(NASA-CR-175440) TERRESTRIAL WHISKER GROWTH EXPERIMENTS WHICH ANTICIPATE SOME SPECIAL EFFECTS OF A SPACE STATION ENVIRONMENT Final Report (George Washington Univ.) 21 p HC A02/MF A01 CSCL 11D G3/24
N84-20647
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# FINAL REPORT

NASA Contract # NASW-3754

Entitled:

Terrestrial Whisker Growth Experiments Which Anticipate Some Special Effects of a Space Station Environment

Submitted by:

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## Part I: Summary of Results

### Primary Goal:

The primary goal of this research was to determine, using methods and apparatus developed by the principal investigator, whether the absence of gravitationally driven thermal convection (to be expected in the space station environment) would prevent or drastically effect growth of whiskers by chemical reduction of metal salts. This goal has been achieved in that it has been possible to accomplish nearly complete suppression of such convection here in our laboratory. The results of experiments carried out under this project show that suppression of the convection does indeed effect the growth but in subtle, not necessarily detrimental ways: none of the changes observed are such as to hamper efforts to produce whiskers in space!

### Other Goals:

While all other goals in this project were addressed, and some measure of progress made in each, it should be kept in mind that the period of performance of this contract was extremely short and required that precedence be given to the primary goal. Many aspects of this work are of profound and fundamental scientific interest and it is hoped that NASA may see its way clear to extend support on a more long-term and appropriate basis. The following is a short statement on each of the remaining goals.

1. "Determine which materials show most promise for growth in gravity-free environment."

The experiments, thus far, suggest that copper whiskers grown from cuprous iodide respond most positively to the suppression of convection; therefore, they are strongly recommended for tests in the space environment. On the other hand, cobalt whiskers grown from cobaltous bromide show the greatest independence from conditions of convection and applied electric fields of any material studied; therefore, this medium is highly recommended.

2. "Study the electric currents accompanying the growth in applied electric fields".

This effect, quite possibly the most important from a long-term scientific point of view, was necessarily given secondary importance in this project because of the shortage of time. The most dramatic result is a clear demonstration that these currents are <u>not</u> simply a side effect of the large convection loop in this growth apparatus. Currents were measured whenever possible and the effects on them of suppression of the convection carefully noted. The effects are, again, subtle rather than drastic, and are shown in the body of this report.

3. " Formulate procedures for growth in gravity-free environment".

The lack of any drastic effect due to suppression of the convection makes it possible to take over, with only minor modifications, the procedures described in Appendix I. That type apparatus, with suitable safety precautions, may be used but with electric fields just strong enough to promote alignment of the whisker leaders. A strong pulse of electric field may be occasionally applied to the plates to extract the whiskers from the molten substrate and greatly facilitate harvesting the growth.

## Part II. Description of the Experiments

Appendix I of this report is a reprint of the paper which describes the method developed by the author for growth of whiskers by chemical reduction in applied electric fields. The results described herein were obtained using that method with suitable modifications and extensions; for example, the convection studies apply to the convection loops occuring in the Vycor growth tubes described in that paper etc. It is therefore suggested that the reader first peruse Appendix I unless already familiar with that work. Background and contemporary references for this work will also be found in the bibliography of that paper.

### Evidence for Existence of Strong Convection Currents in the Growth Apparatus.

The author first became aware of the strong convection loops in this growth apparatus upon noting the spiral patterns which occasionally appear at the entrance and/or exit of the furnace. These patterns are produced only during very long runs, are sometimes very faint, and are deposits of growth source material (such as cuprous iodide). They represent intersection of flow patterns with the walls of the tube, but the impressive thing is that the crispness of the pattern which is laid down very gradually (runs lasting over ½ hour) suggests that the currents must be very very stable! Figures 1 and 2 show such patterns and also show that scale is not a factor, since the growth tube in Figure 2 has twice the diameter of that of Figure 1. The convection loops were studied as a part of this project and a rough description of the loops gleaned from visual observation is shown in Figure 3. The currents were rendered visible by releasing small quantities of ammonium chloride at various locations inside the furnace. This decomposed forming a white "smoke" which rendered the flow patterns visible. Estimates of flow velocities were made by observing the flight of individual particles of ferrous chloride released during the growth of iron whiskers. These particles are thin plates which "float" along the flow lines and provide very graphic views of the convection currents. The convection loop is roughly the same at entrance and exit, but the division between the two loops is not not necessarily at the exact center of the furnace. Figure 5 illustrates the kind of photographic data available in this apparatus. The flow had maximum speed near the top and bottom of the tube in the region labeled A in Fig. 3.

| Typically: | | |
|---|---|---|
| | Speed of flow in region A ---------------- | 5 to 15 cm/sec |
| | Gas in tube-------------------------------- | Nitrogen |
| | Linear flow rate of gas------------------- | 0.062 cm/sec (3.7 cm/min) |
| | Furnace temperature | 700 °C |
| | Tube diameter------------------------------ | 45 mm |

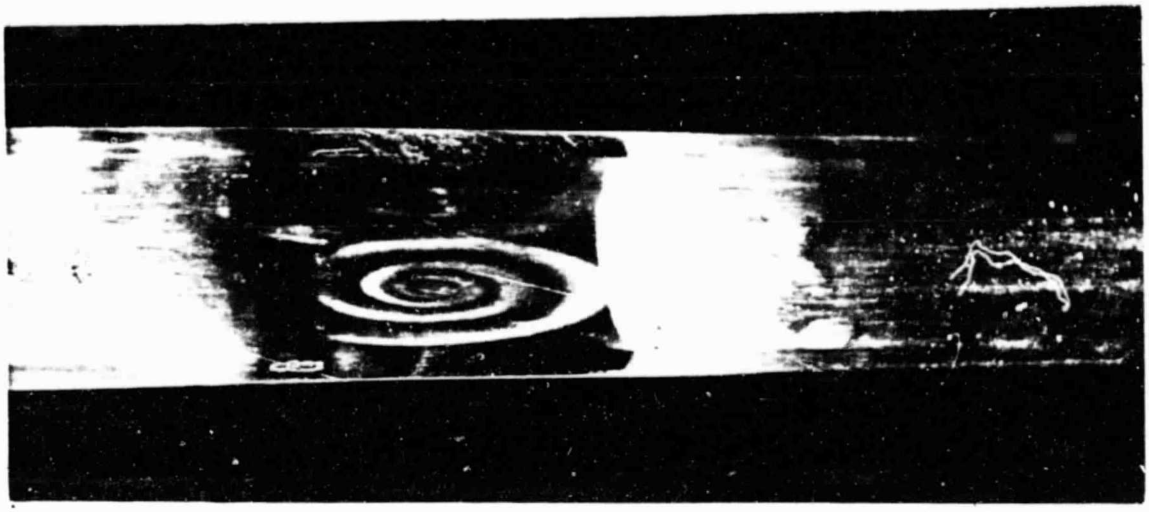


Figure 1. Spiral patterns at entrance to furnace on Vycor growth tube ( 25 mm I. D. tube).

