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ON BROAD-AREA COPPER AND NIOBIUM ELECTRODES

by

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Abstract

It has been experimentally demonstrated that micron-sized particles of graphite deposited on the surface of copper and niobium electrodes can promote the field emission of electrons in the range of 5-20 MVm⁻¹. From measurements of the current-voltage characteristic, electron spectrum and emission image of such sites, it has been concluded that electrons are emitted by a mechanism similar to that operating at the naturally occurring sites responsible for pre-breakdown electron emission. A hot electron based metal-insulator-metal model is considered.

1. Introduction

There is a growing body of experimental evidence which strongly suggests that carbon, in certain forms, can promote the field emission of electrons at anomalously low fields, typically in the range of 5-20 MVm⁻¹. In particular, filamentary carbon fibres have been extensively studied as point field emission electron sources (1-4) and, in the form of a felt weave, as extended cold-cathode electron sources (5). Copious field emission has also been observed from bulk specimens of pyrolytic graphite (6), and from a carbon film deposited on an insulating substrate (7). There is also evidence from studies of prebreakdown electron emission from broad-area high voltage electrodes that carbon, as a localised impurity, can stimulate the emission of electrons in the same field range. For example, gold electrodes, which are known to have a high level of carbon contamination, have been observed to be strongly emissive (8), whilst more recently, electron emission sites have been shown to be located in the vicinity of surface carbon concentrations as identified by Auger analysis (9). Lastly there is evidence from vacuum arc studies that the initiation mechanism, which depends on a primary electron emission process, may be also associated with the presence of carbon concentrations (10).

On the basis of this evidence, and that discussed elsewhere (11), which emphasises the similarities between the electron and optical spectroscopic data obtained from the prebreakdown emission processes on high voltage electrodes and carbon fibre emitters, an investigation was initiated to create artificial carbon sites on broad-area metal electrodes and to determine how closely their emission behaviour simulates that of naturally occurring sites.

2. Experimental

2.1 Artificial site production

Two techniques have been developed, both very simple in concept. In the first, originally demonstrated with copper electrodes (12), a micromanipulator is employed to lower gently a finely sharpened pencil lead to a known position on the surface of a planar electrode that had previously been polished and ultrasonically cleaned in readiness for introduction to the vacuum system. By taking care to 'touch' the surface of the electrode only lightly it is possible to produce a faintly visible carbon spot of

typical diameter ~ 0.2 mm. In the second and more recent technique, a fine glass capillary tube is similarly used to deposit a ~ 0.5 mm drop of colloidal graphite (Aquadag) onto an electrode surface, which, after drying, typically leaves a visible deposit of somewhat smaller dimensions. At higher resolution, such deposits are found to consist of a random distribution of carbon particles of varying size and orientation; this is illustrated by the scanning electron micrograph of Figure 1 which shows a typical region of a 'pencil' spot. It is particularly important to note the bright appearance of the carbon particles, which suggests they are electrically insulated from the substrate metal electrode, i.e. similar to the appearance of naturally occurring sites (13).

Fig. 1 A scanning electron micrograph of a 'pencil' site showing the randomly distributed carbon particles (labelled C).

2.2 Emission site characteristics

Using the experimental facilities previously developed for studying the emission properties of the sites that occur naturally on broad area electrodes (11,14-16), measurements have been made of the current-voltage characteristics, electron spectra and emission images for pencil and Aquadag sites on both copper and niobium electrodes. In all cases the most strongly emitting site was found to be at the location of the graphite deposit. However, no consistently reproducible difference in emission properties were identified between the two types of site on a given material, or indeed between a given type of site on the separate materials. Accordingly, the following examples of experimental data are to be taken as representative of all the systems studied.

Thus Figure 2 is a typical single-site current-field characteristic of the initial field cycling (i), together with the resulting reversible Fowler-Nordheim (F-N) plot (ii). This illustrates how the current from a virgin site initially increases in a very erratic and unstable manner from a near-zero current level (i.e. 10⁻¹¹ A) to a level of ~ 10⁻⁷ A and then exhibits a spontaneous switch-on into a

Fig. 2 A typical example of (i) the current-field characteristic (x) and (ii) the associated F-N plot (•) of a carbon site.

final and more stable emission mode that is subsequently reversible over the whole field range. It is to be noted that the hysteresis associated with the initial field cycling is so marked that whereas a field of $\sim 9 \text{ MVm}^{-1}$ was initially required to obtain a current of $\sim 10^{-10} \text{ A}$, the same current could subsequently be drawn by a field of $\sim 3 \text{ MVm}^{-1}$ after the switch-on process. The F-N plot corresponding to the switched-on state can often be divided into two fairly clearly defined linear regions above and below current levels of $\sim 10^{-6} \text{ A}$: typically, the low-field range is characterized by β -values in the range 300–1200, whilst within the limited high field range one finds $\beta > 1000$. In the plot of Figure 2, this parameter has the respective values $\beta_1 \sim 1000$ and $\beta_2 \sim 1700$.

