The Growth and Properties of Metal Whiskers

By S. M. Arnold*

Introduction

Much of the communication equipment used in the Bell System is protected from atmospheric attack by means of a finish coating of electrodeposited metal. Some seven years ago electrically conducting filaments were found protruding from the zinc plated surfaces of components in certain apparatus and causing circuit trouble. The occurrence of such filaments was not limited to one type of unit nor to one lot of zinc electroplate. Close examination of equipment fabricated over different periods revealed the presence of similar filaments on other zinc plated surfaces.

The trouble-making particles were metallic-looking, highly-reflecting discrete filaments, approximately 1–2 microns (40–80 millionths of an inch) in diameter, and so easily flexed that they were moved by the slightest current of air. Projecting from the metal surface of a bracket in the channel frequency filter shown in Figure 1 are some of the filaments which actually extended to the post of a capacitor 3/16 of an inch away. As a result, what was intended to be an insulating spacing between parts in an electrical circuit had become instead a conducting path as shown in Figure 2. The phenomenon is thus similar to that reported by Cobb[1] in 1946 who referred to trouble experienced in the radio industry with cadmium plated air capacitors short-circuited by filaments between adjacent plates. At that time, the presence of such filaments generally was attributed to factors in the plating technique. It was decided to study the phenomenon more fully in controlled laboratory experiments to determine the prevalence of filamentary or "whisker" growth and the conditions conducive to its occurrence.

Growths on Electroplate

A typical group of specimens, the supporting rack and the type of container used in most of the studies are shown in Figure 3. An early finding, that metal whiskers such as those in Figure 4, form on tin as well as on zinc and cadmium plated parts within a few months after electroplating, resulted in the inclusion in the study of most of the common metals. These were electroplated under a variety of conditions to obtain coatings of different characteristics. Specimens were exposed at temperatures ranging from −40° C to 150° C and at several relative humidities.

While differences in exposure time were required, whiskers developed on susceptible metals regardless of the method of plating. Most of the work has been done with tin, but enough observations have been made on zinc and cadmium as well to indicate that whisker growth is largely independent of the following variables:

1) Type of plating bath, acid or alkaline, with or without additives, or made up with high-purity chemicals.
2) Prior cleaning treatment, whether chemical, abrasive, or omitted, and whether rinsed thoroughly or incompletely.
3) Post-plating treatment, whether plating bath residues were left on the specimens or scrupulously removed.
4) Plating current density—low, high or continuously varied.
5) Fusion (in the case of tin plate) or, conversely, abrasion of the plated metal.

Fig. 1—Channel Frequency Filter. Pencil indicates gap bridged by filaments

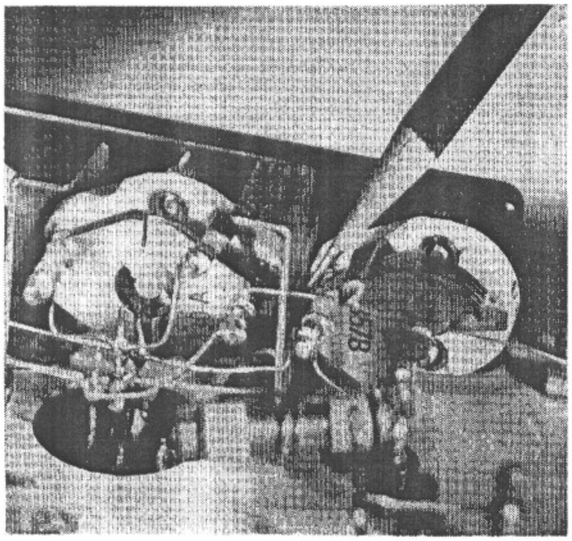
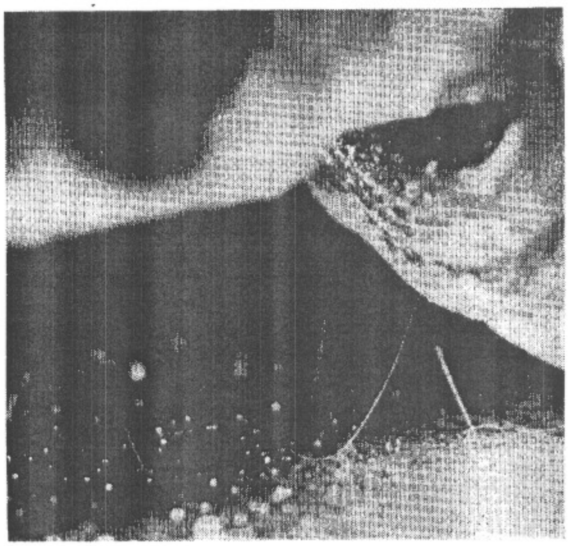