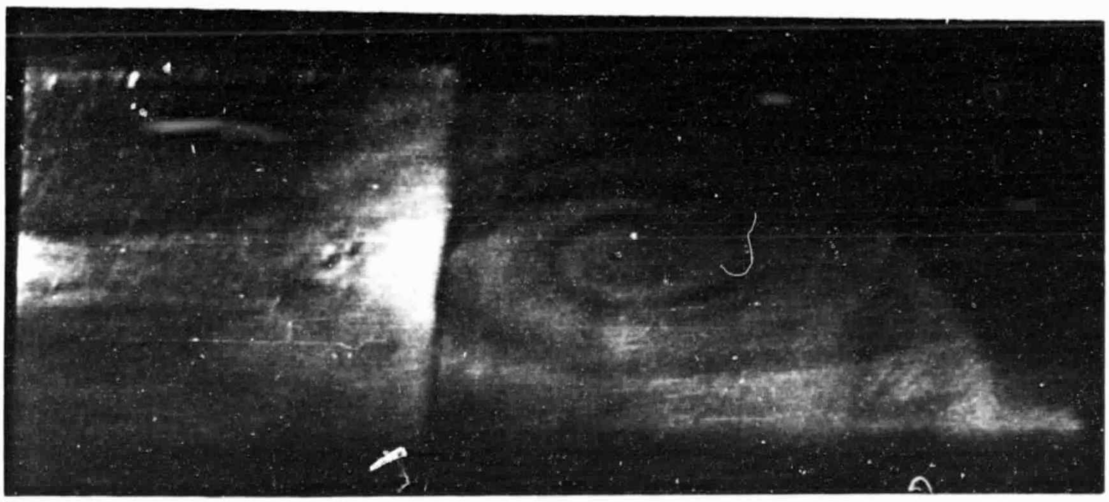


Figure 2. Spiral patterns at entrance to furnace on Vycor growth tube ( 45 mm I. D. tube).

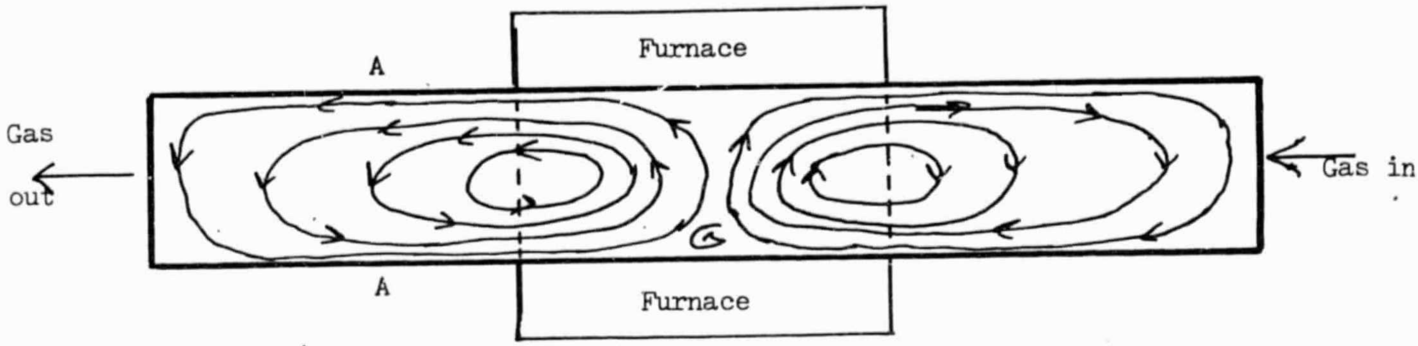



Figure 3. Flow lines deduced from observations of smoke patterns, and particles drifting with the flow. G is the growth region.

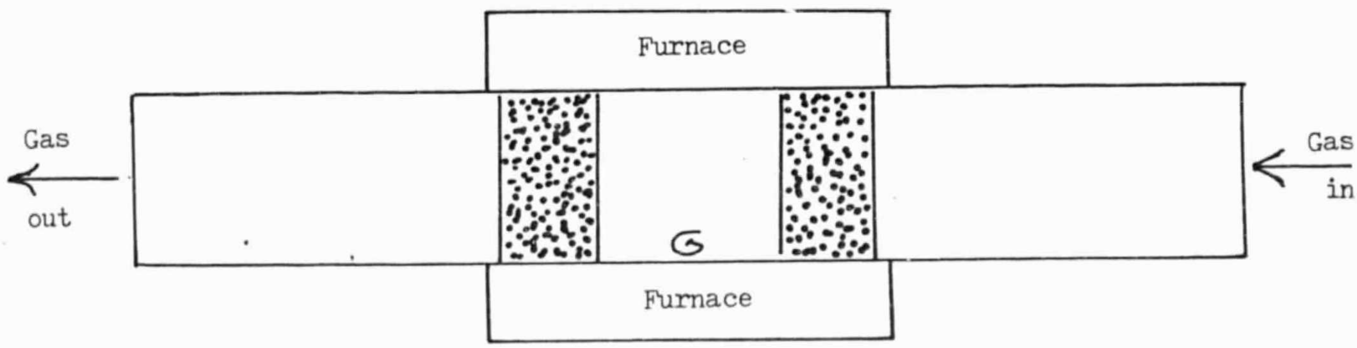
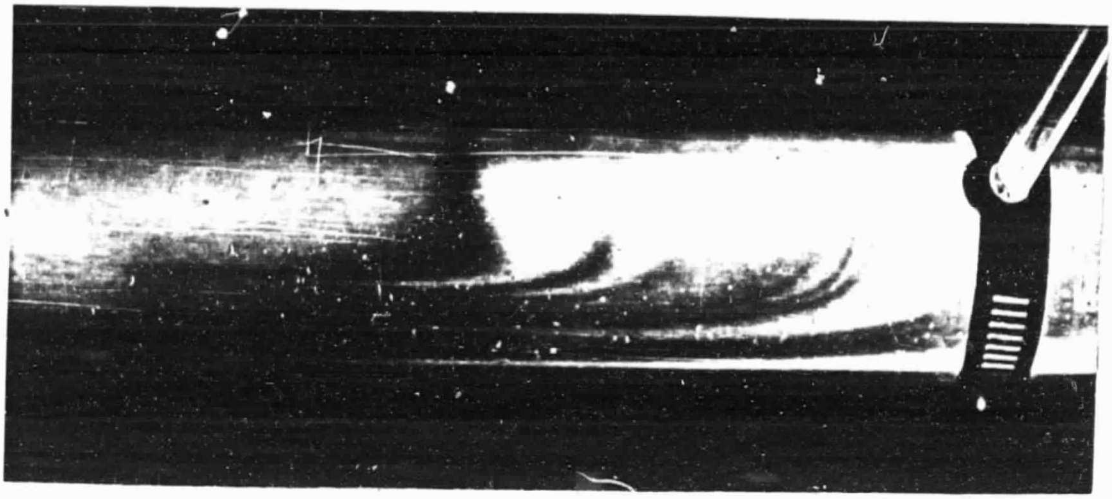
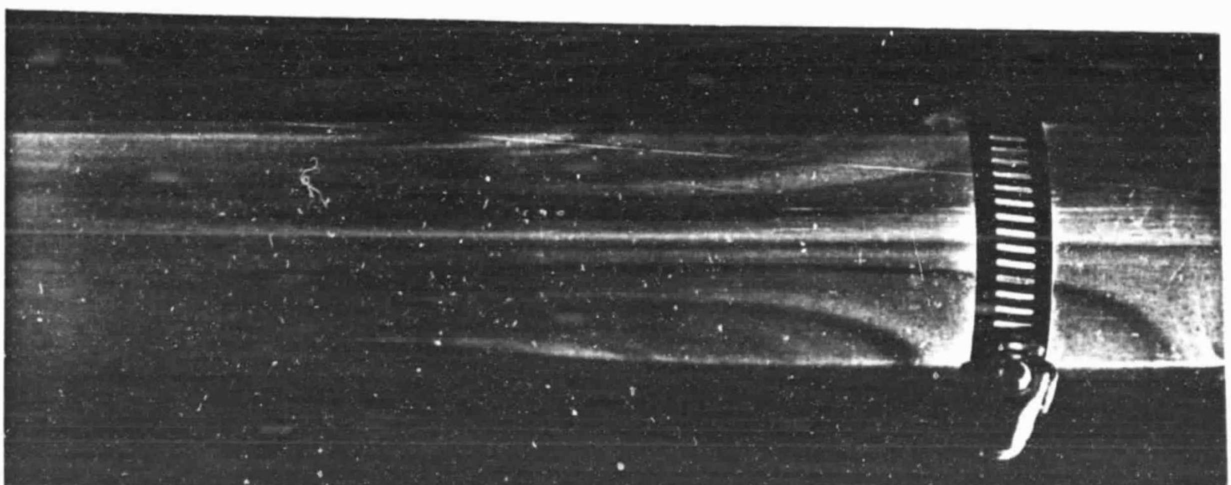



