023 (1957).
47. ———, unpublished.
48. P. Hirsch, *Prog. in Metal Phys.* 6, 236 (1957).
49. F. C. Frank and W. T. Read, *Phys. Rev.* 79, 722 (1950).
50. N. F. Mott, *Phil. Mag.* 43, 1151 (1952).
51. R. Gomer, *J. Chem. Phys.* 28, 457 (1958).
52. W. W. Webb, R. D. Dragsdorf, W. F. Forgeng, *Phys. Rev.* 108, 498 (1957).
53. W. Gorsuch, in preparation.
54. H. G. Smith and R. E. Randle, *J. Appl. Phys.* 29, 679 (1958).
55. R. V. Coleman and N. Cabrera, *ibid.* 28, 1360 (1957).
56. E. N. da C. Andrade, *Inst. Metals (London) Monograph and Rept. Ser. No. 13* (1953), p. 138.
57. E. Jenkel, *Z. Elektrochem.* 38, 569 (1932).
58. G. F. Taylor, *Phys. Rev.* 23, 655 (1924).
59. A. Seeger, personal communication.
60. R. V. Coleman and C. G. Scott, *J. Appl. Phys.* 29, 526 (1958); ———, *Phys. Rev.* 107, 1276 (1957); C. G. Scott and R. V. Coleman, *J. Appl. Phys.* 28, 1512 (1957); R. W. DeBlois and C. D. Graham, Jr., *ibid.* 29, 528 (1958).
61. R. W. DeBlois, *J. Appl. Phys.* 29, 459 (1958).
62. J. F. Green and A. A. Woolf, *Research (London)* 11, 38 (1958).
63. D. A. Vermilyea, *J. Chem. Phys.* 27, 814 (1957).
64. O. S. Lutes, *Phys. Rev.* 105, 1451 (1957).
65. R. S. Eisner, *Acta Met.* 3, 419 (1955).
66. R. V. Coleman, P. B. Price, N. Cabrera, *J. Appl. Phys.* 28, 1360 (1957).
67. R. Bacon, paper presented at the Cambridge Conference on Strength of Whiskers and Thin Films, 1958.
68. W. W. Piper and W. L. Roth, *Phys Rev.* 92, 503 (1953).
69. W. G. Johnston, personal communication.

Biological Sulfate Activation and Transfer

Studies on a mechanism of group activation and its role in biosynthesis are described.

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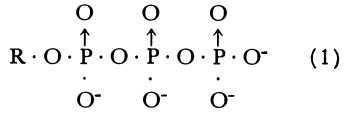
Sulfate is bound, mostly in ester linkage, in a fairly large variety of compounds present rather commonly in living organisms. Of most importance among these compounds are the sulfated mucopolysaccharides, such as chondroitin sulfuric acid, the ground substance of cartilage, and the similar mucoitin-sulfuric acid in mucosous tissues. Heparin belongs in this group; it is outstanding for its high sulfate, partially bound here to the amino group of the glucosamine moiety. Furthermore, a sulfurylated cerebroside is present in the brain and other tissues. On the other hand, conjugation with sulfate is a means of phenol detoxication in the animal body. This sulfate conjugation of the phenols, mainly in liver and the intestine, has been used for many years for the study of the mechanism of sulfate transfer.

With such a large number of metabolically-formed sulfurylated substances, it appeared likely that there was a common metabolic carrier for activated sulfate which would serve as general sulfate donor in the enzymatic set-up of cells. This was all the more indicated when DeMeio (*1*), who pioneered in the field of sulfate activation, demonstrated that, in cell-free systems, ATP (*2*) could serve as the source of energy for sulfate activation. The kind of mechanism that occurs in sulfate activation was further clarified by Bernstein and McGilvery (*3*). All this work with the liver system indicated strongly that conjugation with phenol was a two-phasic process, the activation of sulfate being the primary, the transfer to phenol being a secondary and separate, step.

Since, therefore, in the process of activation the energy of a phosphoanhydride link of ATP



(1)

apparently was transmitted to the sulfate, it seemed likely that the formation

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