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Signature Date

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(NASA-CR-192701) WHISKER GROWTH STUDIES UNDER CONDITIONS WHICH RESEMBLE THOSE AVAILABLE ON AN ORBITING SPACE STATION Final Technical Report, 1 Jun. 1990 - 31 Dec. 1992 (George Washington Univ.) 16 p

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ABSTRACT

Minimal funding was provided by NASA with one designated "mission" being the clear demonstration of the relevance of previously supported whisker growth studies to microgravity research. While in one sense this work has shown the converse: namely, that ambient gravitational fields as high as 1 Earth normal have no relevance to growth of whiskers by hydrogen reduction of metal halides, a case is made that this does not demonstrate lack of relevance to microgravity research; on the contrary, the driving forces for this growth are precisely those which must be understood in order to understand growth in microgravity. Results described suggest that knowledge gained from this work may be highly fundamental to our understanding of the genesis of metal crystals. Time and money ran out before this work could be considered complete. At least another year's study and analysis will be required before publications could be justified.

SUMMARY OF WORK PERFORMED AND RESULTS OBTAINED

General Remarks

After several years attempting to obtain further funding for work begun under grant # NASA NAG 3-642, this grant, a one year grant with a budget limited to 2 month's salary for the Principal Investigator, was funded in 1991 and extended without further funds until December 1992. It was strongly suggested by the director of the Microgravity Section that the work under this short grant be devoted to clearly demonstrating the relevance of this work to microgravity research. This became the "mission" of the research and was adhered to quite faithfully in spite of a number of very tempting side issues which were clearly unrelated to the mission.

There have been no further publications from this work but the last paper from the preceding grant (published in 1989) provides a good background to the work and is included as Appendix I. Much data has been accumulated (some at a furious pace) in the attempt to provide a clear, graphic, and unambiguous dependence of this growth on the ambient gravitational field; however, as will be seen, the one unambiguous conclusion reached, so far, is the converse: so far as "protowhiskers" (see Appendix I) are concerned there is no connection to gravity at all! It is estimated that full assimilation of implications in all of the results obtained during this grant, and during the many years of work preceding it, will take several years of intense theoretical work. This, the Principal Investigator is prepared to do, and one or more significant publications should be a natural outcome. NASA will be kept informed of any and all future developments.

Description of the Work

Altogether, about 100 growth runs were performed. None of the growth runs had growth of mature whiskers as a goal: rather, the inception of whisker growth, which is mostly manifested as protowhiskers, which are often "free" whiskers (not anchored at either end) and are less than one micron in diameter. A typical "run" consisted of quickly drawing a low heat capacity tray containing a cover glass (half of which was clean, half of which was covered with a polished graphite coating) quickly into the furnace (in hydrogen); leaving it for 1 to 30 seconds; and quickly drawing it out into a cool region. Temperatures ranged from 270 to 670° C. Most runs used cuprous bromide but occasionally other materials were used: namely, cuprous iodide, cuprous chloride, silver bromide, ferrous chloride, cobalt bromide, nickel chloride, and yttrium bromide. In addition, some whiskers were grown from solution using sodium chloride, potassium chloride, sodium nitrate, and sodium potassium tartrate-tetrahydrate. The latter were used to confirm the ubiquity of the protowhisker phenomenon only: otherwise not related to the reduction grown whisker phenomenon. Other work involved the modification of an evaporator for vacuum deposition of thin films of metal halides and the development of techniques for extremely rapid heating and cooling of the growth plates.

Preliminary Results

Whiskers were grown from thin films of metal halides of thicknesses ranging from about 1 micron to about 5 microns. These films were vacuum deposited on glass, on nickel sheets, on copper sheets and on polished graphite. Protowhiskers were easily formed on glass, graphite, and nickel; but on nickel, roughness of the surface made them hard to find. Many runs consisted of three plates: one horizontal with the film on top, one vertical, and one inverted (horizontal with film underneath). There was no detectable difference in the growth behavior between these differently oriented plates: thus we conclude that ambient fields of 1 earth gravity have no effect upon this type growth.

