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EFFECT OF ADSORBED NITROGEN ON THE THERMIONIC EMISSION FROM LANTHANUM HEXABORIDE

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EFFECT OF ADSORBED NITROGEN ON THE THERMIONIC EMISSION FROM LANTHANUM HEXABORIDE

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SUMMARY

The emission properties of lanthanum hexaboride in an atmosphere of nitrogen were investigated. The emitter was not poisoned by adsorbed nitrogen. This result should have application to magnetohydrodynamic devices in which electron flow from channel walls is required.

INTRODUCTION

A study of possible applications of magnetohydrodynamics, with emphasis on plasma accelerators, has shown that one of the walls of the channel through which the plasma flows must become an emitter of electrons to close the current circuit through the plasma. Reference 1, in fact, cites the problem of obtaining current flow through a wall as being of particular significance. A plasma accelerator of one type that has been proposed requires that there be no discharge and therefore requires low electric gradients. It follows that field emission or emission by positive ion bombardment of the surface cannot be used. Thus, thermionic emission must be considered. The usual condition of a good vacuum, however, cannot be realized, but the emission must occur in the presence of a gas at pressures up to atmospheric. Air would be a desirable choice for the gas, of course, but at the high temperatures ($3,000^{\circ}$ Kelvin) required for thermal ionization of seeding material, oxidation is too much of a problem. Nitrogen would be a good second choice because it is a major constituent of air. The presence of nitrogen, however, frequently poisons (greatly reduces) the electron emission from a surface whether the emission be thermionic, field-induced, or photoelectric. This poisoning is thought to be caused by the gas molecules adsorbing on the surface and becoming polarized in such a direction that the work function of the surface is increased. The emission current I is an inverse exponential function of the work function ϕ divided by the temperature T $\left(I \propto e^{-\phi/kT}\right)$, and the work functions of good emitters and the temperatures at which they can be used (which are limited by evaporation and/or melting of the emitter) have values such that their ratio is rather large. This ratio is large enough that the change in its value due to poisoning by adsorbed gases can change the emitted current by a factor of several powers of 10. (See ref. 2.) Some typical examples of poisoning of emitters are: (1) the adsorption of oxygen on thoriated tungsten at 10^{-14} millimeter of mercury (ref. 2), (2) the adsorption of a few parts per million of oxygen on barium-strontium oxides (ref. 2), and (3) the adsorption of nitrogen on tungsten (refs. 3 and 4). There is evidence that nitrogen in some cases decreases the work function (ref. 5), in some cases increases it (refs. 3 and 4), and in some cases has no effect (ref. 6). Available evidence and prevailing opinion were against the expectation of any appreciable rate of thermionic emission of electrons in the presence of nitrogen at pressures of the order of an atmosphere.

The solution to the problem of poisoning appeared to be so necessary, however, that considerable attention was given to the problem. In vacuum technique, surfaces can be outgassed by heating them, in a good vacuum, to temperatures that approach their melting points. Glass, for example, that softens at 425° C is usually outgassed by heating to 400° C. Tungsten, which melts at 3,350° C, can be outgassed by heating to about 2,700° C. This procedure results in rather rapid outgassing. Much slower rates, of the order of hours, result when the temperature is much less than the melting point. It was thought that possibly a thermionic emitter could be depoisoned (outgassed) by heating it almost to its melting point, even in the presence of gas, rather than in a good vacuum. In the experiments reported herein, the emitter was not heated to a high enough temperature to drive off the adsorbed nitrogen rapidly, but the attempt led to the discovery that nitrogen not only did not poison the emitter that was used (lanthanum hexaboride) but actually enhanced the emission rate.

APPARATUS

Lanthanum hexaboride was chosen as the emitter. It has been studied and developed by Lafferty (ref. 7), who made a thorough investigation of its properties, of which there are a number of desirable ones. It is commercially available and ready for use in powder form, but, when sintered, it can be machined. It is therefore physically rugged. It is chemically stable, unaffected by oxygen or moisture at room temperature, easy to activate, and has an emission rate per unit surface area that, at a given temperature, exceeds that of any other known emitter except those of the barium-strontium oxide type. It has a reasonably high melting point (2,175° C) and the lanthanum evaporated from its surface is completely replenished by diffusion from within at temperatures up to 2,000° C.