Figure 4. Sketch of growth tube in furnace with porous plugs. (Porous plugs are the stippled objects.) G is the growth region. Plugs are made of compressed alundum fibers.



Side View



Bottom View

Figure 5. Patterns traced in downstream end of 45 mm Vycor growth tube using "smoke" from ammonium chloride injected into the growth region. In these photographs "downstream"is to the right: that is, gas exits the tube to the right, and furnace with growth region is to the left.

Suppression of the Convection Loop.

The cause of the main convection loop is ~~obviously~~ obviously the tremendous thermal gradient encountered by the gas as it enters or leaves the furnace. During the growth of cobalt whiskers, for example, the temperature drops about 500 degrees in the last 10 cm before the gas exits the furnace. Suppression of the major part of this loop is easily accomplished, in principle, by the insertion of porous plugs in the growth tube as shown in Figure 4. The currents between the porous plugs were not observed but are assumed to be very small by comparison to the unsuppressed currents. The thermal gradients in the central regions of the furnace were measured and found to be less than 0.05 $^{o}$C/cm with the porous plugs in place.

In practice insertion of the plugs was found to be extremely difficult with the original apparatus (as in Appendix I) because of the two thermocouple wells and the delicate growth plates affixed to their ends; accordingly, a new configuration was developed using one cylindrical electrode which just fits inside the growth tube and a single graphite-coated thermocouple well on the axis of the cylindrical electrode. The growth material is placed on the bottom inside portion of the cylindrical electrode and growth proceeds much as before. Of course, this step complicates estimates of the applied electric field which increases in intensity as the axis is approached. Electric fields quoted here are rough values and apply to the region near the surface of the cylindrical electrode (where the whisker leaders appear). Whiskers will now be growing into stronger electric fields as they increase in length. The porous plug is now moulded around the single thermocouple well and inserted into the growth tube after the cylindrical electrode with its growth material is in place. The plug in the downstream end is easily inserted. The porous plug which contacts the thermocouple well must be changed after each growth run since it also contacts the wire which connects the cylindrical electrode to the outside of the growth tube. It tends to become contaminated by the vapor of the growth material as well as by reduced metal and gives rise to spurious electric currents. More than 100 runs were made in various versions of the apparatus with and without plugs, and with various growth materials. The results are deemed sufficient to put to rest any notion that absence of the large convection loop would stop or even hinder the whisker growth process. The effects were clear and observable, but subtle and different for different growth material. A summary of results are shown below. Effects of convection suppression on growth currents will be shown in a later section of this report.

Effect of Suppression of Convection on Whisker Yield

| | |
|---|---|
| Copper whiskers grown from cuprous bromide | Yield of long fine whiskers slightly better. Total number in yield about the same. |
| Copper whiskers grown from cuprous iodide | Yield of long fine whiskers dramatically improved. |
| Cobalt whiskers grown from cobaltous bromide | Yield of all types about the same with or without convection. |

Other Methods of Suppressing Convection.

As mentioned in the proposal, it was also considered useful to try to change the convection by using the growth tube and furnace in a vertical configuration. An apparatus was constructed using a cut-down Vycor tube, vertically oriented in a crucible furnace. Even though it worked, after a fashion, and actually grew cobalt whiskers, it had special problems and was too time consuming (runs took about 4 hours each) for the time frame of this project.

As a final check on the porous plug experiments, a few runs were made in the original configuration (as in Appendix I) but with a Vycor cylinder sandwiched between the growth plates. This completely isolates the growth region from any currents in the main tube (see Figure 6).The runs made with this apparatus showed results quite similar to those with the porous plugs and so will not be discussed further here. Although this scheme was conceived late in the project and not used extensively, it is the neatest, the most convenient, and will probably be used in future studies.

Attempts to Extend the Range of Available Growth Materials.

A number of new materials and procedures were tried and,while some showed promise, the shortage of time required that they be set aside as temporarily unsuccessful: these were, nickelous bromide, chromous chloride, and cobaltous chloride. In addition, a procedure using methane as a reducing agent in place of hydrogen was tried but set aside without notable success. Silver whiskers were produced from silver bromide, and actually constitute a "first" since that source material has not been used before, but again time did not permit further development of that material.