Fig. 2—Capacitor grounded by metal filament approximately 3/16 inch long



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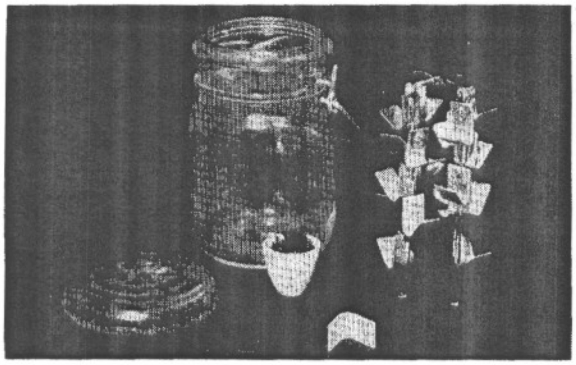


Fig. 3—Type of Specimen and Container Used in Study. Specimens 1½ inches x ½ inch x 1/32 inch

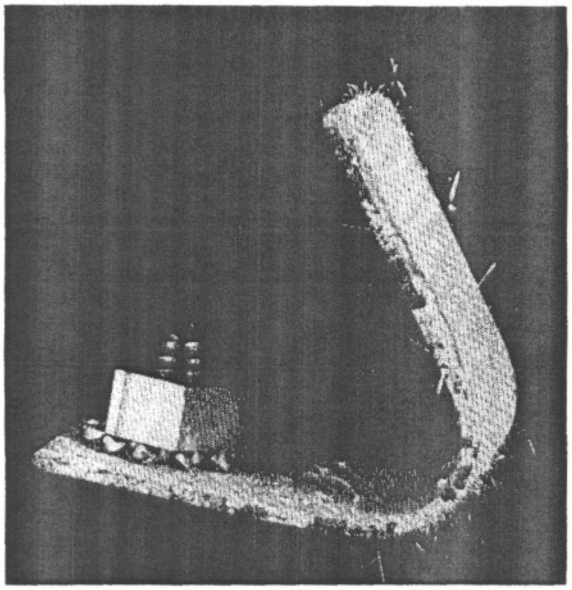
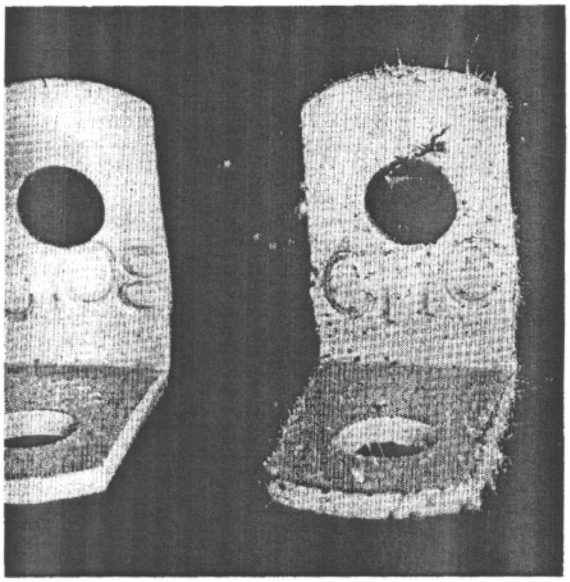


