MECHANICAL PROPERTIES OF WHISKERS AND THIN FILMS

On March 17–19 some sixty scientists met at the Cavendish Laboratory, Cambridge, and Tube Investments Research Laboratories, Hinxton Hall, for an informal discussion of nineteen papers on "The Mechanical Properties of Whiskers and Thin Films", invited from universities and industrial research laboratories in Great Britain and the United States. The main purpose of the meeting was to review the present state of knowledge on the high mechanical strength observed when one or two dimensions of a test specimen are reduced to a small value. The organizing committee consisted of Dr. F. P. Bowden, Mr. J. E. Gordon and Dr. J. W. Menter.

D. Turnbull (General Electric Co.) opened the proceedings with a survey of mechanisms of whisker growth. Whiskers can be grown either by spontaneous extrusion or by growth into physically or chemically supersaturated media. The former are very strong in bend tests (Galt and Herring) but not in tension tests. Plausible dislocation mechanisms for the observed growth from the root have been advanced by Eshelby, Frank and Seitz.

By contrast, whiskers appearing in physically supersaturated media grow at the tip although they appear to be nucleated at singularities on the substrate. A typical example is mercury, which, after an initial period of growth to a considerable length at a constant thickness of about 100 A., begins to thicken abruptly. Sears suggested that growth occurs by the action of a single axial screw dislocation, and this is supported by the field emission studies of Gomer. Whiskers grown in this way are strong both in bend and tension tests.

Similar mechanical properties are observed in whiskers grown from chemically supersaturated media, which have been extensively studied by Brenner. The growth mechanism is not clearly understood, but Frank has suggested that in some cases it may be controlled by the rate of chemical reduction at the tip or root.

Metal Whiskers

A number of papers then followed on the mechanical properties of metal whiskers. S. S. Brenner (General Electric Co.), in a paper on the plastic deformation of metal whiskers, first summarized the observations of himself and others on the elastic behaviour of whiskers. Elastic strains from 1 to 5 per cent have been reported with a maximum tensile strength of 1,400 kgm./mm.^{2} in an iron whisker about 2μ in diameter (but see Bacon below). Brenner has found that the plastic deformation of copper, silver and iron whiskers occurs by the motion of a Lüders band at a stress sometimes as small as 1 per cent of the yield stress. The local plastic strain in the Lüders band remains constant at values ranging from 0·25 to 0·40 during propagation, depending on the diameter of the whisker. Cross-slip can readily occur at these strains, suggesting that slip may extend along the whisker by a double cross-slip mechanism. Lüders bands are more difficult to observe in iron since extensive local deformation occurs within the band. This local slip is very sensitive to the applied stress, with the result that at high stresses fracture occurs before much of the whisker has slipped. No appreciable part of the elastic strength of whiskers can be recovered by annealing at temperatures up to 600° C. Creep has been observed in iron whiskers and a linear region can usually be observed in which the creep-rate varies roughly exponentially with the applied stress.

N. Cabrera described experiments on the creep of vapour-grown zinc and cadmium whiskers carried out at the University of Virginia with H. H. Hobbs and P. B. Price. An initial non-linear region is observed in the stress – strain curve followed by yield at strains of the order of 1 per cent. If the stress is maintained constant below yield for several hours, creep is observed, the initial creep-rate increasing with the applied stress. A saturation value is finally reached, and once creep has been exhausted at a particular level no more creep is observed at any other level. These results are tentatively interpreted as due to pinned-down dislocations (of the order of 10^8–10^9 cm.$^{-2}$) already present, most of which are pushed out of the whiskers during the creep process, leaving a much more perfect crystal, which then yields at higher stresses (1·5–2 per cent strain). The pinning may be associated with impurities which may be present in concentrations of the order of 10^{-4} impurity atoms per pure atom if the residual resistance observed at liquid-helium temperature is interpreted as due to impurities.

From optical and electron microscope replica studies of copper whiskers, G. A. Geach and P. E. Charsley (Associated Electrical Industries Research Laboratories, Aldermaston) deduced that slip in the Lüders band occurs on only one system, with the implication that the band is not propagated by a double cross-slip mechanism. In whiskers with a $< 211 >$ axis it appears that the slip system in the Lüders band is not that corresponding to the maximum resolved shear stress. The slip distance is observed to depend on size. 5-μ whiskers showed slip steps with up to 0·7μ glide, whereas the amount of glide was only a few hundred angstroms or less for the slip steps on a 20-μ whisker.