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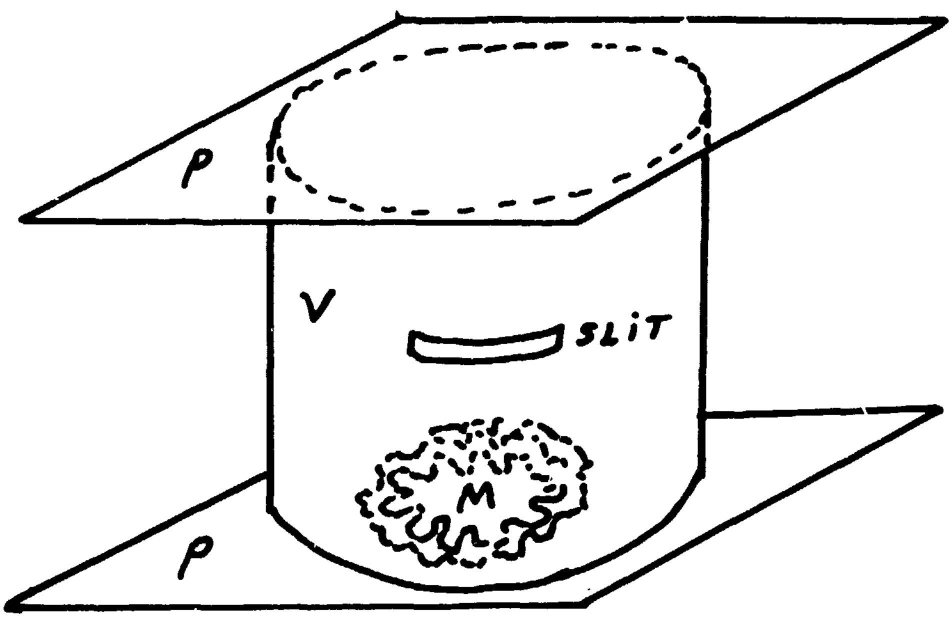


Figure 6. Sketch of Vycor cylinder, V, enclosing the growth region. Cylinder diameter is 25 mm I.D. The metal plates P (as in Figure 1 of Appendix I) are in contact with the ends of the cylinder. Gaseous exchange between the growth region and the ambient gas flowing through the growth tube is by diffusion through two slits (only one shown in sketch) in the side of the cylinder.

Production of Long Cobalt Whiskers.

Since Brenner's definitive work it is commonly assumed that cobalt is not a good medium for whisker work because of the impossibility of growing cobalt whiskers longer than about one or two millimeters (See Refs. 1, 2, 3, 4 of Appendix I). This project has produced a new approach which produces cobalt whiskers which are very fine and frequently longer than 10 millimeters. The surprising thing about the cobalt is that once the crux conditions are established, the drive to remain in the whisker mode is stronger than in many other materials. The crux is twofold: first, the hydrogen must be withheld from the growth region until the growth material (cobaltous bromide) has melted, and second, the hydrogen is introduced only at very low partial pressure ( 5 % of normal atmospheric pressure, or less). The procedure developed here will be the subject of a paper to be published as soon as possible, but for users of this report the detailed procedure is as follows:

Using the cylindrical electrode set-up described earlier, start with 140 milligrams of cobaltous bromide (Spex UHP) spread over 2 square centimeters of the center portion of the cylindrical electrode (at bottom of growth tube). Purge the growth tube with pure nitrogen (Carrier grade UHP) and with the growth region outside the furnace (as in Appendix I) bring the furnace to 700 °C. Now insert the tube so that the growth region is centered in the furnace and monitor the temperature. As the temperature passes through the melting point of cobaltous bromide (678 °C in nitrogen) start the flow of hydrogen at linear flow rate of 3.7 cm/minute (in 45 mm I. D. tube). Growth will occur whether or not the tube has porous plugs, and whether or not an electric field is applied across the electrodes. The best crops occurred in this laboratory with an applied field of about 100 volts per cm (near the surface of the cylindrical electrode).

As mentioned above, one very impressive thing about the cobalt growth is the tremendous tendency to maintain whisker-like (high aspect ratio) growth once proper conditions have been achieved. This tendency is perhaps exemplified by some unusually long and not very pretty specimens which maintain the growth in spite of kinks, branches, changes of orientation, and growth in a tight helix. One such specimen required 30 photographs at the magnification of Figure 7 to tell its story. It had a length of nearly 2 cm, which is something like 5000 times its diameter. Figure 7 is an example of this persistence of the whisker form.

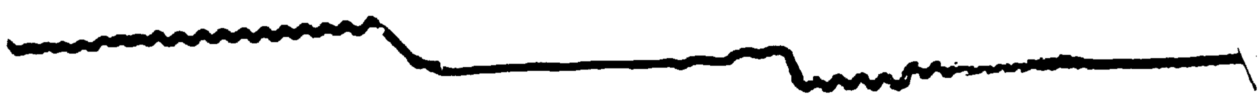

Figure 7. Highly magnified view of a portion of a cobalt whisker. At the left side the whisker has just changed from straight (not shown) to a low pitched helix. After two pitch changes and a short straight portion, there is a wiggle, then a long straight portion followed by several more helical modes etc.

Studies of Currents Accompanying the Growth.

These currents, referred to as "growth currents", remain a mystery as discussed in Appendix I, but their behavior has been monitored wherever possible and has been further explored during the course of this work. The most valuable contribution of this project to their understanding is, of course, the clear demonstration that they are not a direct result of the convection loop. Suppression of the convection changes them subtly, but they persist and in fact are somewhat stronger in the absence of convection. They remain an excellent indicator of the state of the growth process during a given run: virtually no growth has been observed after the current passes through its maximum point. The shape of the "growth current curve" has a shape characteristic of the source material: a sort of "signature". It is even sensitive to the "batch" of source material, as is the whisker growth itself. The cylindrical version of the growth apparatus is better suited to studying these currents than the parallel plates and gives more reproducible results. The currents shown in Figures 8 through 13 illustrate some of these effects. They are "typical" currents: that is, reproducible providing everything else stays the same and there are no "glitches", such as leakage across insulators, whiskers growing across the gap and shorting, open circuits along the graphite coating on the thermocouple well, etc. Some 100 runs were made and the tapes are on hand for further study.

Remarks on Figures 8 through 13.

Figures 8, 9, and 10 are tracings of dual pen recorder tapes of runs # 221, # 225, and # 227, in that order. All started with 140 milligrams of cuprous bromide in hydrogen flowing at a linear flow rate of 3.7 cm per minute. All were with applied electric field of roughly 100 volts/cm directed vertically upward (bottom plate positive), and all in the 45 mm I.D. growth tube. Figure 8 is with the convection loop present, Figure 9 is with the convection loop suppressed (porous plugs in place) and Figure 10 (which should be the same as Figure 8) is with convection loop present but using cuprous bromide from a different batch of starting material.