Fig. 4—Tin Whiskers on Tin Plated Steel. Specimen 1½ inches long

Fig. 5—Whisker Growth as Affected by Substrate. Specimens ½ inch wide



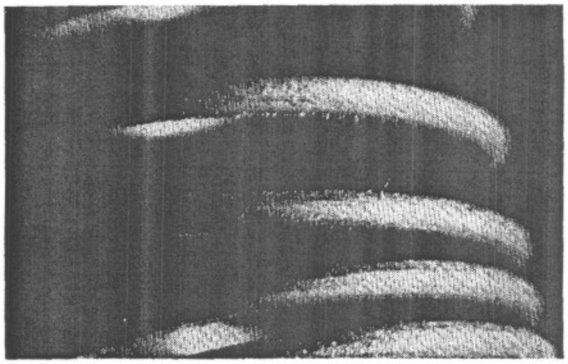


Fig. 6—Whisker Growth on Tinned 22 Ga Copper Wire

It was found that the character of the specimen surface and the thickness of coating affected whisker growth but only in degree. (Three types of deposit had been applied: a "flash" coating of 0.00001 inch, a "nominal" coating of 0.0001 inch and a "heavy" coating of 0.0005 inch.) The effect of coating thickness also was studied by means of wedge-shaped deposits applied to long specimens by electrodeposition during gradual immersion into or withdrawal from the plating bath. Although whiskers developed on all thicknesses of electroplate the greatest growths were found on the thin coatings. In line with these findings, it has been noted that after shearing a plated specimen, whiskers often develop in considerable number both at the interface between coating and substrate and on exposed base metal surface over which the coating has been smeared.

The substrate metal itself influences whisker growth, as is shown by the two identical brass brackets in Figure 5. The left-hand bracket was tin plated directly. The right-hand bracket was first iron plated and then tin plated. After an exposure of two years, there was a heavy growth of whiskers on tin over iron and practically none on tin over brass. Similar decrease in whisker growth resulted when tin was plated over gold, copper or other copper alloys. Although reduced, growth was not entirely prevented, as can be seen in Figure 6 which shows some very short whiskers on the surface of tinned copper wire. The variation in whisker growth on electrodeposits over different substrate metals may be associated with the specific basis metal, differences in thermal expansivity between the two metals, the degree of crystallographic coherence between substrate and coatings, or may be due merely to differences in the physical character of the substrate surface. Causes for the variations in growth are being studied.

Whisker growths are not confined to the metals cadmium, zinc and tin. Even some alloy coatings, such as tin-zinc and tin-cadmium occasionally used on electrical components, develop whiskers. The tin-nickel coating now being applied to a limited extent has not been in test long enough to be judged as to its whisker growth tendencies. Although perhaps of less general interest, whiskers have been found on electrodeposited antimony.

Growths on Other Finishes and on Bulk Metal

Whisker growths are not limited to electroplate. Hot-dipped, sprayed and evaporated metals have developed whiskers. In addition, the substrate need not be metallic. This was demonstrated by the growth of whiskers on tin films evaporated onto paper and onto freshly cleaved mica.

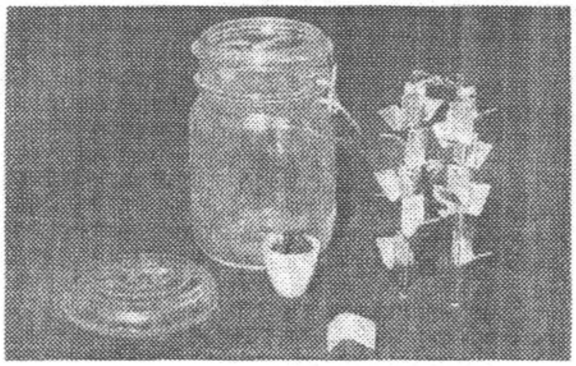


Fig. 3—Type of Specimen and Container Used in Study. Specimens 1½ inches x ½ inch x 1/32 inch