The surface characteristics of copper whiskers have been studied by D. Vermilyea (General Electric Co.). D. Turnbull, in presenting this work, suggested that both the physical and chemical behaviour of whiskers free from dislocations except for an axial screw might be unique if their side-walls are perfectly smooth and densely packed. Vermilyea has studied the overpotential required to discharge cupric ions or dissolve copper metal at the surface of copper whiskers. On bulk copper these processes occur at relatively small overpotentials (about 5 mV.) and apparently uniformly over the entire surface. However, overpotentials of about 100 mV. and 20 mV., respectively, are required to discharge cupric ions or dissolve copper metal at the surface of a 3-μ copper whisker, and the electrolytic action occurs only at a few small areas not including the whisker tip. These observations suggest that the surface of these whiskers may indeed be very smooth and with certain reservations may be taken to imply that the density of dislocations in the whisker may be very low.

G. A. Bassett (Tube Investments Research Laboratories, Hinxton) briefly described a new technique for revealing surface steps down to atomic dimensions, which might be useful for studying the surface perfection of whiskers. Evaporated gold layers are found to be nucleated preferentially along step edges on some ionic crystals. These nuclei are detached by means of a carbon film and used as a 'decoration replica' for observations on surface-step structures. It is not known whether similar effects could be obtained on metallic surfaces.

Some qualitative evidence on the dislocation structure in iron whiskers 10–200μ in diameter with axes in < 100 >, < 110 > and < 111 > directions was presented by R. V. Coleman (General Motors Corp.). Well-defined etch pits connected with dislocations are observed on {100} faces using 4 per cent picral or 2 per cent nital etchants. Perfectly oriented {100} surfaces do not in general develop etch pits, although random groups of pits are observed on some other surfaces. These are of two types: a 'sharp-bottomed' pit which develops rapidly, and a rounded flattened pit which develops more slowly. Larger numbers of the former develop after plastically deforming the whiskers, the density increasing with deformation and remaining constant with time for a given deformation. After annealing at 850° C. for some hours and etching, polygonized and other arrays of dislocations can be seen.

Non-metallic Whiskers

C. C. Evans, D. M. Marsh and J. E. Gordon (Tube Investments Research Laboratories, Hinxton) described observations on the properties of non-metallic whiskers of hydroquinone, nickel sulphate, sodium chloride, potassium chloride and potassium permanganate. Optical studies show that growth occurs from an initial very thin 'leader' crystal in the micron range, which then thickens by the longitudinal spreading of growth layers. A needle habit can be induced in sodium chloride by the addition of very small quantities of polyvinyl alcohol or sucrose to a saturated aqueous solution. Mechanical tensile tests on crystals of sodium chloride between 1 and 200μ^2 grown in this way have been made with a special testing machine developed by Marsh. Below 2μ^2 the whiskers are fully elastic up to fracture at a strain of about 1 per cent, but with increasing size the elastic limit falls and an increasing region of plastic deformation is observed. In the ductile region, slip bands and local necking are observed, and the largest specimens show some work hardening. The machine is not at present suitable for detecting a sharp yield point.

P. E. Charsley (Associated Electrical Industries Research Laboratories, Aldermaston) has investigated the structure of whiskers of sodium and potassium chlorides by electron microscopy and diffraction. Sodium chloride shows a predominant < 100 > orientation with occasional < 110 >, whereas potassium chloride whiskers are invariably < 110 >. The most common shape of sodium chloride whisker is bounded by two parallel {100} planes, the other surfaces being irregular, since the edges of growth layers appear to originate in the centre of the {100} faces. These whiskers frequently disintegrate during direct examination under the electron microscope, the larger ones revealing a substructure bounded by < 100 > directions and the smaller (a few tenths of a micron in diameter) showing no regular substructure. This dependence of the substructure on size is correlated with evidence for a layer structure obtained from carbon-replica studies, and it is suggested that layer growth results in lattice imperfections which may be the cause of the decrease in tensile strength with increasing diameter observed by Gyulai.

