1993 European Study Group with Industry Micro-Droplet Formation in High Current Vacuum Electroplating

(proposed by Multi-Arc (U.K.) Ltd.)

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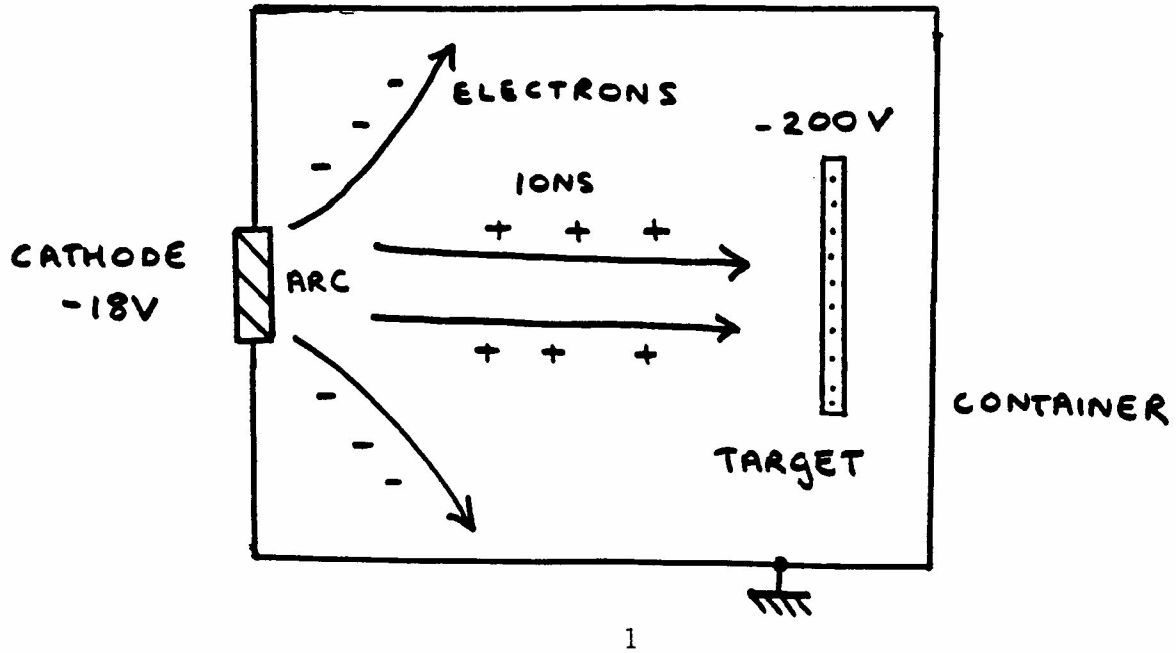
February 16, 1994

1 Introduction

A technique used to coat metal surfaces with Titanium Nitride is to vaporise a Titanium cathode by using a high temperature electric discharge or arc. If the cathode and the metal target are placed in an evacuated chamber containing a low pressure of Nitrogen gas, then the Titanium vapour becomes ionised and, if the target is at a negative potential with respect to the cathode, the ions will move toward it and react with Nitrogen at the surface to produce a thin layer of Titanium Nitride. The resulting geometry is illustrated below



A major disadvantage to this process is that as well as Titanium vapour, the arc also produces micro-droplets of Titanium liquid. These droplets have a size of up to $20\mu m$ in diameter and move at speeds upwards of $100ms^{-1}$. When they strike the target the resulting surface coating becomes uneven. Attempts to avoid this problem by changing the location of the target with respect to the cathode, result in reduced efficiency for the process.