The emitter was mixed with amyl acetate to form a paste which was packed into a graphite cup. The inside diameter of the cup was

0.207 centimeter and the area of the emitter was thus 0.034 square centimeter. The cup was held in a small hollow molybdenum cylinder. (See fig. 1.) The cathode-to-anode gap was set at 0.08 centimeter. Ample heating power was provided by two 100-watt tungsten-filament heaters mounted adjacent to the molybdenum cylinder. Three molybdenum cylinders surrounded the assembly to serve as radiation shields. The anode was made of tantalum, and all leads were of tantalum wire. Cleaning of the components and the assembly was effected by washing with trichloroethylene (reagent grade). The complete assembly was mounted on a heat-resistant glass base for ease in handling and was set under a glass bell jar.

The vacuum system uses a mechanical pump backing an oil diffusion pump. A liquid-oxygen cold trap keeps any oil vapor from reaching the test section. The vacuum system was so designed, cleaned, and assembled as to avoid leaving volatile contaminants inside. Brass was used throughout except for the stainless-steel base plate and the glass bell jar. Before assembly, each brass component was cleaned thoroughly by etching in a solution of sulfuric acid and potassium dichromate and washing in distilled water and in methyl alcohol (chemically pure) to remove any traces of acid. During assembly, all soft-soldered joints except the final ones were flushed with distilled water and cleaned with alcohol to remove any acid flux. On silver-soldered joints, dilute sulfuric acid was used to remove the borax flux and the joints were washed with distilled water and then with alcohol.

Three gages were used to cover the desired pressure range. A Knudsen gage covered the range from 1×10^{-6} millimeter of mercury to 1×10^{-3} millimeter of mercury, a thermopile gage from 1×10^{-3} millimeter of mercury to 1 millimeter of mercury and a diaphragm-type dial gage from 1 millimeter of mercury to atmospheric pressure. A needle-type leak valve with a Teflon seat was designed and constructed to admit nitrogen in any desired quantity. The temperature was measured by an optical pyrometer that was directed at the graphite cup through holes in the radiation shields. The radiation from the graphite is not black-body and therefore a temperature correction was made. The value of emissivity was taken as 0.8 which, with a 4-percent loss by reflection from each of the glass bell-jar surfaces, gives an effective emissivity ϵ of 0.74. This value is used in Wien's law to obtain the true temperature T from the apparent temperature $T_{apparent}$ by the equation (ref. 8)

$$\frac{1}{T} = \frac{\lambda \log_e \epsilon}{c_2} + \frac{1}{T_{apparent}}$$

where $\lambda = 0.65\ \mu$ and $c_2 = \frac{hc}{k} = 1.438 \times 10^4\ \mu\text{-}^{\circ}K$ (h is Planck's constant, k is Boltzmann's constant, and c the velocity of light). The probable error in true temperature is ±5° C because of the uncertainty in emissivity ($\epsilon = 0.74 \pm 0.05$) and about ±25° C because of the uncertainties in reading the pyrometer.

RESULTS AND DISCUSSION

First, the lanthanum hexaboride was activated and partially sintered by heating to 1,375° C for about 25 minutes at a pressure of about 5×10^{-4} millimeter of mercury. Then its emission rate was measured as function of anode potential at 1,340° C. The results are shown in the lower curve of figure 2. The saturation value shown in reference 7 for the same temperature and area is 13 milliamperes. There are a number of possible reasons that the emission rate per unit surface area was less than that obtained by Lafferty. The lanthanum hexaboride was not very well sintered and it could easily be flaked off the surface with a sharp-pointed instrument. Also, the anode voltage could not be raised high enough to obtain saturated emission because of anode overheating. Pulsing equipment for the anode voltage would solve this problem but it was not readily available.