Similar growth runs were performed on the same substrates using fine powder lightly dusted on the surfaces. Results were quite similar to those on the films, but, since the films were so difficult to manufacture in the laboratory, many of the later runs were done with powder. Even below the bulk melting point of the materials, the powder quickly formed a film on the substrate and this justified its use for our purposes (see comment below on lowering of melting point of the halides by gases). In no case was there evidence of any effect of direction of the ambient gravitational field on the growth.

Please note that if proof of clear, graphic, unambiguous dependence of the growth on gravity is our main mission, then our experiment is negative and it is over! The Principal Investigator felt that there was another way of looking at these results (see conclusions); moreover, that there was perhaps a deeper significance to some of the behavior observed during the growth runs.

One really complex result of the growth runs involved an unexpected lowering of the melting point of both the thin films and the fine powders. Clear evidence of melting was observed in the films on all substrates at temperatures more than 40 centigrade degrees below the listed melting point.! A quick, separate, study was made of this effect and it was found that all gases tried had this effect, but the effect was strongest with hydrogen, less strong with argon, and still less (but nevertheless present) with nitrogen. This, of course, needs further study, but was set aside for the time being. One thing became clear: no claims for growth "from the solid" could mean very much with melting surface films occurring so far below the melting point: especially since hydrogen is always present in this type growth. Another extremely complex aspect of all of the growth runs was the effect of the substrate. Clearly the most rapid, prolific, and varied type of growth happened on the polished graphite substrate. The slowest and smallest amount of growth happened on clear glass with the nickel substrate being intermediate between the other two. The growth on the graphite substrate provides another unexplained effect: while there are some straight and even some free whiskers present, there are also a majority of very crooked, curled up, filaments which look as though a straight whisker had been raised above its melting point. (Remember, however, that at typically 500° C we are 580° below the melting point of copper! Such behavior must be explained! Presently it appears likely that such whiskers grow as CuBr whiskers (which are at or above their melting point) and convert to copper at a later point. The startling thing is that, if this is true, it is possible that all copper whiskers grow this way, with only some of them losing their straight shapes before converting to copper. Clearly if, indeed, these whiskers grow first as CuBr protowhiskers, then convert to copper (also as protowhiskers) we have a brand new and hitherto unsuspected mode of crystal growth. Such curled up whiskers have their curvatures in three dimensions and are virtually impossible to photograph at the high powers required to see them. Therefore, though they are present in Figure 1 they appear only as smudges.

The above growth possibility was deemed sufficiently important to justify a number of other experiments. Most significant of these was the confirmation of the existence of CuBr whiskers by performing the same type growth runs without hydrogen. CuBr powder was sprinkled on both glass plates and polished graphite substrates and subjected to similar growth procedures but with nitrogen or argon (only) as the ambient atmosphere. On the glass substrate many free whiskers of CuBr were clearly seen. Some were also seen on the graphite substrate, but surprisingly some reduction to copper also took place. This is probably reduction due to the reaction of CuBr with the graphite forming C_8Br.** Such reduction, incidentally, probably accounts for several of our observations, in the past, of what we called "hydrogen-less" reductions, since graphite was present during all such observations but was thought by the PI to be inert to CuBr and other metal halides. Existence of CuBr whiskers was clearly demonstrated here. (See Figure 2.)

Another observation confirming the complex growth process alluded to above was the observation in many of these runs of strings of whiskers or what clearly appears to be interrupted growth (See Figure 1). We are far below the melting point of copper; far below any temperture where dissipation of copper could possibly take place. Such behavior, just as with the curley whiskers, can be explained only if this were another material (probably CuBr) at the time this happened, with a subsequent conversion to copper prior to the actual observation. Generality of these results is strongly suggested by the fact that similar behavior has been observed in CuI, CuCl and $FeCl_3$. Obviously, a set of experiments focussing on this phenomenon alone was not a part of our "mission", but now that the grant has expired work will continue in that direction.

** W. Rudorff, *Zeitschrift for Anorganische Chemie*, 245, 383, (1941).

Additional Aspects Worth Noting

1. Speed of growth. Large numbers of protowhiskers are formed within as little as 1 second on the graphite substrate. Equipment was rudimentary for high speed reactions and the times are only roughly estimated. The actual time at growth temperature is estimated by subtracting draw-in and draw-out times from total time in the furnace. Some rudimentary measurements suggested that the tray itself took only about 1 second to reach 90% of ambient temperature but estimates are very crude. There are clear theoretical implications to such rapid development of literally tens of thousands of crystals.