The objectives of the study group were as follows

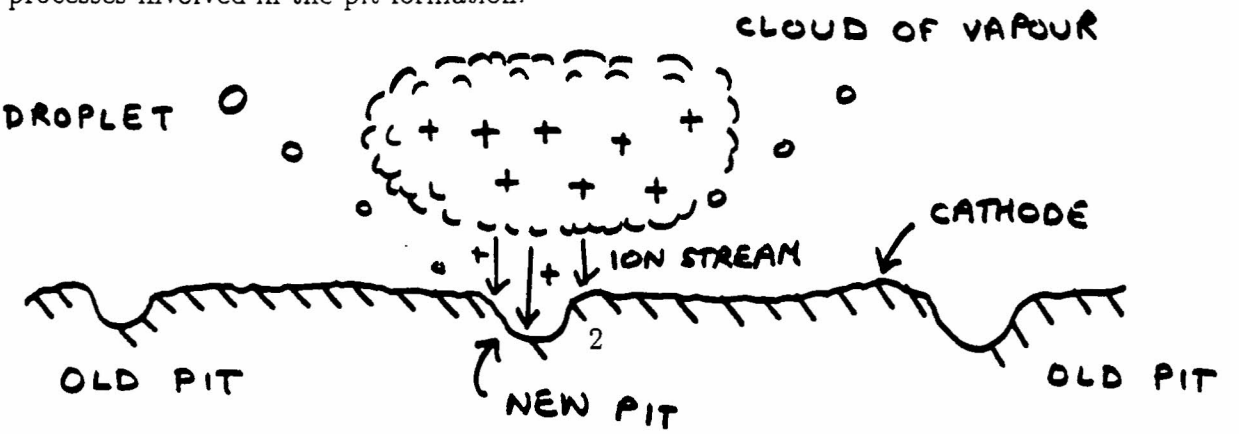
- to identify the underlying mechanisms leading to droplet formation,
- to clarify ways in which the size and number of droplets could be reduced
- to understand how the efficiency of the process depends upon the shape and position of the cathode.

2 Formation of pits by an electric arc

The electric arc in the coating process is initially formed by placing an earthed wire in contact with the cathode. The arc formed by this procedure vaporises some of the Titanium of the cathode forming a cloud close to the cathode. The arc is subsequently maintained by a flow of high energy positive ions from the cloud to the cathode. The effect of the bombardment of the ions is to heat up the cathode. This not only melts and vaporises the cathode but releases electrons from the cathode surface. The electrons ionise the Titanium vapour and the process continues. During arcing there are currents of about 50A due to the electrons emitted from the cathode and about 5A due to the ions leaving the cloud surface, eventually reaching the target which they coat with Titanium.

The bombardment of the cathode by the energetic Titanium ions results in the formation of pits on the cathode surface which are the source of both the Titanium vapour and the Titanium droplets. Typically a pit will grow and when it reaches a critical size will stop growing and a new pit will form at another point on the cathode.

Experiments indicate that a typical pit size is around $10\mu m$ and a typical time for pit formation is around $50ns$. We tried to do some experiments to see how the pit **size** was related to arc **current** but were unable to make the required measurements. Some of the literature indicates that pit size is proportional to the arc current. We indicate below the processes involved in the pit formation.



- Experimental measurements of pits indicate that they look like splashes - i.e. they look as though a molten pool of metal has been suddenly struck by a large object, causing droplets to "splash out" at an angle of about 20 deg with respect to the cathode. A typical such pit is indicated below. It seems unlikely that such a pattern would be the result of **steady** ion bombardment.