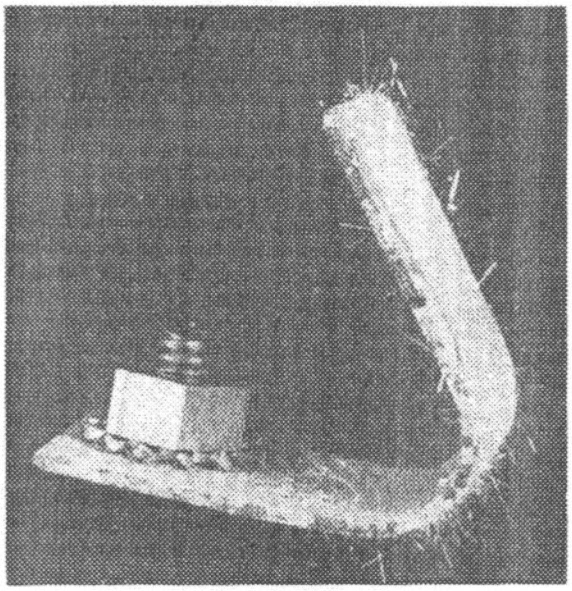
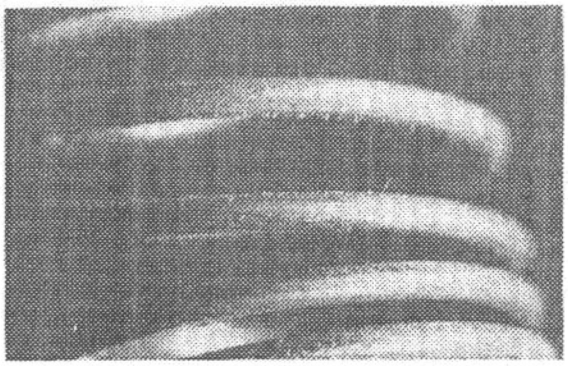


Fig. 4—Tin Whiskers on Tin Plated Steel. Specimen 1½ inches long

Fig. 5—Whisker Growth as Affected by Substrate. Specimens ½ inch wide



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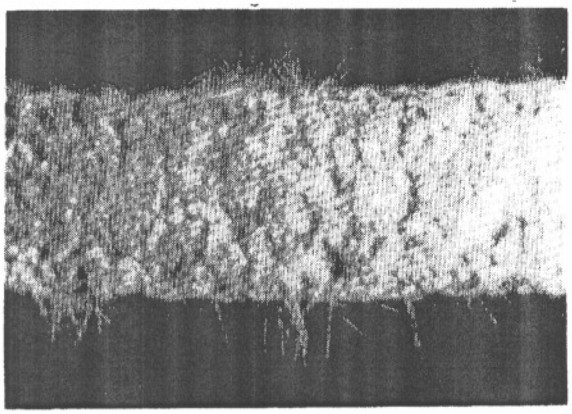


Fig. 7—Whiskers on 1/32 inch thick Bulk Zinc

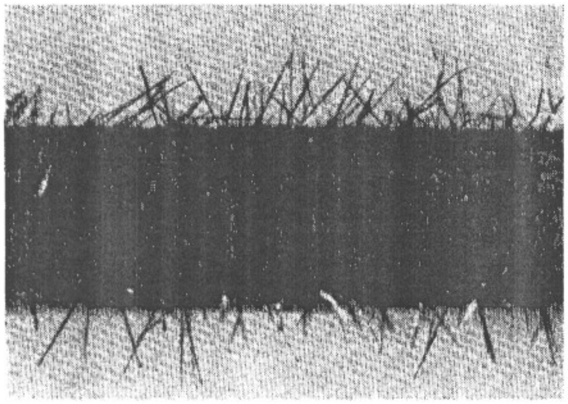
While growth is not as great and usually requires a longer time, even bulk metals produce whiskers on their surfaces. After exposure periods of 2–3 years, numerous filaments have been found on polycrystalline tin, cadmium and zinc specimens. Whiskers on bulk zinc are shown in Figure 7.

High tin-lead alloys are susceptible to whisker growth at room temperatures but growths have not been observed on lead. The minimum lead content required to avert growth in tin-lead alloys is not yet known. Whiskers have been found, however, on a tin-lead solder containing 30 per cent lead, and also on a tin-lead-silver solder containing 34 per cent lead and 6 per cent silver. Tin-aluminum alloys develop whiskers on the tin rich phase and growths actually have been observed on tin-aluminum bearings.[2]

As yet, whisker growths have not been observed on metal of the highest purity, such as zone-refined tin of better than 99.9999 per cent purity now in test, nor on single crystal specimens of nominal purity. Many whiskers have been found at grain boundaries in polycrystalline materials and also over the surfaces of the individual grains.

Another type of growth has been observed on silver and copper exposed in the presence of sulfur or sulfur-bearing materials, such as hard rubber. These growths, however, developed only on severely tarnished areas and were in general quite unlike the metal whiskers under discussion. They were brilliant black and usually tapered or spear shaped, as shown in Figure 8.