2. Effect of substrate: Slowest growth (and smallest quantity) on glass; next nickel. On graphite, growth was at least 10 times more prolific, with much overgrowth of "curley" whiskers (as mentioned above). Observations of bare areas of substrate indicate that wetting probably is markedly different on the graphite. There is also probably an augmentation of the reduction by formation of CsBr (as mentioned above) and perhaps catalysis.

3. Chaos? As mentioned above, the glass plates usually had half polished graphite and half clear glass substrates. Growth runs always showed markedly different behavior in the vicinity of the edge of the graphite. This is clearly indicative of the extreme criticality of the growth conditions. This is thought to suggest possible chaotic behavior of the growth, which would explain the traditionally mysterious nature of the whole field of whisker growth. This will be pursued further. That all of these growth phenomena are limited by the proximity of chaos is further substantiated by independent results mentioned in item 4.

4. Ubiquity: In an attempt to test the ubiquity of the protowhisker phenomenon, independent experiments using crystallization from solution were performed. NaCl and KCl whiskers were grown by observing a droplet under high power in an optical microscope. Supersaturation was provided by evaporation. Protowhiskers (free whiskers) became visible when they reached a fraction of a micron in diameter but lack of control of supersaturation (which increases with time) caused these to quickly thicken or transform into platelets. Most spectacular was a series of experiments done with sodium-potassium-tartrate-tetrahydrate. In this case, supersaturation is strongly temperature dependent so that simply cooling a nearly saturated solution will provide a gradually increasing supersaturation. Several growth runs produced quite spectacular results. In a 500 Ml beaker, slowly cooling, thousands of free whiskers suddenly became visible. They increased in thickness and length (to 2-3 microns X 1 cm) while more and more were formed until the entire solution became a solid mass of whiskers. Quick estimates suggest at least a billion whiskers in the single container. This behavior is so unlikely, however, that the next 20 tries failed to produce such whiskers: instead, plates, blocks, or large single crystals were produced. Subsequently, other tries were successful, but the tremendous variation of outcome from carefully controlled initial conditions very strongly suggest that chaos is manifested in such growth. This is probably worth further study. In any case, the Principal Investigator hopes eventually to show that the protowhisker is fundamental in nature and precedes all commonly accepted mechanisms of whisker growth. (One possible exception is the "squeeze" or "proper" whisker grown by subjecting metals to high pressure.)

5. High Density Growth Regions: As mentioned in item 3, growth varies widely across the growth plate, and this is assumed to be due to subtle and small changes in the growth conditions. In regions where such conditions happen to be exactly right the density of protowhisker starts is extremely high : estimated to be more than one million per square centimeter (See Figure 3). From the strict point of view of production of whiskers, it would clearly be worth while trying to seek out: (a) What distinguishes such regions from other less productive ones and (b) methods to reliably achieve and maintain such conditions over large areas.
If this is truly chaotic behavior, however, a continuous variation of conditions across the field of growth may well be the only way to achieve such growth.

6. Applied Electric Fields: Fields applied by an apparatus similar to that described in Appendix I have no detectable effect upon the genesis of protowhiskers and therefore little effect upon the outcome of the runs which are terminated in 1 to 3 seconds; however, if the growth is allowed to proceed past the protowhisker stage so that ordinary whisker growth occurs, many whiskers are plucked out and appear on the top plate. This is because the levitating force is proportional to the square of the length. Clearly, regardless of the strength of the field (maximum fields used here were about 50000 V/M), there will be always be a length below which effects of the field are negligible. Results observed here must be correlated with results which go back at least a decade, and all conclusions re-examined. Scanty evidence exists that in the strongest fields applied some of the CuBr whiskers may be "plucked"! This should lead, soon (but unfortunately after expiration of this grant), to proof of claims for existence of the CuBr whiskers and some of the most definitive results yet!