After the data shown in the lower curve of figure 2 were obtained, prepurified nitrogen (99.996 percent pure) was admitted over a period of 22 minutes until a pressure of 735 millimeters of mercury was reached. The temperature was held at 1,340° C; the anode voltage, at 10 volts; and the current was measured as function of pressure. (The results are shown in figure 5 and are discussed subsequently.) Then the system was exhausted to its initial pressure of about 5×10^{-4} millimeter of mercury. Current-voltage data were then obtained and the results are shown by the upper curve of figure 2. Comparison of the two curves indicates that exposure to nitrogen increased the thermionic current by 2 or 3 times.

At a later time, after the system had been exposed to atmosphere, it was evacuated and the emitter was reactivated by heating for 25 minutes at 1,315° C. Then the heaters were turned off. After an hour and a half, nitrogen was admitted until the pressure reached 740 millimeters of mercury and the system was allowed to sit for a half hour. Then 10 volts were applied to the anode and heater power sufficient to raise the temperature to 1,322° C was suddenly applied and current-time data were taken. These data are shown in figure 3. The current rises quickly to about 50 microamperes and then decreases. In 7 minutes it falls to 13 microamperes. The decrease in current as time increases is believed to be due to the loss of adsorbed nitrogen from the emitter.

In what chemical form the nitrogen may have been adsorbed was not ascertained in the present investigation. Dr. J. M. Lafferty of the General Electric Research Laboratory, Schenectady, N. Y., has pointed out to the authors that the adsorbed nitrogen probably combines with lanthanum on the surface to form there a surface layer of LaN. Dr. Lafferty has found that bulk LaN has, at a given temperature, a greater emission rate than LaB_6. This result would explain the increase in emission current that results from adsorption of nitrogen and would also explain the decrease in emission current with increasing time as probably being due to evaporation of LaN from the surface.

Further information on the effect of nitrogen is shown in figure 4. After the emitter had been activated, nitrogen was admitted to a pressure of 1 millimeter of mercury and this pressure was held for 20 minutes. Temperature was kept at 1,250° C during this time. Then the system was evacuated to 3×10^{-4} millimeter of mercury. With an anode potential of 10 volts the variation of current with time at different temperatures was determined. At 1,257° C, the current was about 210 microamperes. When the temperature was suddenly raised to 1,476° C, the current rose to 1,050 microamperes and then dropped linearly in 5 minutes to 800 microamperes. This drop is believed to be due to the loss of adsorbed nitrogen. When the temperature was returned to 1,257° C, the current was little more than half its original value at that temperature. This result seems to indicate that driving off the adsorbed nitrogen decreased the emission rate, probably by increasing the effective work function. Then as time increased, the current increased; this condition probably indicated that at the rather low temperature of 1,257° C nitrogen was again adsorbed on the surface and the work function was therefore decreased.

Further results are shown in figure 5, which shows current as a function of pressure. The maximum of 390 microamperes for an anode potential of 10 volts (which, with an anode-cathode distance of 0.08 centimeter gives a gradient of 125 volts per centimeter) is set by the simple version of Child's law for space-charge-limited emission in a vacuum. The experimental results are seen to approach this value at low pressure and to fall considerably below this value as the pressure increases. The electron mobility, of course, decreases as the mean free path decreases and becomes small compared with the anode-cathode distance.

The calculated curve shown in figure 5 results from Child's law with consideration of electron mobility. Cobine's derivation (ref. 9) gives

$$J = \frac{9.95 \times 10^{-14}\ KV^2}{x^3}$$

where J is current density, K is the mobility, V is the voltage, and x the gap width, all in practical cgs units. Theoretical values of the mobility K, derived either on the basis of kinetic theory or of Ramsauer cross sections, are shown in reference 10 to disagree with experimental values. The experimental values, taken from figure 1.24 of reference 10, were therefore used in obtaining the calculated curve shown in figure 5.