Fig. 8—Growths on Silver Plated Steel in Presence of Sulfur. Specimen 1/32 inch thick



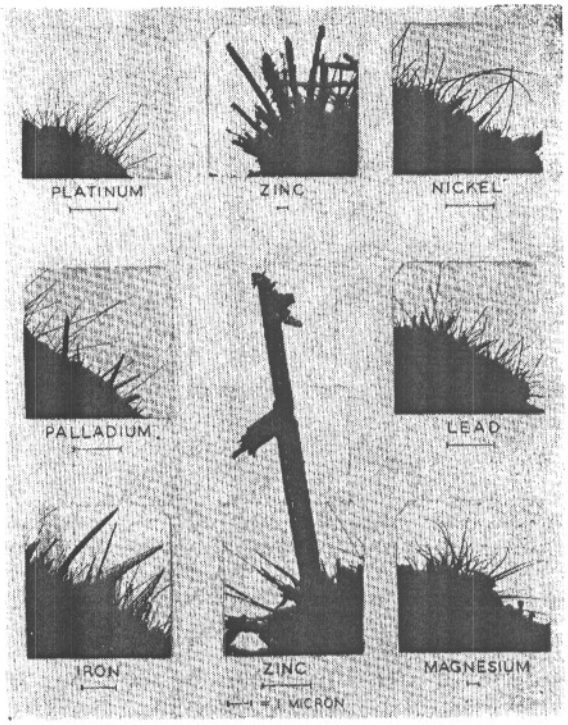


Fig. 9—Growths at Elevated Temperatures

Growths at Elevated Temperatures

Studies have been made to determine whether metals resistant to whisker growth at room temperature develop filamentary growths under favorable conditions. Bulk metal was used in the form of cold rolled 0.010 inch sheet. Small annular rings were punched from the sheet material and heated in air in quartz tubes for various periods and over a range of temperatures. The rings were examined at intervals in the electron microscope for evidence of whisker growth.

These studies have shown that brass (65 copper–35 zinc), columbium, copper, gold, iron, lead, magnesium, molybdenum, nickel, palladium, platinum, silver, tantalum, titanium, tungsten and zinc develop filaments on heating. In Figure 9 are electronmicrographs of a few typical growths. With the exception of the lead whiskers, which grew at 200° C, all those in the illustration formed at 400° C over periods of 60 to 140 hours. Most of the growths are much smaller than those which normally form on tin, and generally require magnifications of the order of 10,000-15,000 to detect their presence.

The actual compositions and structures of the filaments which developed at elevated temperatures have not been determined. Some may be compounds, probably oxides. Metals such as gold and platinum, however, do not readily oxidize and the surface growths may be metal filaments.

Inhibition of Growth

It is important not only to determine the extent to which growth will take place, but also to develop means of completely preventing the formation of whiskers. One possible method prescribed for the prevention of whisker growth was the application of a coating to the metal surface. Oils, greases, silicones, waxes, lacquers and a number of proprietary materials were applied in the form of thin surface films. Whiskers penetrated all such