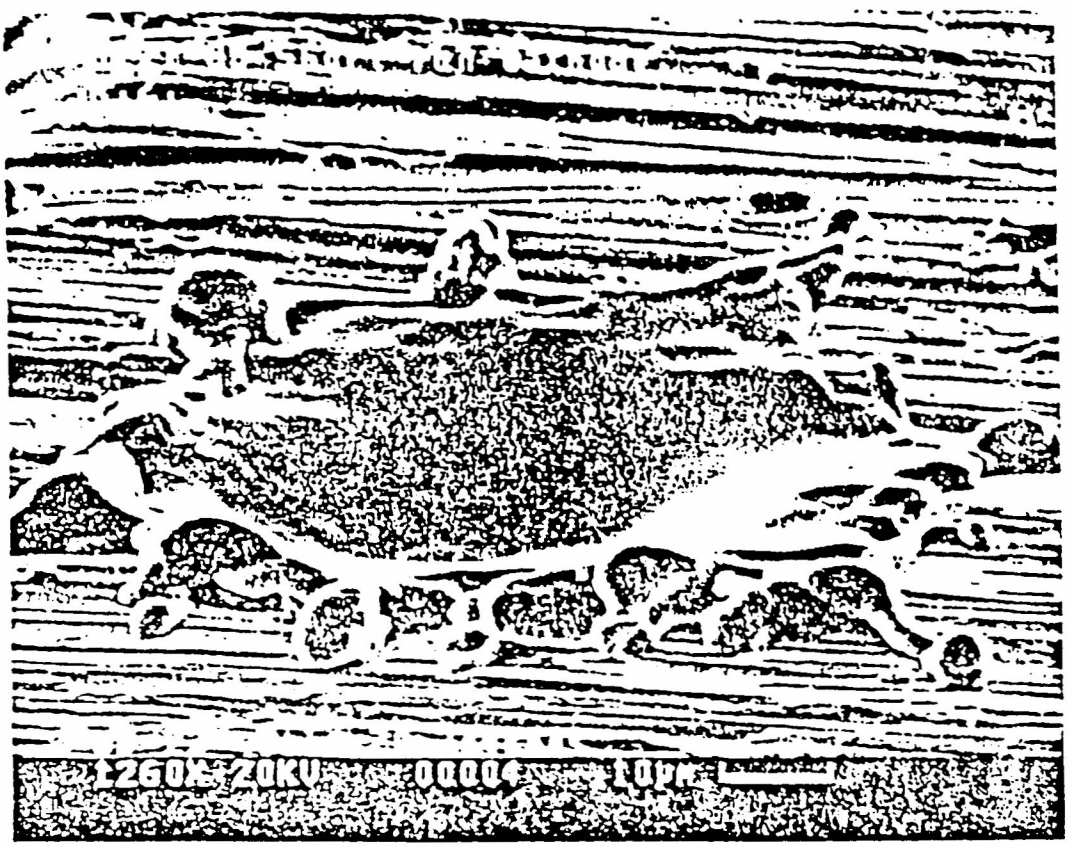


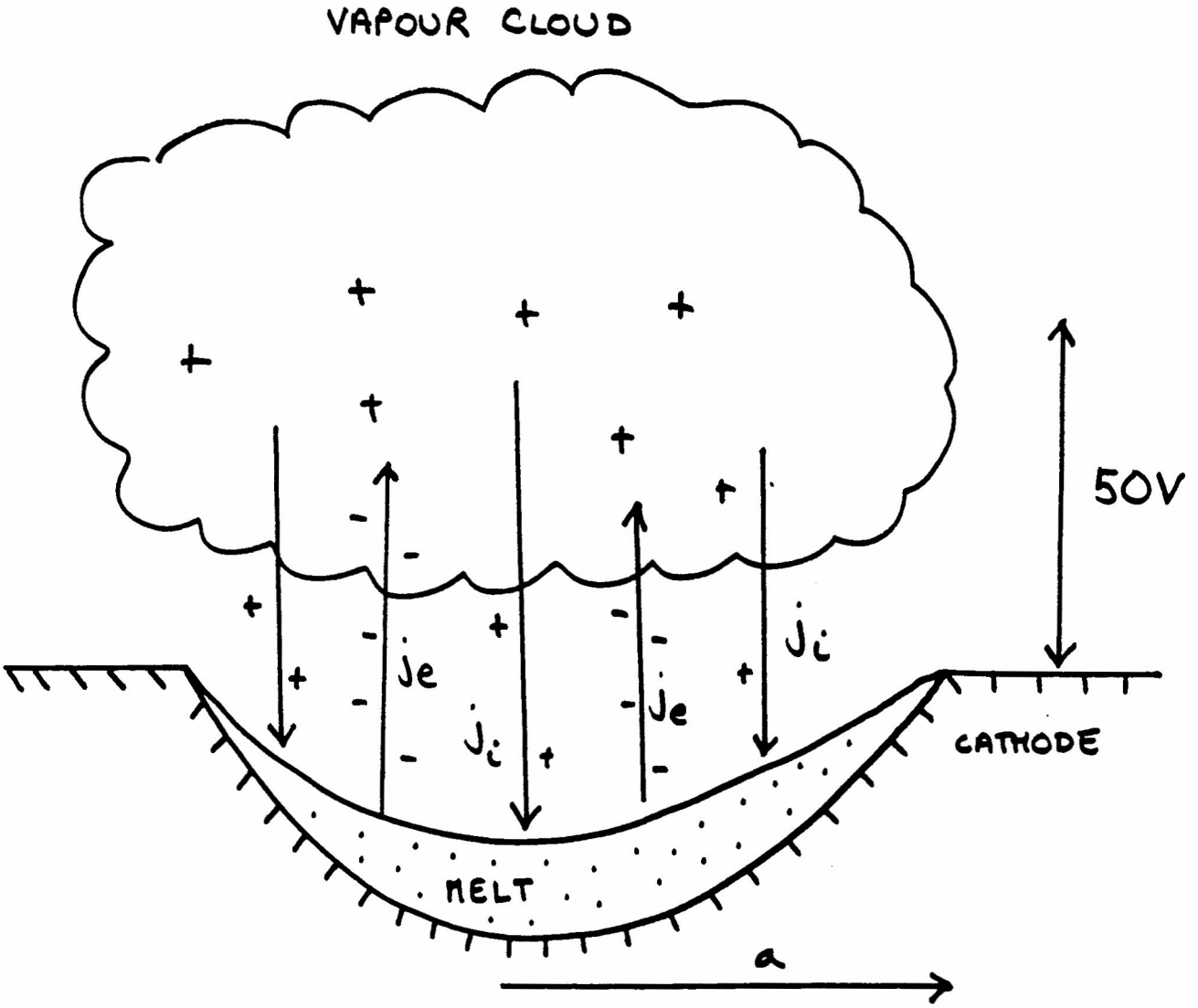
Figure _ - Scanning electron photomicrograph of Arc crater

- Further experiments indicate that the pit size is **increased** if an Aluminium cathode is used rather than a Titanium one and that it is **reduced** if Nitrogen is introduced into the chamber. The location of the pits can be partially controlled by the application of an external magnetic field but otherwise the location of the arc (and the current "active" pit) tends to move erratically over the electrode.

Our study of the formation of the pits attempted to explain these observations.

3 Processes involved in the growth of a pit

The mechanisms involved in the formation of a pit can be summarised by the following figure



Here the ion cloud is at an (observed) potential of about $50v$ with respect to the cathode. From this cloud there is an ion current density of j_i bombarding the cathode which releases an electron current density of j_e. The pit is of size a and temperature T.

The energy input to the pit is a combination of the energy of the bombarding ions and the ohmic heating effect of the electron current.

This energy is lost through conduction, melting the Titanium, vaporising the Titanium and in ejecting the micro-droplets.

It is possible to compare the magnitude of these effects by using known properties of the materials.

Energy in

- Measured electron current = 50A
- Electron current density for a pit of radius $10\mu = a$

$$j_e = \frac{50}{\pi \times (10^{-5})^2} = 1.6 \times 10^{11} Am^{-2}.$$

- Ion current density

$$j_i = 1.6 \times 10^{10} Am^{-2}.$$

- Power of ion bombardment per unit area

$$w_B = U j_i$$

where U is the "cathode drop" potential of about $50v$. Thus

$$w_B = 8 \times 10^{11} wm^{-2}.$$

- Power of ohmic heating per unit volume

$$W_0 = s(j_e + j_i)^2$$

where $s = 150 \times 10^{-8}$ is the conductivity of Titanium. Thus

$$W_0 \approx 3.75 \times 10^{16} wm^{-3}.$$

We note that $W_0 \times a \approx W_B$. This indicates that the effects of ohmic heating and of ionic bombardment are comparable.