Figures 11, 12, and 13 are a similar series. They are runs # 252, # 255, and # 279. Each used 140 mg of cobaltous bromide in diluted hydrogen admitted in accordance with the schedule described in the text. Figure 11 is with convection loop present, Figure 12 is with the convection loop suppressed (plugs in place), and Figure 13 is same conditions as Figure 11 but using a different batch of material. The material in the runs of Figure 11 and 12 is Spex U.H.P, and grew excellent whiskers, That in run of Figure 13 is Fisher Purified and grew a very poor crop.

In all of these figures the temperature pen is offset from the current indicating pen by 1.1 cm which amounts to about 1 minute at the speeds used in these runs. This means that the temperature graph is 1 minute ahead of the corresponding current reading. To synchronise temperature and current the temperature graph must be displaced 1.1 cm to the left.

In the cobalt run of Figure 12 the large residual current remaining after normal growth time has expired is caused by contamination of the alundum of the porous plug by the growth material and by reduced cobalt. This is a serious drawback to any critical analysis of currents with the plugs present.

Temperature (Each unit represents 100 °C) (Broken Line)
Growth Current (Each unit represents $3 \times 10^{-7}$ amperes) Solid Line

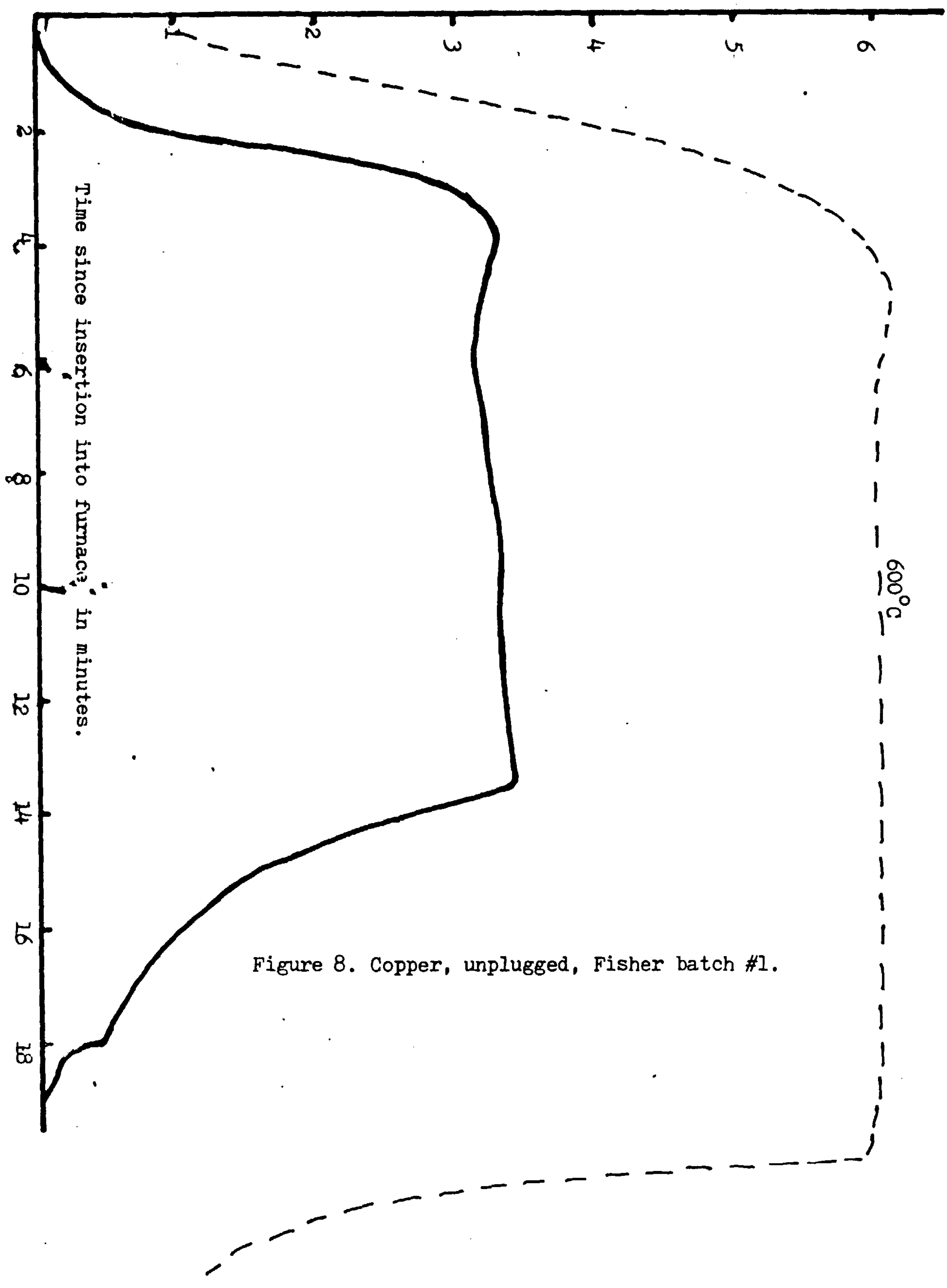


Figure 8. Copper, unplugged, Fisher batch #1.

Temperature (Each unit represents 100 °C) (Broken Line)
Growth current (Each unit represents $3X10^{-7}$ amperes) (Solid Line)