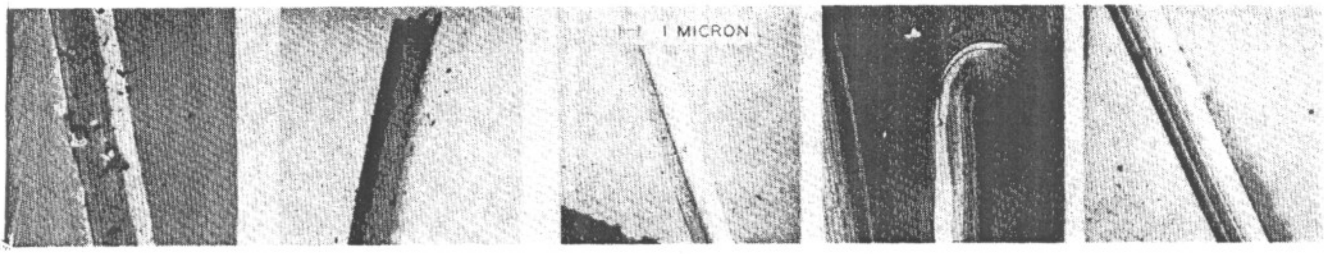


Fig. 10—"Fluting" on Sides of Whiskers

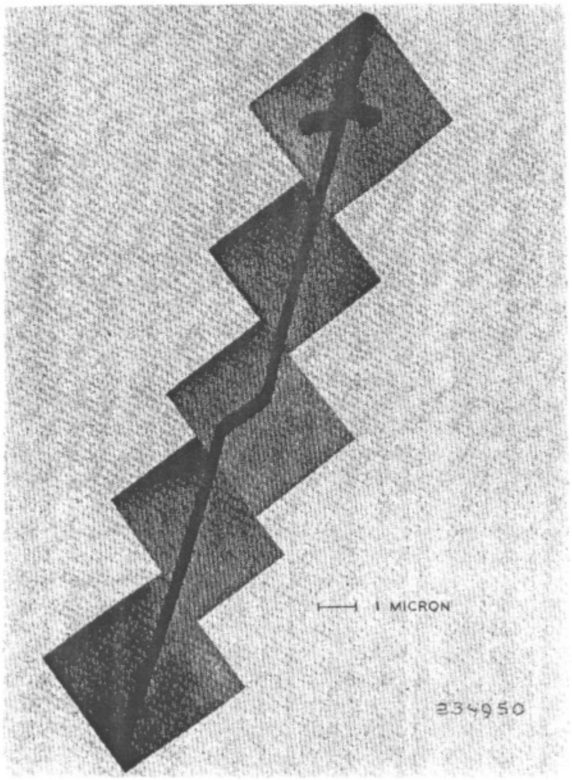
coatings and even developed on parts completely immersed in oil. Films of lacquer approximately 0.0007 inch thick were not satisfactory. Heavy resin coatings of the order of 1/16 inch or more prevented whisker growth so long as the coating remained entire. However, where the coating pulled back at an edge or where cracks developed, whiskers pushed through.

Conversion coatings, such as the chromate coatings often developed on zinc and cadmium to increase their corrosion resistance, are not satisfactory for the prevention of whisker growth. Many chromated parts have been examined and found bearing the typical metal filaments.

Acceleration of Growth

Actual growth rate is difficult to specify. Whiskers are just beginning to appear on some specimens maintained at 25° C for approximately seven years. On seemingly identical specimens in the same environment there are numerous whiskers ranging in length from those barely distinguishable to others over ⅜ inch long. Some whiskers grow for a short time only, others continue for varying periods before growth ceases. Individual whiskers have been observed to grow approximately 750 microns in a month, corresponding to 25 microns or 1 mil per day.

Fig. 11—Offset Variation in Growth Direction



While periods of weeks or months generally are required before there is evidence of whiskers on a metal surface, growth may be tremendously accelerated by application of pressure as reported by Fisher, Darken and Carrol[3]. In a matter of seconds at a pressure of 3000–4000 psi, whiskers are formed equaling in length many of those requiring several months of growth time under normal atmospheric pressure. The growth rate falls off after the pressure has been applied for some time, but an increase in pressure will again accelerate growth.

In another study, a number of tin plated specimens were exposed to neutron bombardment at Brookhaven National Laboratory for approximately 30 days at a flux density of $10^{12}cm^{-2}sec^{-1}$. Examined after twelve months, it was found that a dense growth of whiskers had developed. In comparison, control specimens not irradiated showed very little growth. Similar studies are underway in which specimens are being subjected to β particle bombardment. No accelerating effect has been observed with specimens merely supported in electric or magnetic fields.

There is a considerable temperature range over which metal whiskers develop. Tin whiskers have been grown at −40° F, but the optimum temperature is in the neighborhood of 125° F. Relative humidity also affects whisker formation in that growth may be accelerated by increasing the humidity. However, high humidity is not required. Whiskers have developed in dry atmospheres and even on specimens in highly evacuated containers.

Structure and Properties

X-ray diffraction studies have established that the whiskers which grow spontaneously at normal temperatures are metal single crystals. More than one crystallographic direction has been found as the growth axis: thus, in the case of tin the <100,> [001] and the <101> growth directions have been observed.