CONCLUSIONS

This work, which began many years (and several grants) ago as an examination of the growth of whiskers under the levitating force of applied electric fields (thus approximating microgravity), has gradually, and unavoidably, redirected itself to a study of the genesis of whiskers. This new focus was strongly re-inforced by the discovery that under a wide variety of circumstances the ordinary growth of a whisker is virtually always preceded by formation of a whisker-like nucleus. These entities are not actually the whiskers so well described in the literature: in fact, are invisible in all of the older optical equipment used before a state of the art modern metallurgical microscope (Nikon Epiphot) was obtained (under grant # NASA-NAG-3-642). In need of a name for this hitherto un-reported entity the Principal Investigator has used the term "protowhisker" to describe them. All evidence accumulated ,so far, suggests that protowhiskers may grow by totally different mechanisms from any suggested in the literature up to now: in short, it is quite possible that we deal here with fundamentally new concepts in crystal growth. It is this that has driven the Principal Investigator to expend a major portion of his career on the project. It seems worth the gamble.

With funds running short and demands upon NASA to show "relevance" increasing and the Microgravity Section's patience decreasing, the project was given this short and vastly underfunded grant with the express requirement to show relevance to microgravity research. Have we suceeded? There are two possible answers, depending upon point of view:

1. If "relevance" means a clear, graphic, dependence of whisker growth on the presence of a gravitational field, so that such growth would be markedly changed by microgravity conditions, then we have failed.

2.If, on the other hand, "relevance" means whisker growth under conditions obtaining in the absence of gravitational fields, then we have probably suceeded rather spectacularly! Growth in vacuum deposited thin films (or in the automatic*** thin films provided by fine powders) takes place under total domination of the phenomena which control all growth in microgravity: surface tension forces, viscous drag, surface wetting forces, self diffusion, gas/solid diffusion, chemical gradients, etc. Effective gravitational forces are 10000 times smaller than those of surface tension and surface wetting. Any transport effects are totally controlled by non-gravitational convective effects such as Marangoni convection, and by diffusion. At least in this setting, we are studying growth in the very conditions which control all crystal growth in microgravity: thus we fulfill our mission daily.

***Films provided by rapid melting and spreading of fine powders.

These experiments are ploughing new ground: providing Earth-based observations of behavior under conditions not identical to, but mimicking relevant microgravity conditions exactly! Perhaps more importantly, it could also turn out that the protowhisker is actually a fundamental entity involved in the genesis of many, if not all, crystals! Those who would attack this work (as some referees already have) as not theoretically interpreted should read very carefully the fine piece by P. W. Anderson in Physics Today wherein he says, in part "we don't want to lose sight of the fundamental fact that the most important experimental results are precisely those which do *not* have a theoretical interpretation." Further: "Much more serious is the distortion of priorities, of communication, and of the refereeing process that occurs when excess weight is given to theoretical interpretation." ****

It is unfortunate that the work could not be finished within even the extended time period. It is actually a far bigger task than it appeared initially and was vastly underfunded. The Principal Investigator will continue (though unfunded) as long as circumstances permit, but unfortunately this laboratory is scheduled to be dismantled in a few months so that subsequent work will necessarily be theoretical. Clearly, each of the items numbered 1 through 6 requires more work: experimentally, more carefully controlled conditions and better instrumentation for examination of growth fields; theoretically, for meaning and generality of results. As an example consider item #5: the high density regions of protowhisker starts (hard to photograph, but shown in Fig. 3) could easily be looked upon as cusps in patterns of Marangoni-Benard instabilities, driven microvortex networks, or some analog thereof. What about items 3 and 4? is there a possibility of applying chaotic theories to such behavior? Or conversely: could such studies contribute to our fund of experimental examples of chaotic behavior? All of these items require additional work: none should be ignored.

Finally, in any measuring of the work against the funding level, it should be borne in mind that, while the Principal Investigator has expended much of his own time and resources, the actual funding level amounted to just 2 months salary for one individual plus a modest additional amount for supplies. The Principal Investigator has no regrets except for his inability to finish in time to justify further (and more adequate) funding. The results above plus those likely to come from further unsupported work should amply justify all past expenditures.