Energy out

- The timescale to **heat** a volume a^3 of Titanium with density $d = 4\,500 kgm^{-3}$ and heat capacity $c = 500$ to its melting point of $T_m = 1\,600K$ is

$$t_H = T_M dca/(w_0 a + w_B) \approx 30ns.$$

This figure agrees with the experimentally observed value for the time of pit formation.

- The timescale to **melt** a volume a^3 of Titanium with latent heat of melting Λ_m is $t_m = \Lambda_m da/(w_0 a + w_B) \approx 10ns.$ which is again about right.
- The timescale to **vapourise** a volume a^3 of Titanium liquid with latent heat of vapourisation $\Lambda_v = 9 \times 10^6$ is

$$t_v = \Lambda_v da/(w_0 a + w_B) \approx 400ns.$$

This is rather longer than the time for the existence of the pits. We conclude that during pit formation only part of the molten Titanium will be vapourised and that the ramainder must be ejected as micro-droplets.

(We also note that the timescale for heat loss by conduction, given a conductivity $k = 20$ is

$$t_c = dca^2/k \approx 1\,000ns \gg 50n.$$

Thus heat loss by thermal conduction may be neglected.)

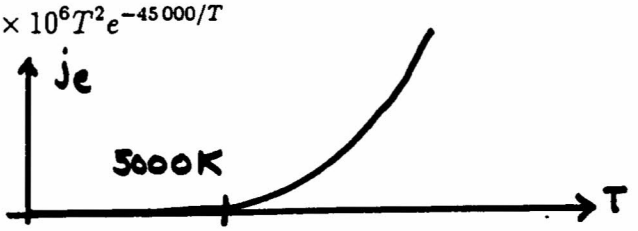
4 Electron Emission

During the ion bombardment, electrons are emitted from the surface of the cathode and it turns out that understanding this process gives a vital clue into the mechanisms behind the formation of the micro-droplets.

The emision of the electrons is (according to literature) governed by three processes, thermionic emission, quantum mechanical tunnelling and (appropriately) a mysterious process called "Nottingham heating". Of these, only thermionic emision is significant. In this process the electron current density j_e is proportional to temperature T so that

$$j_e = 1.2 \times 10^6 T^2 e^{-45\,000/T}$$

A graph of this function is given below



Essentially the thermionic emission process acts like a switch in that j_e is quite insignificant if $T < 5\,000K$ and takes the, measured, valve of $1.6^{11} Am^{-2}$ when

$$T = 7\,600K$$

which is significantly greater than the melting point of Titanium at $3\,300K$. We conclude that to reach this high temperature the molten Titanium in the pit must be superheated.

This superheating may be caused by the high pressure P of the ion bombardment given by

$$P = j_i \left(\frac{2Um}{e}\right) = 2.21 \times 10^7 Pa$$

where $m = 7.68 \times 10^{-26} Kg$ is the ion mass, e the electron charge.

(We note that the impulse I due to this pressure is $I = Pa^2 t_p$ where t_p is the pits formation time. If this impulse is transferred to the Kinetic energy of a microdroplet travelling at speed v then

$$I = da^3 V.$$

This gives an, approximately correct, value for the droplet velocity.)

5 A possible mechanism for micro-droplet formation

Existing models for pit creation postulate a "steady state" in which the electron-emision is just sufficient to ionise the cloud of Titanium vapour to produce more ions and thus more electrons. In these models it is postulated that the pit grows until it is so large that the total current $\pi a^2 j_e$ is greater than the available current from the power supply.

We find this unsatisfactory for two reasons, most significantly the photographs of the pit resemble those of a **sudden** explosion and secondly the extreme sensitivity of j_e to the cathode temperature would seem to rule out any "slowly evolving" process.

An alternative mechanism was proposed to overcome these objection, starting from the presumed existence of an ion-cloud and no "active" pits.

1. The ion cloud would drift over the cathode (perhaps under the action of a magnetic field) until it encountered an imperfection at which the electric field was higher than elsewhere.

2. Positive ions would move to wards the cathode under the action of the field. These ions would bombard the cathode melting it and raising its temperature.