By electron microscope examination of plastic replicas of the whiskers and also by fine polishing of whiskers mounted in a transparent molding resin, it has been shown that the external surfaces of the whiskers have striations or "flutings" extending longitudinally along the length as shown in Figure 10. In at least some of the whiskers holes extend along the whisker axis[4].

Whiskers usually are straight, but occasionally a filament is found with an offset portion similar to that in Figure 11. A few have been observed in the form of the spirals shown in Figure 12. Although most of the whiskers appear to be approximately 1–2 microns in diameter, considerable differences in size are possible, as shown in Figure 13.

Fig. 12—Spiral Forms of Tin Whiskers

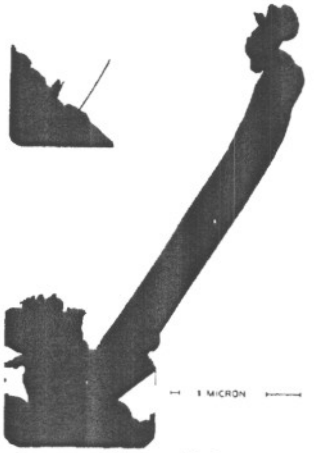


Fig. 13—Observed Variation in Size of Tin Whiskers

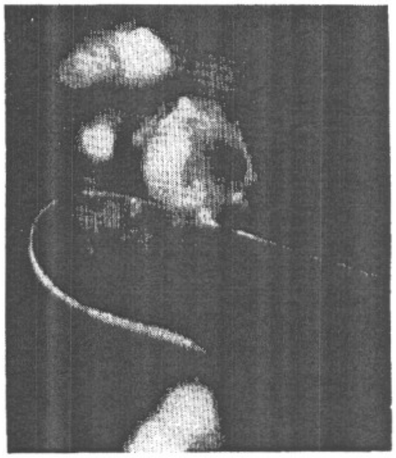


Fig. 14—Bent Tin Whisker. Whisker approximately 1/8 inch long

The smaller is 0.05 microns and the larger 5.8 microns in diameter (or 2 and 240 millionths of an inch respectivel[5]y).

Because of their occurrence on the surfaces of components used in electrical equipment, it was of interest to determine the resistance of the whiskers. Using a condenser discharge method, a fine tinned copper wire was welded to a whisker to secure a stable contact. The average resistance of a number of tin whiskers ⅛ inch long was of the order of 50 ohms. The temperature coefficient of resistance at 20° C was found to be 0.0032/deg C. This compares with a published value for tin of 0.00365[6]. At the same time the surprisingly high current carrying capacity of the whiskers was noted, some carrying as much as 10 milliamperes before burning out. For a 2 micron diameter whisker, this corresponds to a value of more than one million amperes per square inch.

Whiskers possess very high yield strengths. Herring and Galt[7] bent individual tin whiskers, measured the radius of the bend and determined elastic strains of the order of 1–3 per cent, a value much higher than that observed for bulk material. This finding was the first experimental confirmation of the theory that metal crystals can have extremely high yield strains.

Current metallurgical theory proposes that a type of imperfection, the dislocation, is present in quantity in bulk metals. Dislocations multiply and move easily under applied stress and are responsible for the failure of metals to achieve by a thousandfold the yield strength they theoretically should possess if perfect. Because whiskers are of the order of only 1 micron in diameter, they are too small to contain many dislocations and hence should be relatively strong. The bend tests appear to bear this out and indicate that in many cases the whiskers include no dislocations at all. In Figure 14 is shown a tin whisker bent through a small radius. It straightened out elastically upon removal of the probe, without evidence of plastic flow. Metal whiskers thus are crystals which can be used to advantage in the study of the intrinsic properties of a metal, free from the effects of imperfections present in gross specimens.

Mechanism of Growth

The mechanism of whisker growth has not been determined as yet. One significant aspect of growth was shown by a series of shadowgraphs made in the electronmicroscope at intervals during the life of a whisker[8]. A few of the growth stages, shown in Figure 15, reveal that the tip end remains unchanged. Accretion of material must be taking place at the base and is responsible for the increase in whisker length. A dislocation mechanism proposed by Frank[9] is consistent with the observed strength properties.