The experimental values are slightly greater than the calculated values and differ by a factor of about 2 at the most. The two curves are very nearly parallel, however, and again show that nitrogen does not poison the emission. When the mobility is calculated, the temperature of the gas must be taken into consideration. The temperature was not actually known but was assumed to be the same as the temperature of the cathode.

It should be mentioned that the lanthanum hexaboride and the graphite cup were removed and a clean graphite cup inserted in the molybdenum cylinder after the data were taken. The temperature was raised to 1,335° C to determine whether there was any emission current from the components. With an anode potential of 10 volts, a reading of 37 microamperes was noted. This value is about 10 percent of the reading obtained under the same conditions with lanthanum hexaboride in the cup. Inasmuch as the purpose of the investigation did not require that absolute measurements be made, this discrepancy was not taken into account in the data.

CONCLUDING REMARKS

The thermionic electron emission from lanthanum hexaboride is not poisoned by the presence of nitrogen at pressures up to atmospheric. This finding should be useful in practical applications of magnetohydrodynamics in which electron flow from channel walls is required.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Field, Va., November 25, 1958.

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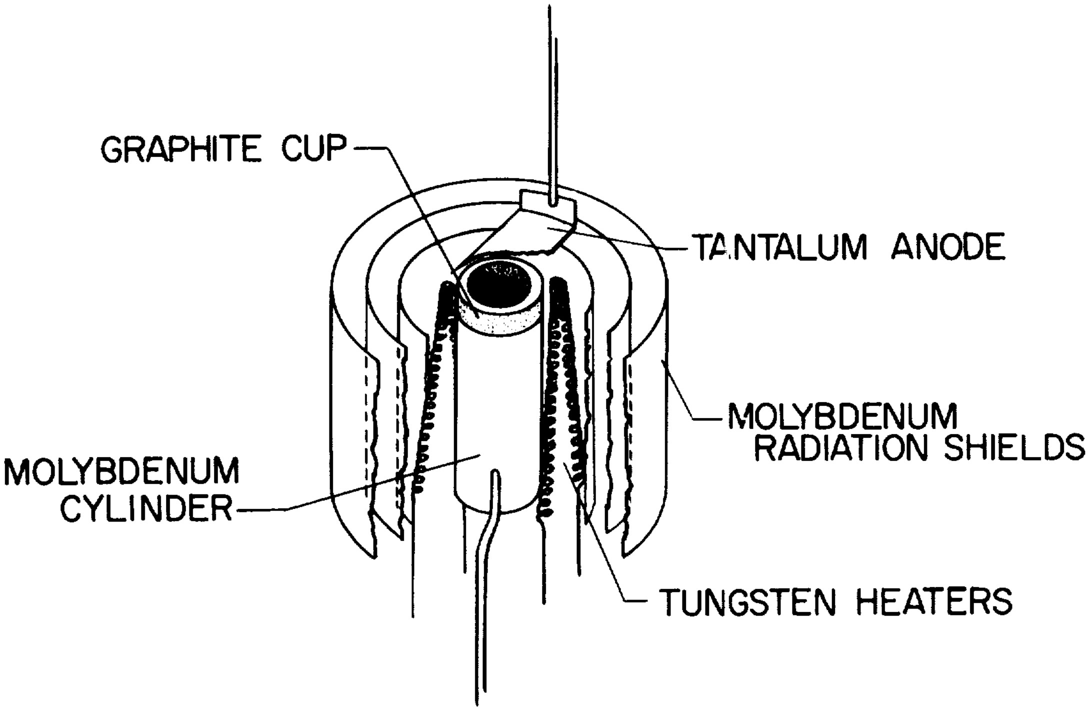

Figure 1.- Details of emission diode construction.