A. Berghezan (European Research Associates) presented a paper by R. Bacon (National Carbon Research Laboratory, Union Carbide Corp., U.S.A.) describing some interesting observations on graphite whiskers grown by a high-pressure arc process. Whiskers 0·5–5μ in diameter and several millimetres in length show a remarkably high fracture strength of 2,000 kgm./mm.^{2} at an elastic strain of 2 per cent. Most of these whiskers exhibit a ribbon-like form which are often single crystal over their entire length, with the *c*-axis perpendicular to the axis of the whisker. Some whiskers are cylindrical, but again X-ray examination shows that the *c*-axis is normal to the axis of the whisker in all azimuths, suggesting a structure consisting of one or more concentric tubes each of which is essentially a large sheet, many atomic layers thick, rolled up into a tight spiral scroll. Growth is thought to occur by addition of carbon to the spiral edge of the rolled-up sheet so that the whisker elongates rapidly (10 in./hr.). The elastic modulus of these whiskers is about 100 times that of bulk polycrystalline graphite.

Some aspects of the theory of dislocations in whiskers were considered by J. D. Eshelby (Department of Metallurgy, Birmingham) and J. P. Hirth (Carnegie Institute of Technology). The former described a method for calculating the twist which an axial screw dislocation produces in a whisker of arbitrary cross-section, and briefly discussed the stability of the dislocation. Hirth considered the possibility of thermally activated slip of dislocations out of metal whiskers, as a possible mechanism for the cessation of whisker growth. Whiskers with radii less than a critical value will not retain a single axial dislocation. Above the critical radius the dislocation will slip out only if it has an edge component of about 0·3 times the Burgers vector with respect to the axis of the whisker. The effects on whisker morphology predicted by this mechanism were shown to be consistent with observation.

Most of the evidence on crystalline whiskers seemed to indicate a fairly definite dependence on size of mechanical properties. Earlier work on non-crystalline glass fibres followed the same trend, but more recently it has been shown that if care is taken to avoid surface damage, strength is virtually independent of fibre size. The problem of size, strength and structure in glass was discussed in a paper by M. E. M. L. Parratt, D. M. Marsh and J. E. Gordon (Tube Investments Research Laboratories, Hinxton). On the assumption that failure is associated with surface defects, an improved sodium decorating technique has been used to study surface crack patterns and definite correlations have been made between their extent and the mechanical strength. These crack patterns present on the surface of all fire-polished glass seem to control the mechanical strength up to at least 3 per cent strain. The origin of these cracks is not clear. Electron microscope studies on thin films of glass showed that devitrification could lead to cracks, but an alternative source was abrasion, the susceptibility to which may be associated with the state of stress of the surface.

The importance of the surface condition was emphasized by D. G. Holloway (University College of

North Staffordshire), who has found that the bending strength of 60–120-μ 'Pyrex' fibres is larger by a factor of 5–6 when drawn and tested under high vacuum compared with those drawn and tested in air or those drawn in vacuum and tested in air. The drop in strength was attributed to atmospheric attack on the surface.

Thin Films

D. W. Pashley (Tube Investments Research Laboratories, Hinxton) has studied the tensile deformation of single-crystal films of gold in (111) orientation, 500–2000 A. in thickness, inside the electron microscope. No movement of the grown-in dislocations (10^{10}–10^{11} cm.$^{-2}$) was observed as the strain was increased to about 1 per cent, and this strain was confirmed as elastic by measurements on electron diffraction patterns from the strained film and by means of stress-strain measurements carried out externally by D. Marsh.

At an elastic strain of about 1 per cent the film was observed to fracture by the propagation of a highly localized region of plastic deformation along the film corresponding to slip on $(11\bar{1})$, $(1\bar{1}1)$ and $(\bar{1}11)$ planes. This led to complete fracture of the thinner films, but with thicker films short regions where fracture occurred were joined by regions of less localized plastic deformation.

T. Evans (Tube Investments Research Laboratories, Hinxton) described experiments in which similar single-crystal films of gold, gold/palladium, rhodium and platinum oriented on substrates consisting of single crystals of silver were deformed as a result of tensile stress applied to the substrate. In this situation the film may become deformed plastically with the substrate up to large deformations, provided dislocations from the substrate are able to pass into and through the film. The important determining parameters are the relative lattice misfit between film and substrate and the relative elastic moduli. Examination by transmission electron microscopy of films stripped after deformation showed that gold and gold/palladium accommodated the strain of the substrate by slip, whereas platinum and particularly rhodium films had many cracks following the traces of slip planes in the substrate, implying that the film had cracked locally due to the stress concentration arising from piled-up groups of dislocations on the substrate slip planes immediately below the film.