The driving force for growth remains an unsettled question. An oxidation reaction has been invoked to supply the energy necessary for whisker formation[9]. If this is the mechanism, the amount of oxygen required for growth is very small because it has been found experimentally that whiskers grow at pressures of 10^{-7} mm of mercury. Present evidence suggests that microstrains present in the metal may supply the required energy. This leads to the view that whisker growth is actually a strain relief or further, as suggested by D. F. Gibbons, may be a manifestation of a recovery or recrystallization process.

Other Studies

Because of their unique properties as well as the increasing number of equipment problems attributable to their presence, interest in metal whiskers has been aroused and several pertinent articles have appeared in the literature. Some have been concerned with the characteristics of filaments which grow "spontaneously," such as those referred to in the present article[9–13] while a number of authors have described other methods of producing filamentary growths.

Filaments of silver have been formed by condensation from the vapor phase by Howey[14]. Growths at high temperatures on molybdenum and tungsten have been reported[15, 16, 17]. Wakelin heated copper in an electric field and produced masses of fibers[18]. Growths on copper and other metals[30] at elevated temperatures have also been observed by other workers[19, 20]. Mercury has been deposited in filamentary form at low temperatures on glass by Sears[21, 22] and he also has grown whiskers of zinc, cadmium, silver and cadmium sulfide by condensation from the vapor[23]. A number of metals, including iron, silicon, gold, platinum, copper, nickel, cobalt and silver, have been obtained in the form of filaments by reducing the corresponding halides in an atmosphere of hydrogen[24–29]. While most of the published work is concerned with the filamentary growths themselves, some work of an engineering nature is being carried on.

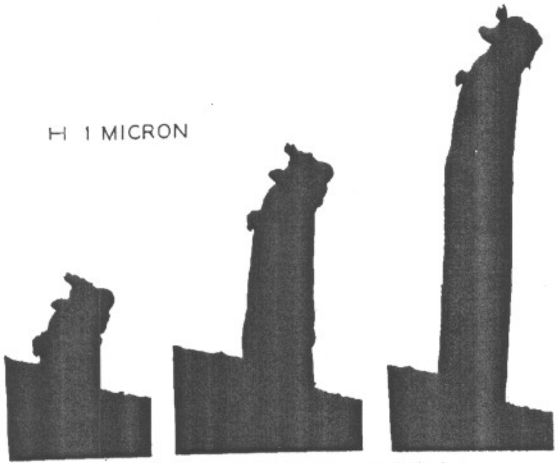


Fig. 15—Stages in Growth of Tin Whisker

That the growth of whiskers is not a new phenomenon may be concluded from the examination of undisturbed old equipment. For example, a number of zinc plated details installed in a telephone central office in 1912 were recently removed for study. Surfaces which had been protected from cleaning operatings and from excessive air circulation had numerous whiskers present. This observation also indicates that the growth of metal whiskers cannot be ascribed to such factors as plating technique or purity of deposit since there have been changes in plating practices and coating compositions over the years.

One reason why there has not been more trouble directly attributable to whisker growth stems from the fact that spacings between components have been much more generous in the past. Smaller and smaller spacings necessarily must result from the trend toward more compact equipment. As miniaturization advances, separation between parts more closely approaches the length of a whisker and increases the probability of formation of a whisker "bridge" and a low impedance or short circuit condition. It is important to consider this in the design and assembly of electrical equipment.

Knowledge of the existence of metal whiskers has resulted in more careful scrutiny of equipment parts before the offending filaments have been dislodged and the evidence destroyed by mechanical shock, handling or cleaning to remove "dust." As a result, their occurrence has been found to be more extensive than was anticipated. Whiskers have been found in equipment from many sources and manufacturers—nor is this problem restricted to domestic producers. In other countries, also, metal whiskers have been observed, and studies of the growths are now being made.

Conclusion

Briefly summarized, studies to date indicate that whiskers are metal single crystals with unique properties. They form on a few metals under a wide variety of conditions and on many metals under specific conditions. Bulk, as well as deposited metal, is susceptible. Factors such as temperature, relative humidity, applied pressure, method of deposition, thickness of metal coat, character and/or surface condition of substrate influence whisker growth but only in degree. No general, practicable method is known at present which will prevent metal whisker growth, but studies, now under way, offer promise of a solution to the problem.

Acknowledgement

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