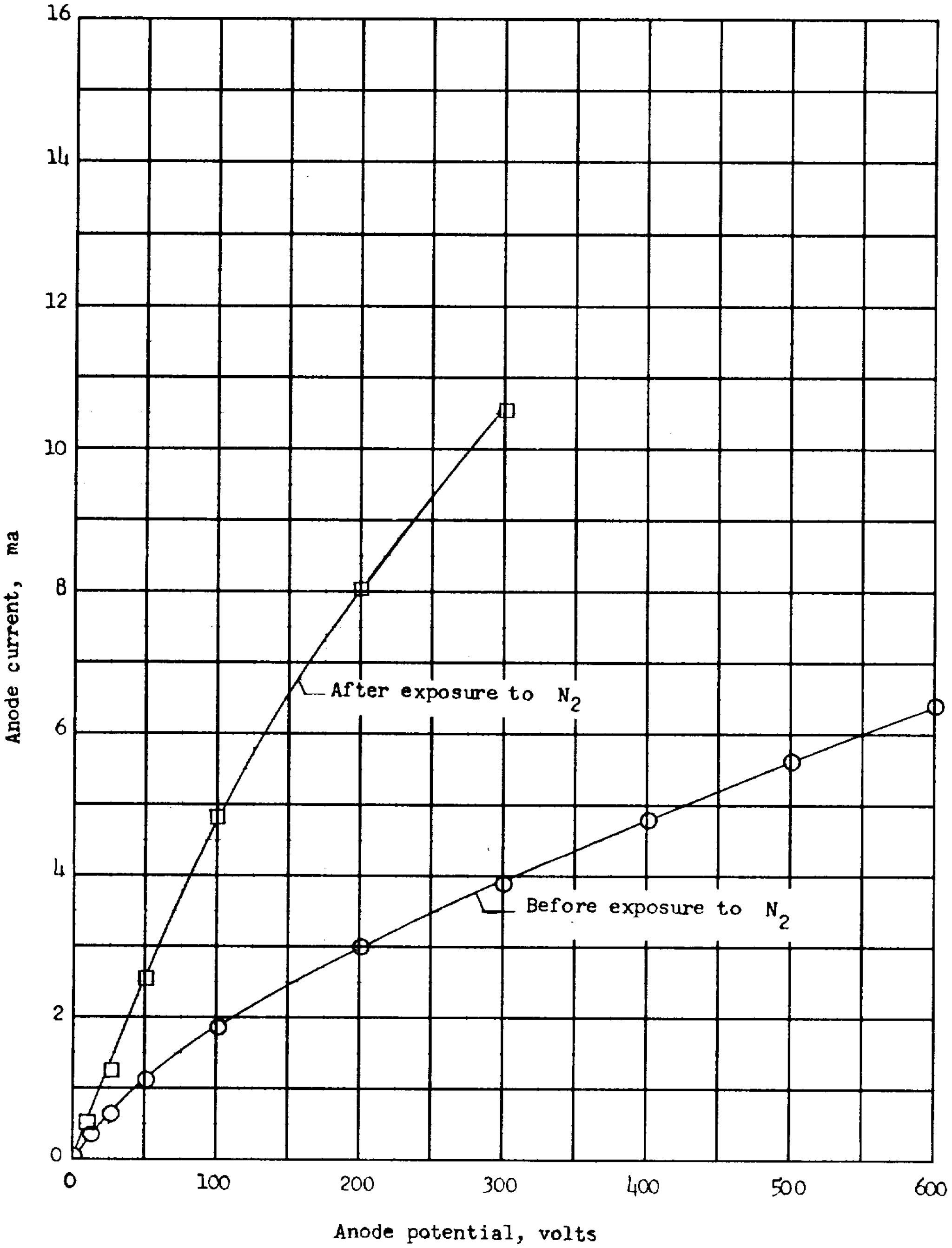

Figure 2.- Variation of anode current with anode potential for LaB_6 before and after exposure to N_2. Temperature, 1,340° C; pressure, 5×10^{-4} millimeter of mercury.