3. At a critical temperature the electron current emision from the cathode would rise rapidly (here the thermionic emission is acting like a switch). The electrons quickly move into the ion cloud causing significant new ionisation.

4. As a consequence of this ionisation there is a huge new pulse of ions bombarding the cathode. This pulse drives out the melt causing the "splash" like picture observed.

Following the expulsion of the melt the remaining cooler cathode cannot maintain the electron emision and the process stops.

A further modification to this picture, proposed by JRO, arises if we postulate a fixed ion density in the cloud. Whilst the ions bombard the cathode the high ion pressure prevents the metal from vaporising. However, if the pressure due to the ions drops (either because their number or their velocity decreases), then the (superheated) melt will explode. The speed of sound in molten Titanium is of the correct order of magnitude for this to be a feasible process. In fact it is not necessary to invoke a supersonic flow for this; vapourisation within the body of the melt will cause a large volume change that will eject molten metal. This picture seems quite plausible in view of the simple arguments below.

We can now make some qualitative predictions from the above model

- If an Aluminium cathode is used then j_e has the same dependence upon temperature but Aluminium has a lower melting point. As a consequence, more Aluminium will

melt until the critical temperature when electrons are released. Thus the size of the pits in Aluminium will be greater.

- If Nitrogen is introduced into the chamber then (it is believed) the critical temperature at which electrons are released is lowered. As a consequence the pits have less time to grow and their size is smaller.

  Both of these predictions agree with experiment.

- Following the critical temperature at which electrons are emitted the melt will heat up by ohmic heating so that

$$\frac{dT}{dt} \propto j_e^2 \propto T^4 e^{-B/T}$$

  where $B = 90\,000K$. Although this equation would appear to provide the possibility of finite-time blowup (T becoming infinite in a finite time) we must recall that other factors such as the electric field are ommitted and that temperatures much above 7 500 would lead to considerably higher currents than the apparatus can support. It is the exponential, with the large value of B in this equation, rather than the fourth power of T, that predicts a rapid acceleration in the growth of temperature. Thus T (and hence j_e) will rise rapidly. This will cause the melt both to heat and to grow (by conduction) although its size a and hence the temperature itself are limited by the available current i.e.

$$\pi a^2 j_e = \pi a^2 \times 1.2 \times 10^6 T^2 e^{-45\,000/T} < I \qquad (*)$$

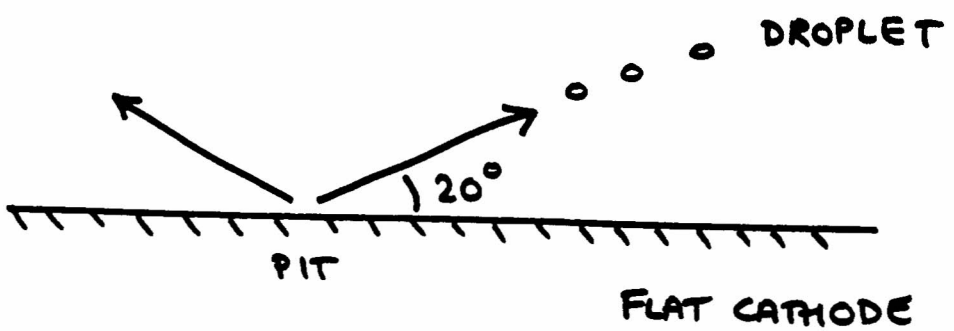
  where I is the available current from the supply.