P. B. Hirsch and M. J. Whelan (Cavendish Laboratory, Cambridge) considered the factors determining the strength of thin metal foils with free surfaces, inferred from their direct observations in the electron microscope. Moving dislocations leave behind traces at the top and bottom surfaces, which are thought to be surface dislocations held up at the interface between the metal and an oxide or other type of surface film.

For a thick oxide film the stresses required to move dislocations approach the critical Frank–Read stress of the dislocation line in the metal film. Estimates of this stress from curvature of the line suggest that some dislocations move under stresses of about $G/1{,}000$ in foils about 1000 A. thick. Although in favourable circumstances it is expected that a Frank–Read source might operate, no direct observation of such a source has been made.

However, dislocations have been observed to nucleate near the edge of a thin foil. The dislocations appear to be half loops which have run in from the edge. Following a suggestion by Cottrell, nucleation of dislocations in a wedge crystal has been considered theoretically. It is found that, for a dislocation with Burgers vector in the surface of a thin foil with a wedge angle of 0·1 radian, the activation energy for nucleation is about 1 eV. at stresses of the order of $G/150$. This theory may possibly account for the observed nucleation in the majority of cases.

B. A. Bilby (Department of Metallurgy, Sheffield) also considered theoretically the nucleation of slip in thin plates, using solutions of elastic equations given by Leibfried and Dietze and by Eshelby and Stroh. For a long straight screw dislocation parallel to the plane of the plate a significant reduction in the activation energy occurs only at very high stresses or for very thin plates. A calculation was also made for the introduction of a pair of screw-dislocations lying normal to the plate, with results confirming in order of magnitude those of Hirsch and Whelan for the thin wedge. The energy of steps forming and disappearing on the surfaces as the dislocations are introduced plays an important part, but more detailed models are required to assess their effect quantitatively.

J. Nutting and D. G. Brandon (Department of Metallurgy, Cambridge) have tested iron foils, 99·97 per cent pure, in tensile deformation, with different thickness and grain size. The yield stress and extent of yield decreased and the rate of work hardening increased with decreasing foil thickness (down to less than 30μ). In coarse-grained foils the yield phenomenon was less affected than in the fine-grained. Factors affecting the behaviour of the foils include stress concentration due to local variation in thickness, decrease of constraints on individual grains, triaxial stress distributions resulting from surface rumpling during deformation and possible changes in the dislocation mechanism for deformation. No evidence for the last had been found by transmission electron microscope studies on thinned foils, although more deformation and kink bands and relatively few slip lines are seen on the surface of the thinner foils.

R. B. Nicholson (Department of Metallurgy, Cambridge) showed that the coherency strains associated with Guinier–Preston zones in aluminium/4 per cent copper alloys could be made directly visible in thin films of the alloy studied in the electron microscope and discussed their effect on the age-hardening characteristics of this alloy. G. Thomas (Department of Metallurgy, Cambridge) has studied precipitation phenomena and dislocation structures in thin foils of aluminium/magnesium/zinc alloys in the electron microscope. When previously aged beyond maximum hardness it is possible to cause movement of dislocations in the foils by heating in the electron beam. The chief sources of dislocations appear to be the grain boundaries. The stresses obtained by heating appear to be insufficient to move dislocations through precipitates.

As was intended, the papers given were essentially accounts of work in progress, and it is therefore not easy to give a considered view of the field as a whole. Explanations of the high strength of whiskers start from two conflicting assumptions about their microstructure. Some whiskers are undoubtedly highly perfect and it is reasonable to expect these to show a long elastic range. Whether surface perfection is essential for strength in addition to interior perfection depends on the view taken of the possibility of nucleation of dislocations or cracks from surface irregularities. The alternative view is that whiskers may well be imperfect, but high strength may still be observed because of the pinning of dislocations and inhibition of sources due to the small dimensions of the specimen. Both the latter strengthening mechanisms have been shown to be plausible for thin films from direct observation in the electron microscope, and it would be valuable to have more direct information of a similar nature about whiskers. Equally it would be valuable to have much more information about the relation between strength and thickness for thin films.

It is important to know more about changes in mechanisms and modes of deformation with thickness and also whether a small thickness alone is adequate to achieve high strength. The structure of the film arising from the particular method of preparation may also turn out to be important.