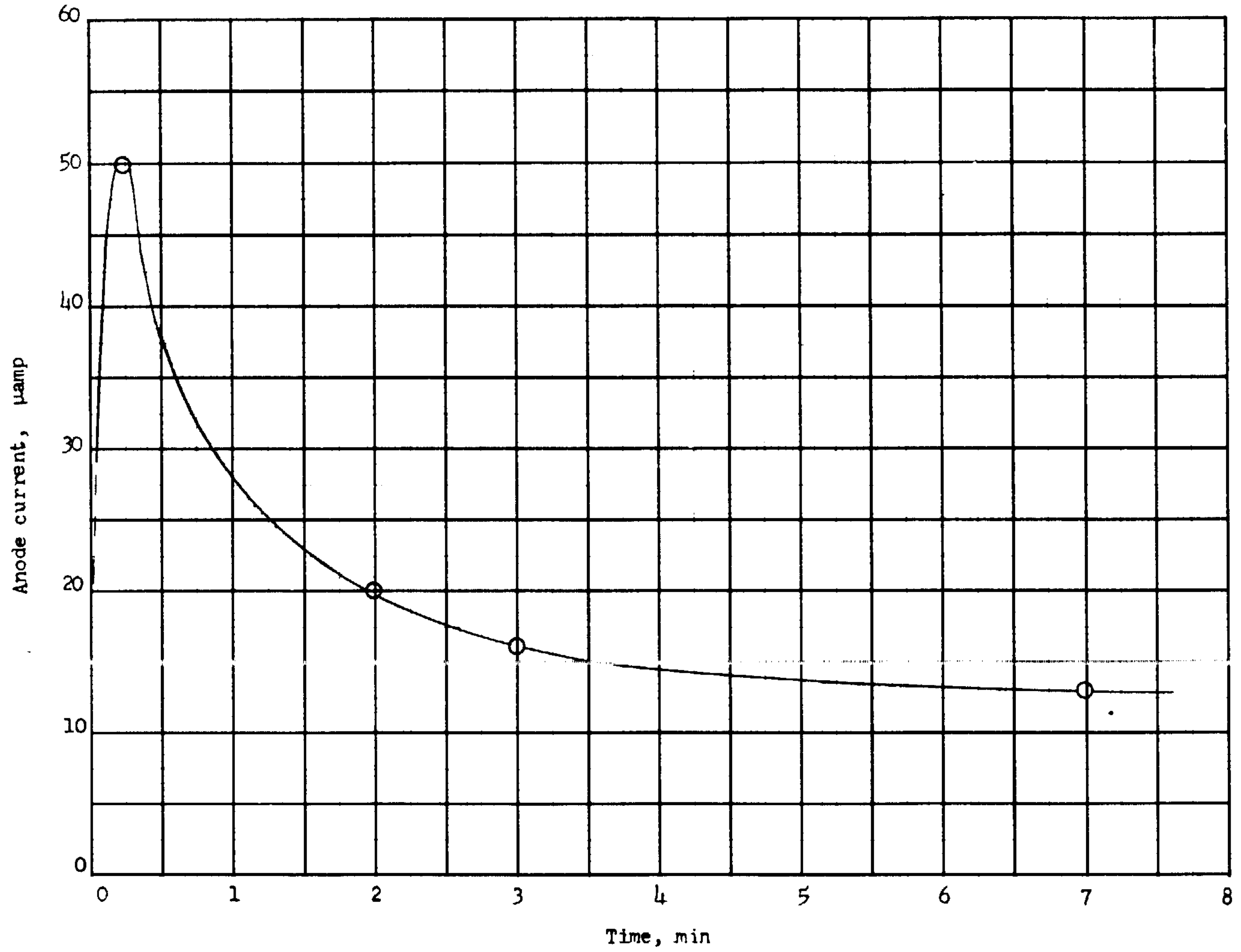

Figure 3.- Variation of anode current with time for LaB_6 in N_2 atmosphere at a pressure of 740 millimeters of mercury when cathode temperature is suddenly raised to 1,322° C. Anode potential, 10 volts.