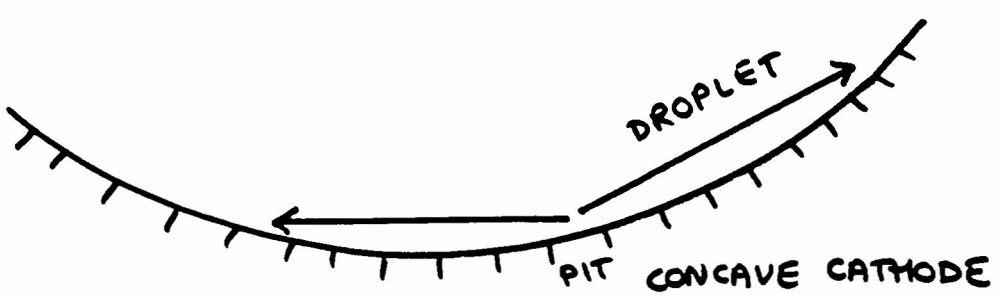
  The current can only stay within limits if the voltage between the cloud and the metal surface drops. This, in turn, will reduce the pressure of ion bombardment allowing the superheated melt to begin vapourising rapidly which, in turn, will drive molten metal away from the cathode. The fact that a reduced ion bombardment will still be taking place suggests that the ejected metal would be deflected sideways, partly explaining the creation of the kinds of "splashes" that are observed.

  The equation $(*)$ indicates that the maximum pit size will depend upon I in some manner. It would be useful to determine this dependence, but although attempts were made at the study group, we were not able to make the relevant experimental measurements and there was not sufficient time to make reasonable theoretical predictions.

6 The effect of the cathode geometry

If our model of an impulsive "splash" or of a deflected ejection of liquid producing the micro-droplets is correct then, as the resulting droplets emerge at a "low angle" with respect to the cathode, there may be ways to change the shape of the cathode so that fewer droplets reach the target. One suggestion is that the cathodes could be concave i.e.