****Physics Today, September 1990, pp 9-11.

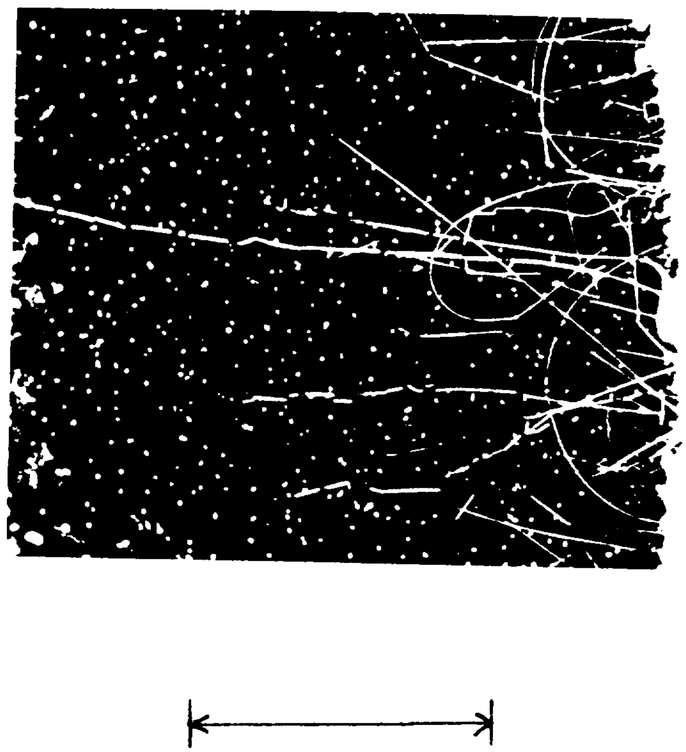

Figure 1. Cu whiskers grown from CuBr. Edge of graphite substrate shows as white area at left edge of photograph. Note several broken or interrupted whiskers: one at center of photo, two others lower down in photo. Note prolific growth near edge of graphite substrate.

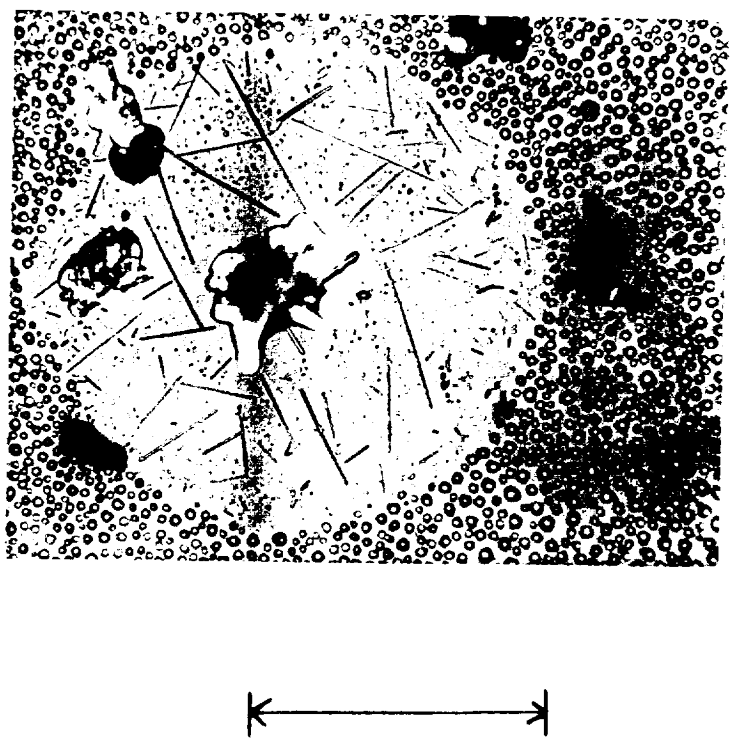

Figure 2. Whiskers of CuBr grown in Argon. Glass substrate. Large lumps are unmelted grains of CuBr powder.