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CHEMISTRY OF PLANT PRODUCTS

The Royal Australian Chemical Institute's Western Australian Branch, in co-operation with the University of Western Australia, held a symposium on "Plant Products" at the Chemistry Department of the University on March 20 and 21. The first day was devoted to general and technological papers and the second mainly to structural chemical investigations. About 45 members and guests attended the two sessions.

After introductory remarks by Dr. D. E. White, president of the Branch, who welcomed the visitors, Dr. J. R. Price (Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne) outlined the development of phytochemistry in Australia, from the pioneers, like the Surgeon of the First Fleet, to its present flourishing state. Work in this field is carried on in most of the Universities and also by the Commonwealth Scientific and Industrial Research Organization. After discussing briefly the role of these institutions, Dr. Price summarized the scope, organization, objectives and potentialities of current work in the Division of Industrial Chemistry. Mr. R. H. Pearce (Kwinana Chemical Co., Kalamunda) described the application of solvent extraction and chromatography to the separation of fractions from *Xanthorrhoea* resins. Variations with species and age of the resin were discussed and some components were found to be unstable in light and air. The techniques used appear much more promising than those previously used in attempts to isolate compounds from this resin.

An account of the use of growth regulators in viticulture was given by Mr. L. T. Jones (Department of Agriculture, Perth), who described the effect of hormone spraying in place of the obsolete and harmful practice of cincturing vines. Local research work illustrated the superiority of such hormones as PCPA, 2,4-dichloro- and 2,4,5-trichloro-phenoxyacetic acids and gibberellic acid, resulting in increased production, improved fruiting, prevention of preharvest fruit drop and the killing of unwanted vines. Reference was made to the disadvantages of hormone spraying, for example, damage to bunches and vines, but these were due to incorrect application of the spray. Mr. Jones pointed out that gibberellic acid (not strictly a hormone), had been used experimentally only recently, and the results obtained suggest a promising future for the use of this material in viticulture. A striking contrast between the sizes of bunches on treated and untreated vines was shown in colour slides.

Mr. W. E. Hillis (Division of Forest Products, Commonwealth Scientific and Industrial Research Organization, Melbourne) discussed chemical aspects of the sapwood-heartwood transformation, referring particularly to the increased polyphenolic content of the heartwoods of Australian timber trees. These components, which contribute to durability, may be derived from the cambium, the leaves or the starch in the sapwood, and evidence indicates that an appreciable portion arises from the latter. The significance of the shikimic acid content of *Eucalyptus sieberiana* leaves of different sizes, before and after shading, was discussed.

Dr. H. Jakobs (Leederville, W.A.) described how chemical research had made possible much of the agricultural development in the Dutch East Indies. He exemplified this in detail by reference to the tea industry, which is now of major importance in Indonesia.

Dr. D. E. White discussed a study made with D. K. Dougall on the 'primary' tars, obtained by distillation of jarrah and karri sawdust *in vacuo*. Among the compounds isolated catechol, 2 : 6-dimethoxyphenol, 1 : 2 : 3-trihydroxybenzene, 5-methylfurfural and D-glucosan (1 : 5)β(1 : 6) were identified. Decomposition of the latter was responsible for the low decomposition temperature of the tar.

The second day's proceedings opened with a paper on the chemistry of stock poison-plants by Dr. C. C. J. Culvenor (Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne) read by Dr. J. R. Price. The liver-damaging pyrollizidine alkaloids and their N-oxides isolated from Compositae, Leguminosae and Boraginaceae were described with special reference to the recognition of monocrotaline from *Crotalaria retusa* as the cause of Kimberley horse disease. Recent work on other *Crotalaria* spp. was also discussed.

Dr. P. R. Jefferies (Chemistry Department, University of Western Australia) outlined the principles of gas chromatography and showed how it could be used for the quantitative analysis of simple mixtures. Complex mixtures as found in essential oils can be studied qualitatively, first on the whole oil, and then on distillation fractions. In this way the isolation of pure compounds is greatly facilitated and the presence of high-boiling components can be easily detected.

The constitution of the sesquiterpene alcohol globulol was discussed by Mr. G. J. H. Melrose in a joint paper with P. R. Jefferies and D. E. White. He described new sources of this alcohol in Western Australian Myrtaceae, and the synthesis of an epimer by the reaction of methyl magnesium iodide with apoaromadendrone. This alcohol also affords aromadendrene on pyrolysis of its 3 : 5-dinitro-