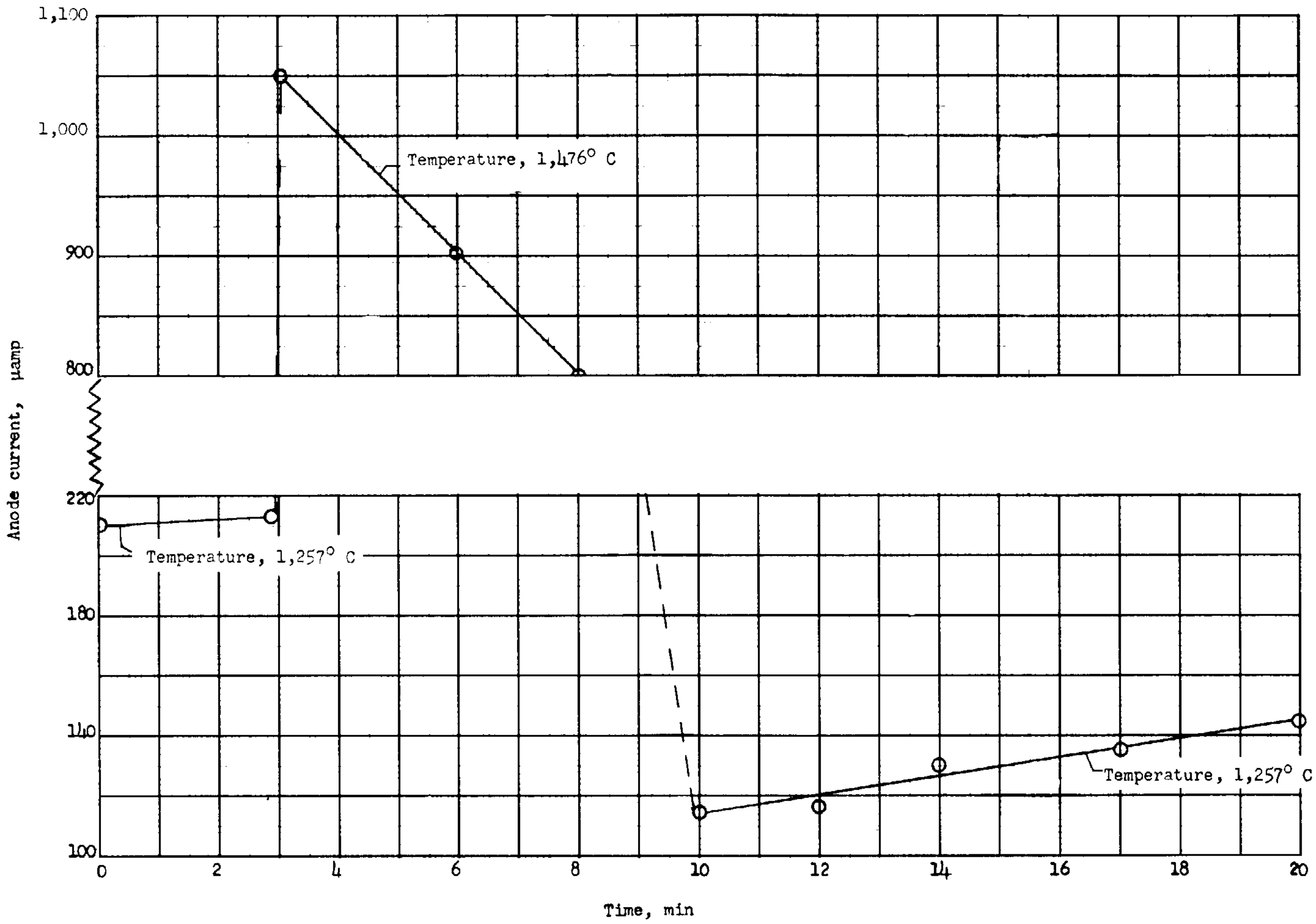

Figure 4.- Variation of anode current with time for LaB_6 (after exposure to N_2 at 1 millimeter of mercury pressure). Anode potential, 10 volts; pressure, 3×10^{-4} millimeter of mercury.