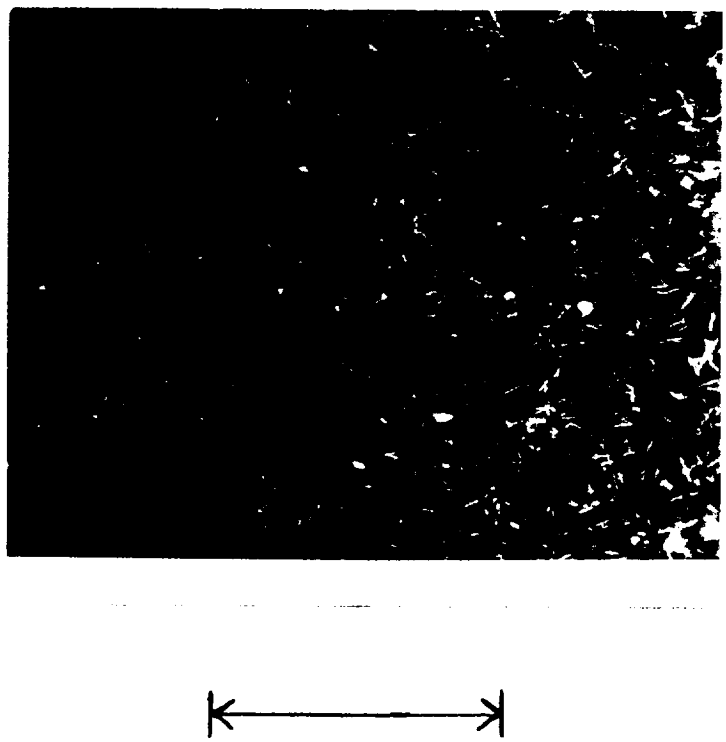

Figure 3. High density growth region. Cu protowhiskers on graphite substrate. These have been mashed down by a cover glass to make them horizontal for photographic purposes. (Such high density growth fields are usually perpendicular to the substrate and virtually impossible to photograph).

Metal Whiskers: A Convection Connection

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ABSTRACT This paper provides a brief review of work leading to a possible linkage between convection in molten growth substrates and the nucleation of metal whiskers which grow during the hydrogen reduction of metal halides.

Background The "convection connection" is but one aspect of a complex and surprising set of results arising from an extensive re-examination of the growth of whiskers during the hydrogen reduction of metal halides (Such growth was extensively studied by Brenner[1] in the 1960's) In an attempt to gain better control of this type growth the present author developed an apparatus in which such growth could be performed in an applied electric field. The new apparatus (Fig.1) also provided for routine direct visual observation of the growth. The latter capability alone provided many new insights to this process: for example, observation of base growth and tip growth occurring simultaneously during the same run. Early results using this electrostatic levitation apparatus [2] led to this project, one mission of which was to study the obvious implications that microgravity might be beneficial to the growth. Among the many avenues explored in this connection were the use of porous plugs to suppress a large and fast gaseous convection loop (which would be clearly absent in microgravity) and to perform the growth under extremely low gas pressures. All such experiments converged on the elimination of gaseous convection as a factor in the growth. Pure electrical effects cited in the original paper [2], and thought to play a significant role in the growth, were also eliminated as a significant factor during the low pressure experiments, which were conducted at pressures down to the onset of glow discharge in the apparatus.

A breakthrough occurred when free whiskers were observed in the substrate of growth runs which were purposely terminated before the onset of visible whisker growth. Subsequently, such free whiskers have been produced by several different means and verified by several means of observation. The discovery of such whiskers led to a hypothesis for a new mechanism for genesis of hydrogen reduction type whiskers which was announced in a recent paper [3] The free whiskers, thought to be formed in the molten growth halide by precipitation of supersaturated metal, are thought to be so fundamental to the growth process that the author is proposing that they be called "protowhiskers" to emphasize this fact. This new mechanism for genesis promises not only to explain most of the "mysteries" associated with the electrostatically levitated growth results, but to lead to fuller understand of all phenomena connected with hydrogen reduction type whisker growth; moreover, it may well provide the necessary directions for vast improvement of such growth.