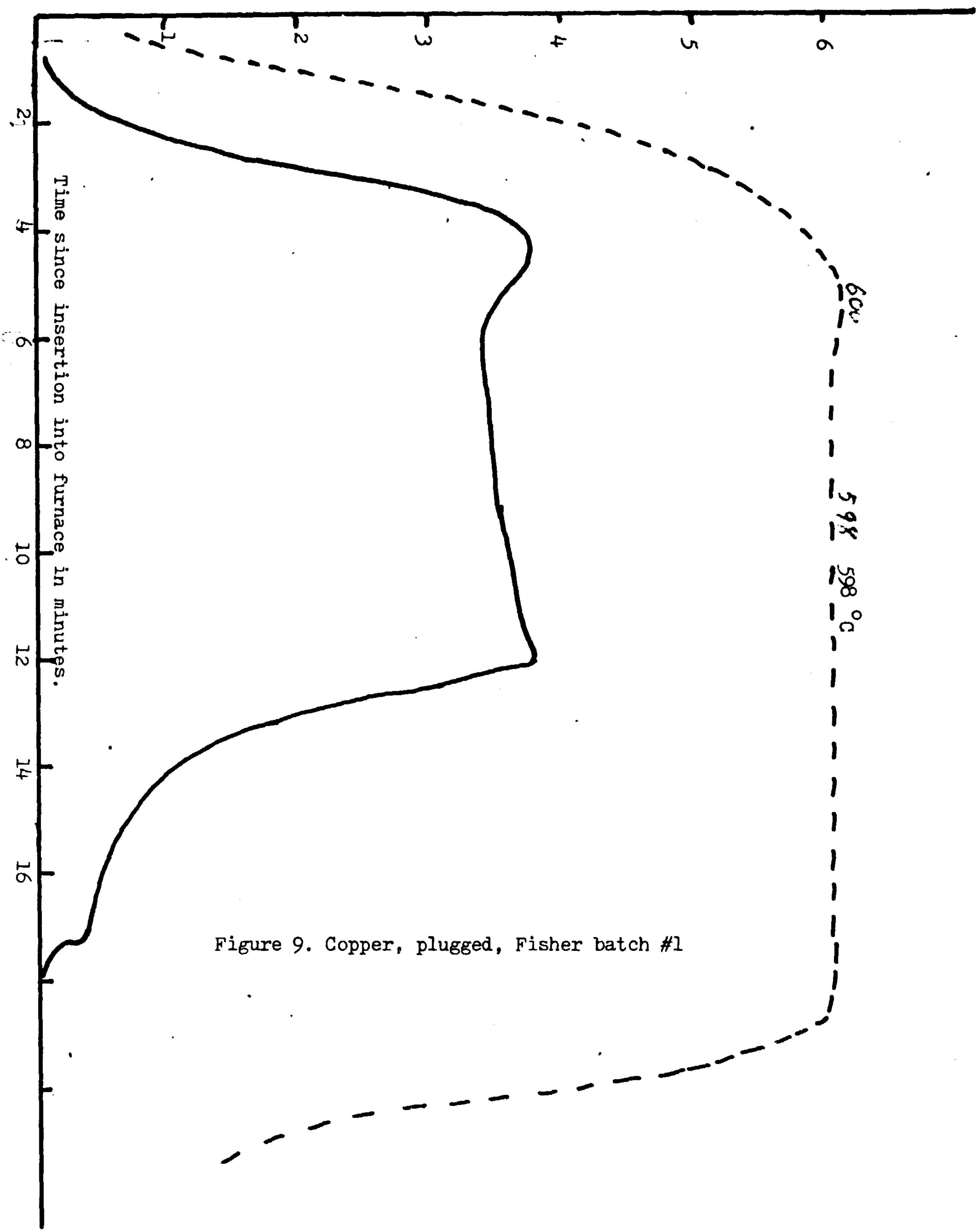


Figure 9. Copper, plugged, Fisher batch #1

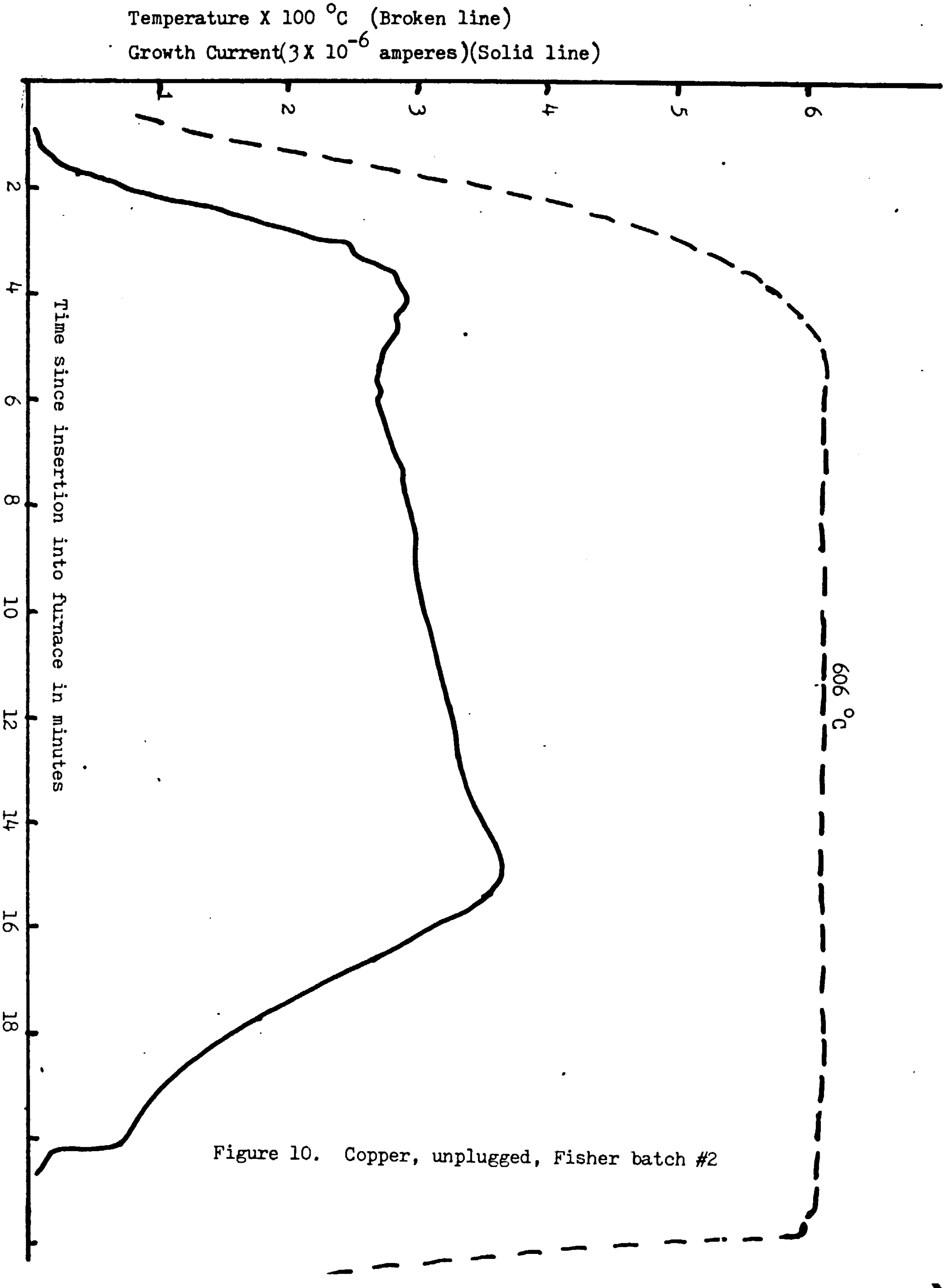


Figure 10. Copper, unplugged, Fisher batch #2