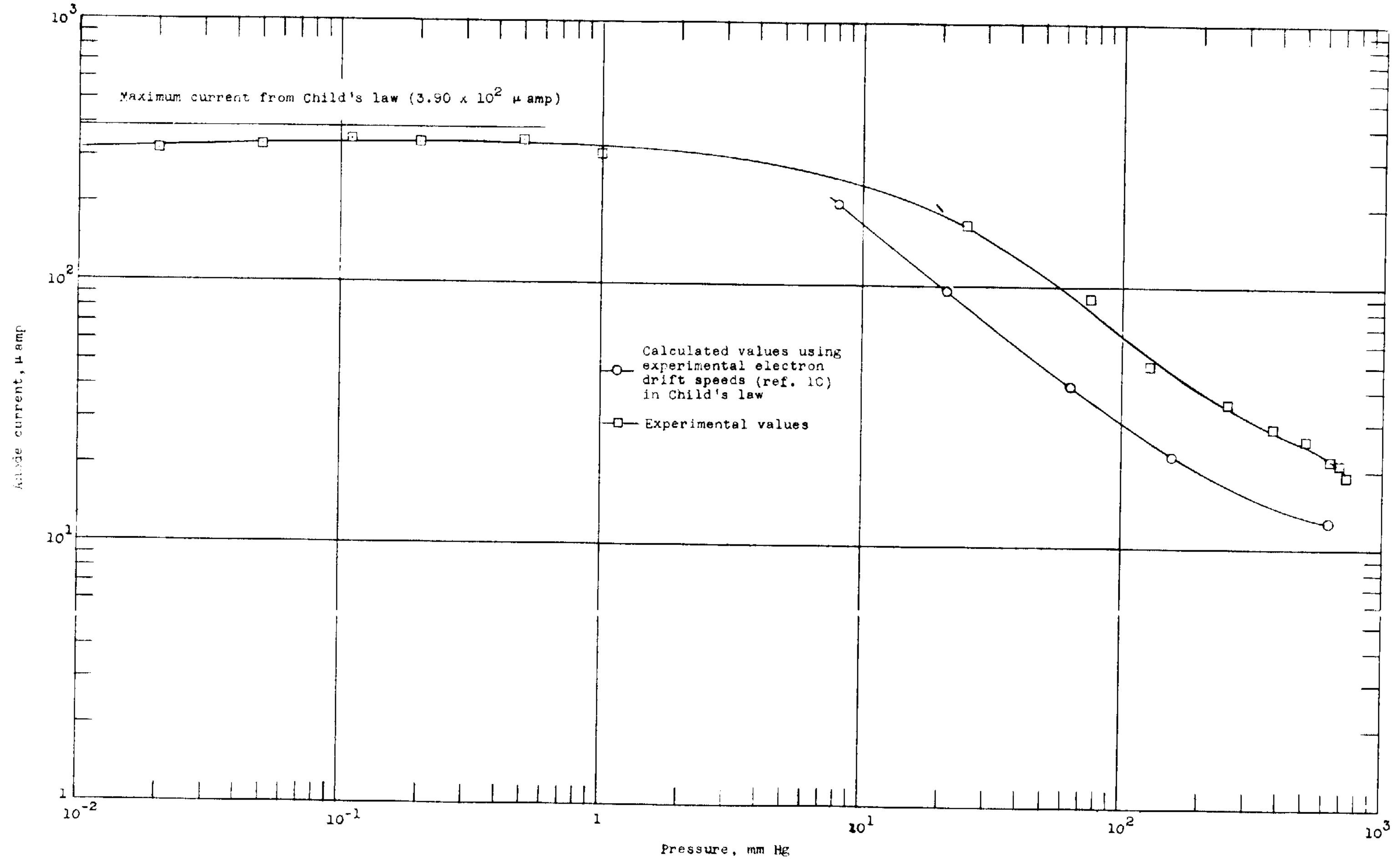

Figure 5.- Variation of anode current with pressure for LaB_6 in nitrogen. Anode potential, 10 volts; gradient, E, 125 volts per centimeter; temperature, 1,335° C.