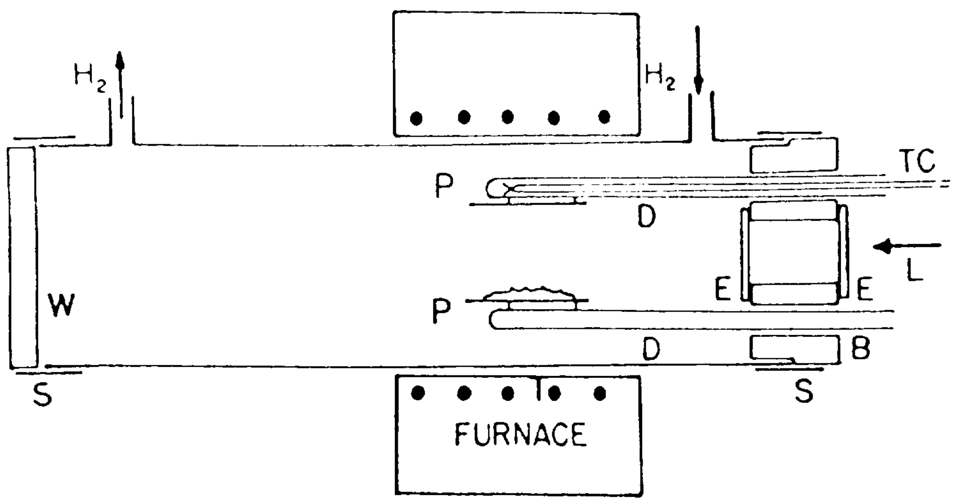

Fig. 1 One version of apparatus for growth in applied electric fields. Field is between plates (P), observation is through window (W), illumination is through windows (E). Tube was Vycor, 45 mm I.D.

Since the details, indeed full confirmation of the "convection connection" may be quite complicated and require much additional work both experimentally and theoretically, it will be presented here in the form of a hypothesis and followed by such experimental evidence as has been accumulated to date.

Hypothesis: That convection in the molten growth substrate plays a critical role in the genesis of whiskers: moreover, can even retard , or entirely prevent whisker growth from being observed.

If, indeed, the growth of (observed) whiskers is preceded by the formation of protowhiskers within the molten substrate, the following scenario is likely: first (using CuBr as an example) there is only molten CuBr immersed in hydrogen gas. The CuBr is evaporating, reduction is taking place in the gas (and at the liquid surface) forming both free copper and HBr. Because of the high accomodation of the liquid surface, much of the released copper will enter the surface. In the absence of convection, the concentration of copper in the CuBr would build up rapidly in a thin layer near the surface and precipitation of copper (as protowhiskers) would be expected. In the presence of convection, on the other hand, the concentration of copper would build up slowly throughout the melt, and such precipitation would be delayed for very long periods (depending upon the surface to volume ratio of the melt). Protowhiskers would form in any case, but after long periods most would be amalgamated into a massive deposit of reduced metal and completely escape observation. Those protowhiskers whose tips emerge from the substrate could grow by any of the accepted modes: that is, by deposition of metal atoms at surface steps provided by emergent screw dislocations, indeed, even by VLS droplets on the tips, as described by Nittono et.al.[4]. If a levitating electric field is present, such emergent whiskers may be drawn out until their bottom tips are within the high concentration thin layer at the surface whereupon growth could proceed both by these various tip mechanisms and by the protowhisker mechanism within the surface! The very long, fine, whiskers occasionally seen when the field is present are thought to be those in which the latter mechanism dominates. Thus we are led to the hypothesis above. Convection in the substrate may play a large and quite negative role in the growth of long fine whiskers, and efforts to counteract, or avoid it seem justified.

Experimental Evidence for the "Convection Connection"

1. In ordinary growth with larger amounts of starting material, it is often the case that the most prolific growth is seen in regions where the substrate was thinnest.

2. Success of electrostatic levitation in producing unusually long thin specimens.

3. Unusually prolific growth when using very small amounts of starting material (which results in spreading of molten substrate into a very thin layer).

4. Unusually prolific growth in thin films of metal halide evaporated and re-deposited in annular regions surrounding a tiny speck of starting material.

5. Extremely rapid growth starts (6 sec) using small amounts of starting material in low heat capacity apparatus designed for extremely rapid temperature rise.

6. Actual growth of protowhiskers within vacuum deposited thin (about 1 micron) films of metal halides.(See Fig. 2)

Experimental Evidence for Protowhiskers (Though not really the subject of this paper, they provide the basis for the "convection connection": thus, evidence for their existence is summarized here.)