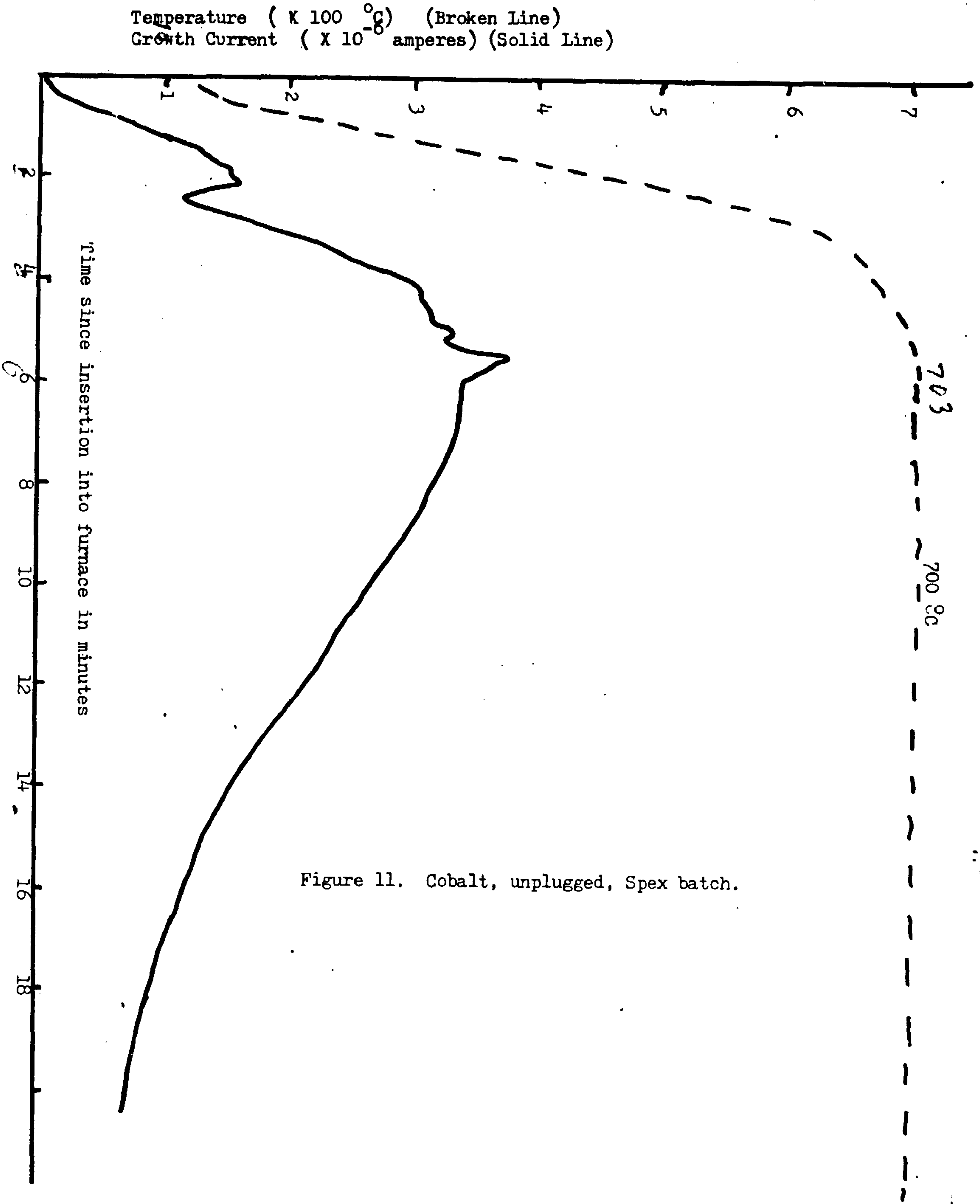


Figure 11. Cobalt, unplugged, Spex batch.

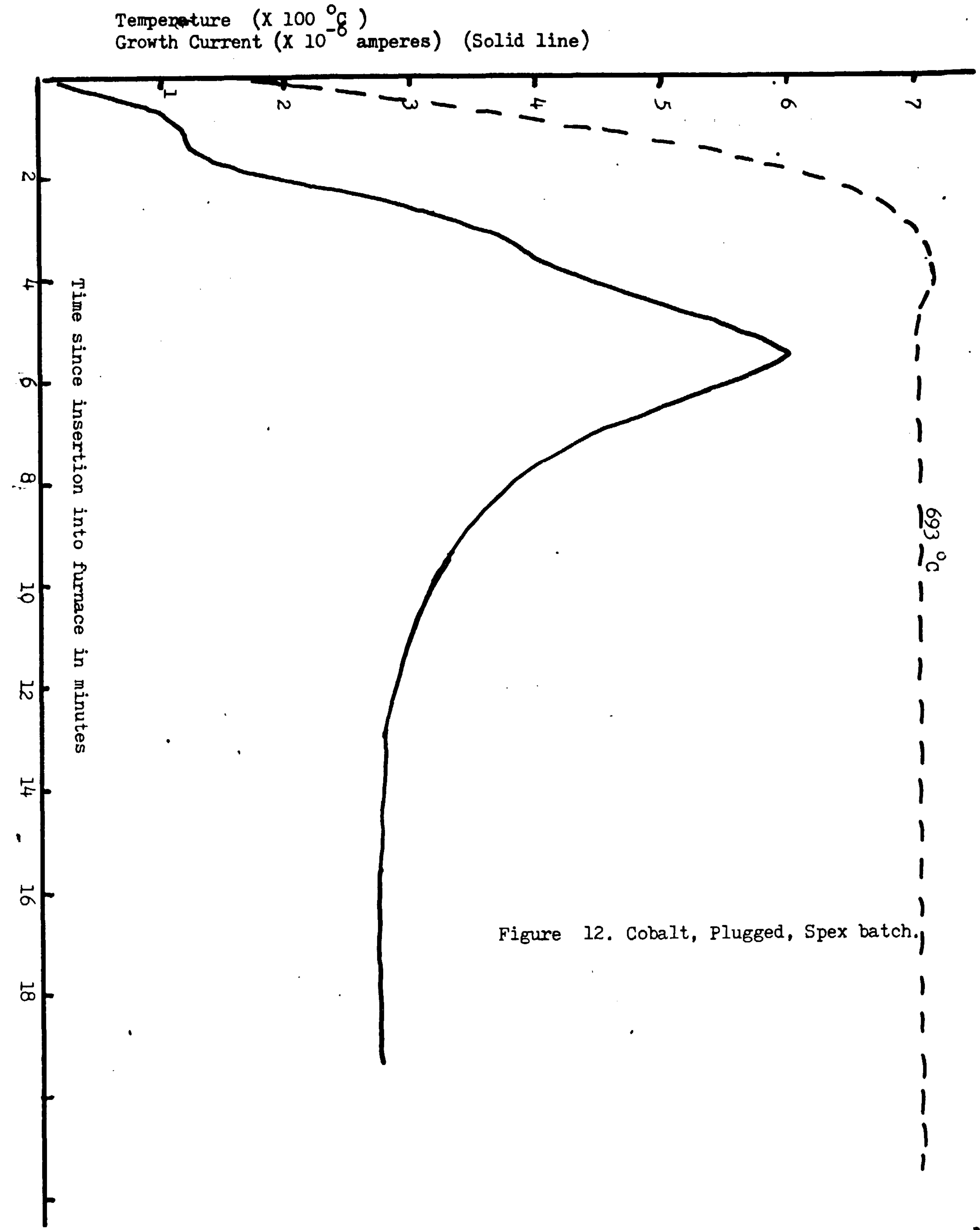


Figure 12. Cobalt, Plugged, Spex batch.