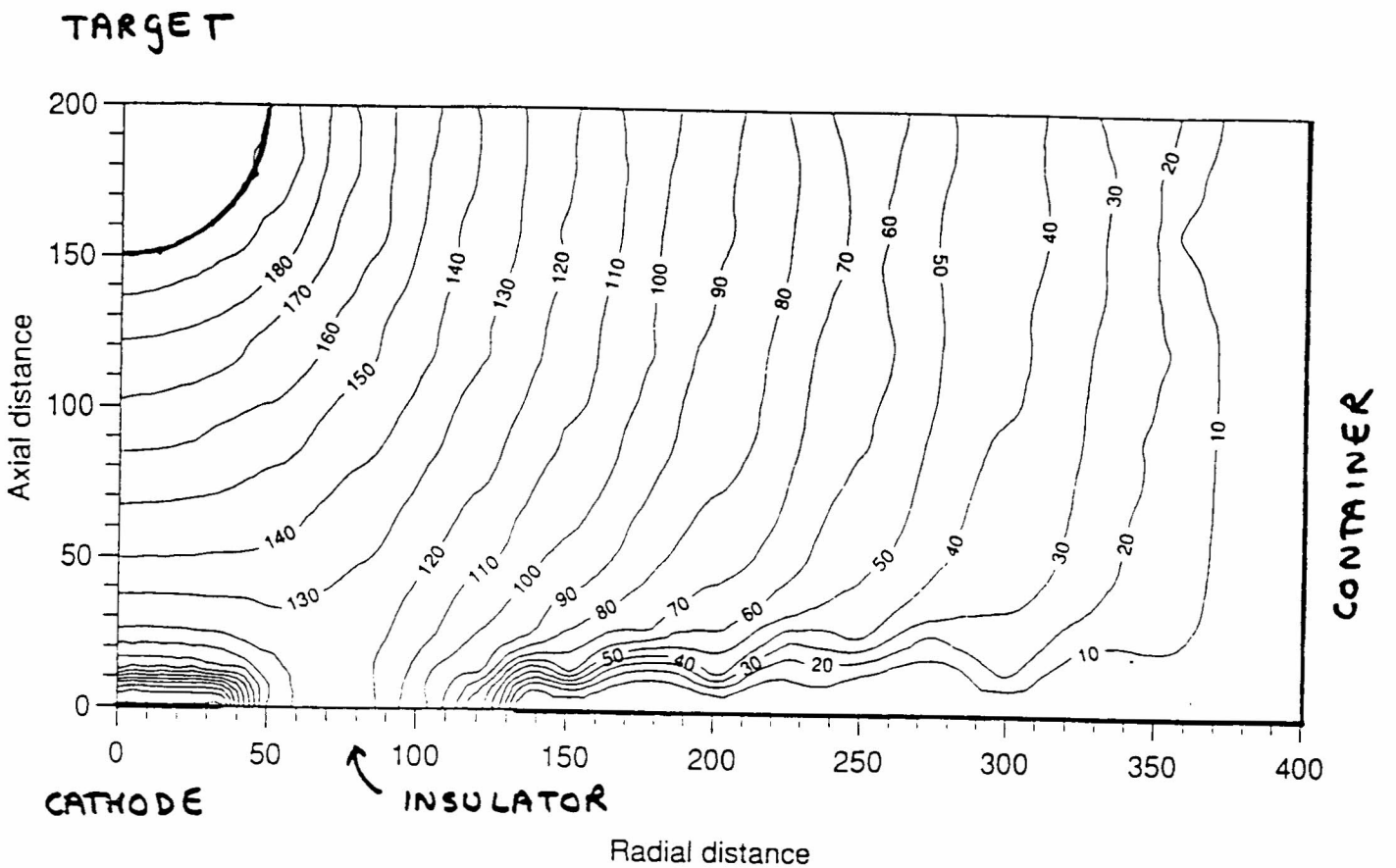


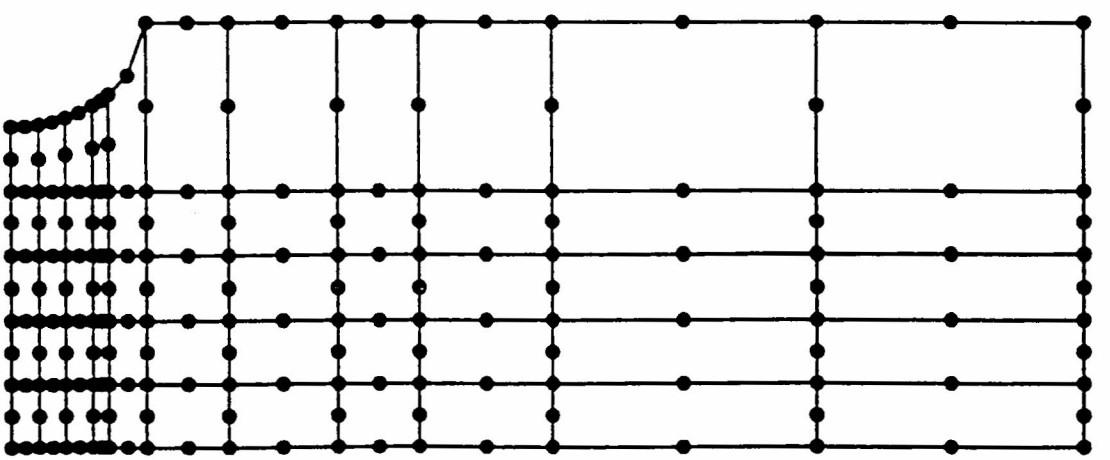


There were two objections to this. Firstly that after a large number of pitting events the **local** surface of the cathode would be so irregular that **global** changes would be irrelevant. Secondly, that markedly reduced efficiencies of deposition on the target were recorded for concave cathodes.

The latter effect is most interesting. Presumably the ion deposition on the target is due to the macroscopic field distribution and using a concave cathode significantly effects this (e.g. by lowering the field and causing more ions to come back to the cathode rather than reaching the target). This would be an interesting area for future work! (See CJB work

Equipotentials for a flat cathode





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on the space-charge equations.) Some preliminary field calculations in an axi-symmetric geometry were made by RS and are included in this report.

7 Conclusions

We appear to have arrived at some reasonable descriptive models for the processes taking place at the cathode. Estimates of time-scales, sizes and currents etc. all seem to be consistent with observations, so that we may be reasonably confident that the models are not wildly incorrect. However, we would recommend that the work be taken further in the following ways:

- Determine the relationship between pit size and arc current
- Determine the relationship between arc current and droplet size
- Calculate the macroscopic field around the cathode in the presence of space-charge and estimate the effect of cathode geometry on ion transport.
- Consider the effect of external magnetic fields.