1. Production and observation by several different means: dissolving away the un-reduced halide from runs terminated before observed whisker growth; looking into solidified (transparent) substrate from incomplete growth runs performed on thin glass plates, growth within vacuum deposited thin films. (see Fig. 3)

2. Observation of protowhiskers by the above techniques within different growth media: copper, iron, silver, cobalt, and chromium.

3. Observation of protowhiskers in halides "doped" with excess metal, then quenched and subsequently annealed or melted.

4. "Hydrogenless" reduction: growth of whiskers by selective evaporation from "doped" halides (halide distilled off thus concentrating the metal).

5. Observation of similar structures in solid silver halide by precipitation of silver atoms released by ultraviolet light by Childs and Slifkin [6]

6. Growth of protowhisker-like structures within vacuum deposited thin films of metal halides.

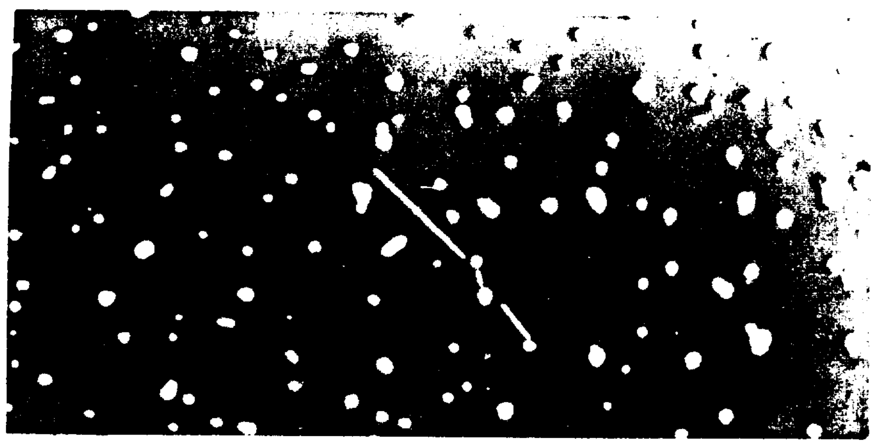

Fig. 2 Copper whiskers grown by reduction of vacuum deposited film of CuBr. (The long one is about 100 microns: diameter less than one micron.)

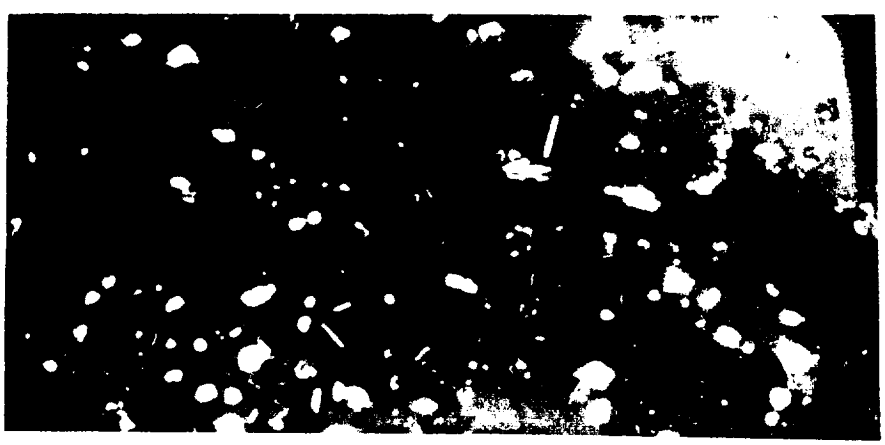

Fig. 3. Copper protowhiskers seen in CuBr from interrupted growth on thin glass plate. Scale is same as in Fig. 2.

Comment on the Relationship Between the Protowhisker Idea and the VLS Growth Mechanism Wherever this work is presented there is always some comment regarding the relationship between the protowhisker precipitation scheme and the VLS mechanism of whisker growth [6]. Clearly, a relationship exists, but it should be borne in mind that the protowhisker is a free whisker grown within a supersaturated growth medium, whereas VLS utilizes the idea of a droplet affixed to the tip of a growing whisker to account for both growth and for unixaiality of the growth. There is little doubt that VLS may be active, but would play the role of one of the secondary growth mechanisms after the protowhisker has emerged from the molten substrate.

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