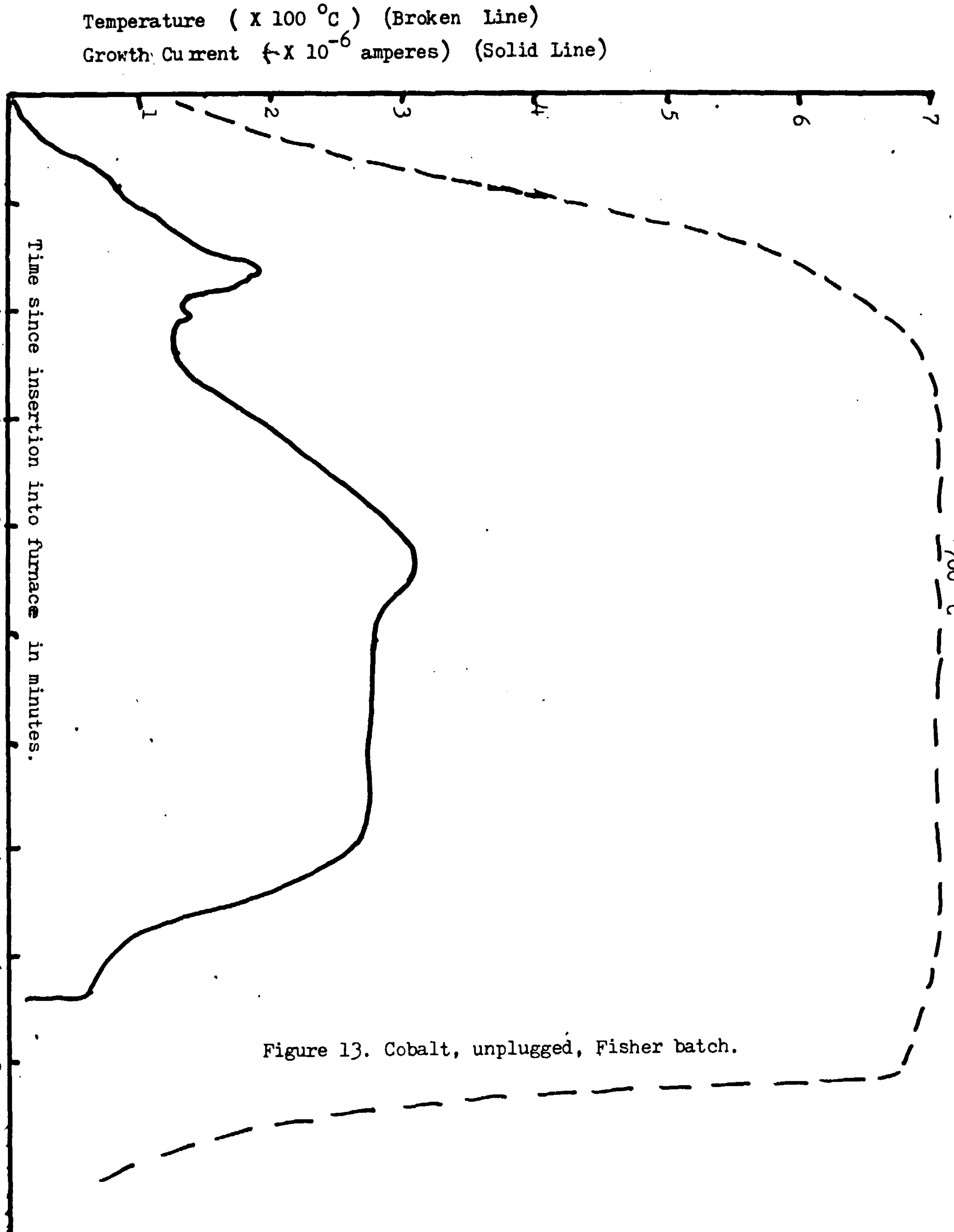


Figure 13. Cobalt, unplugged, Fisher batch.

## Part III. Final Recommendations

Since suppression of the convection subtly modifies but does not prevent, or even noticeably hinder, whisker growth, we may conclude that the absence of gravitationally driven thermal convection in the space station environment presents no obstacle to experiments such as those conducted in this project. Clearly, the procedures outlined in Appendix I could be followed without serious modification. The applied electric fields can be weaker by, perhaps, an order of magnitude: just sufficient to provide alignment of the whisker growth leaders. One additional step, which has been tried in this laboratory, is to apply a strong pulse cf electric field to "snatch" the whiskers from the molten substrate. The "snatched" whiskers rise to the top plate and stick there (probably spot welded by their own residual charge) in a perfect position for study or for "harvesting".

The ready vacuum which is available just outside the space laboratory could be a real asset, especially in the case of growth of cobalt whiskers. These whiskers grown in highly diluted (low partial pressure) hydrogen. Such dilution is the cheap and safe way to achieve low partial pressures in the terrestrial laboratory. On the space station it is recommended that the growth vessels, with their furnaces be mounted outside the laboratory: communitating with the inside by means of double vacuum valves (airlocks) and gas service lines. The pressure in the vessels is then controllable by simple reducer valves exhausting to the zero pressure of space. Note that this is quite safe, even compared to earth laboratories, since all gas pressures are positive and all leaks are to space! On earth, working with hydrogen at reduced pressures and high temperatures is highly dangerous because all leaks are air and are <u>into</u> the apparatus itself. Locating the growth vessels outside the spacecraft also has the advantage of lowering the power requirements of the furnaces. Another safety consideration in the space laboratory is release of noxious fumes ( all of these growth experiments release poisonous gases) which will be neatly and completely taken care of by mounting the growth vessels in space. Exhaust at positive pressure and at the elevated temperatures involved in this growth will drive all gases clear of the vicinity of the spacecraft.

Whisker growth experiments in space will take their priorities from many scientific as well as non-scientific considerations. From the point of view of this worker they are highly recommended and his services are offered herewith in <u>any</u> capacity if the decision is made to include them in the program.