Fig. 3 presents two electron spectra successively recorded at slightly different fields from an Aquadag site on a niobium electrode. This illustrates both how the spectra, with broad half-widths ($> 0.3 \text{ eV}$), are shifted from the cathode Fermi level

Fig. 3 Single and multi-peak spectra successively recorded at (a) 7.2 MVm^{-1} and (b) 8.4 MVm^{-1} from an Aquadag site on a niobium electrode.

and how the emission can switch between a single-peak and multi-peak mode, i.e. in both respects exhibiting a behaviour similar to that observed for naturally occurring sites (11,17). As a consequence of this latter property, it generally proved difficult to measure systematically how the shift of a single peak spectrum varied with field. However, in the case of one pencil site, such a measurement was possible, and it revealed a behaviour broadly similar to that found for naturally occurring sites (18), i.e. where the shift increases rapidly with field. Lastly, Figure 4 is a typical projection image of the emission obtained from such sites, and reveals that, as with natural sites, the total current is derived from several independent sub-sites, each having its own characteristic single-peak spectrum (9,15). From a comparison of this image with that obtained from naturally occurring sites (9,15), known to consist of micron-sized particles (13), it can be concluded that the present emission originates from only a very small localized region of the carbon deposit, possibly just one of the particles. Multi-peak spectra are observed when the emission from two or more sub-sites is simultaneously collected by the spectrometer input aperture. Not revealed on this image is the other important observation, again common to natural sites, that each of the sub-sites intermittently switches on and off with time, with a mean frequency that tends to increase with the current drawn from the site (typically 0.5 Hz at 10^{-6} – 10^{-7} A emission (9,15)). In fact, this 'flickering' of the emission image accounts for the ambient noise on the measured emission current.

Fig. 4 A projection image of the electrons field emitted from a carbon site (9,15).

3. Discussion

The central conclusion to be drawn from the above experimental data is that the emission characteristics of artificial carbon sites are in most respects very similar to those of naturally occurring sites. Thus they exhibit a switch-on phenomenon to give a subsequently smooth and reversible current-voltage characteristic with a linear F-N plot for fields up to $\sim 10 \text{ MVm}^{-1}$ having typical β -values in the range 300–1200 (17). Similarly, there is an apparent equivalence between the electron spectra and emission images obtained from the two types of site. It now remains to discuss how carbon might promote the field-induced hot electron emission mechanism thought to operate at naturally occurring sites (11, 17–20). Two approaches have been considered: firstly, that it is a consequence of the physical properties of carbon, and secondly, that carbon, behaving as a conductor, plays some form of field enhancing geometrical role.

Carbon is a generic term used to describe a wide range of materials having very different physical and chemical properties (21). At one extreme, there are materials such as diamond and many hydrocarbon based 'cokes' that are electrically insulating whilst, at the other extreme, there are the chemically pure pyrocarbons that can exist in either an amorphous 'glassy' form or in a highly orientated 'graphitic' form. There are numerous intermediate forms of carbon (e.g. turbostratic carbons) of which the degree of purity and graphitisation generally depends on the choice of organic precursor and the temperature to

which it is heat-treated. Typically, temperatures in the range 2000-3000 K are required to achieve the purest forms of carbon. In the context of the present discussions of the field emitting properties of carbon sites, attention will be focussed on its highly-orientated graphitic form, since both pencil lead and colloidal Aquadag use this form of the material.

Graphite has the well-known layered structure consisting of stacked basal planes containing closely-packed, covalently bonded carbon atoms arranged in hexagonal rings. The separation between the basal planes (3.35 Å) is nearly 2.5 times the separation of the carbon atoms within the planes (1.42 Å), and they are only weakly bound together by Van der Waals forces. This means that they can readily cleave to form flake-like structures.

Another important consequence of this structure is that graphite exhibits a large anisotropy in its electronic properties: in particular, the ratio of c to a -axis electrical resistivities ρ_c/ρ_a can approach values ~ 5000 at 300 K and exceed 10^5 at ~ 5 K for highly orientated pyrolytic graphite (21) that has been thoroughly annealed to ~ 3000 K. However, for somewhat lower annealing temperatures (say 2000-2500 K), one still obtains a graphite-like structure with stacking of the carbon rings, although in this case they are randomly orientated about the c -axis. These structures also have a somewhat greater mean separation between the basal planes and this can lead to even higher values of the ρ_c/ρ_a ratio, possibly in excess of 10^4 where typically the basal plane resistivity ρ_a at 300 K has a value $\sim 1500 \mu\Omega\text{cm}$. From this brief survey, it is evident that, even in the most favourable circumstances, the anisotropy of graphite never leads to a c -direction resistivity that is greater than that corresponding to a small bandgap semiconductor. Accordingly, it is difficult to envisage how graphite could support the necessary dielectric field penetration to sustain a hot-electron emission mechanism. It may be, however, that amorphous carbon (4) and binding agents (predominantly clay in pencil and organic additives in the case of Aquadag) play a crucial role: in fact, experiments are currently in progress to investigate this possibility.

A more plausible explanation of how graphite might stimulate the hot-electron emission mechanism previously proposed for insulating inclusions (11,17-20) stems from its flake-like structure (21). Thus, for the configuration schematically illustrated in Figure 5, the graphite flake is depicted as forming a metal-insulator-metal (MIM) structure, involving either the ambient surface oxide of the metal or, more likely, some anomalous insulating inclusion such as might be provided by the polishing medium or the non-metallic constituents of the pencil or Aquadag. According to this model the insulating-like material, sandwiched between the metal substrate and the overlying conducting flake, will undergo a switching process similar to that described elsewhere (17) and occurring at some critical gap field in the range $5\text{-}20 \text{ MVm}^{-1}$. This will give rise to a flux of hot electrons that are projected through the flake into

Fig. 5 A schematic illustration of how a conducting flake could form an MIM structure on the surface of an electrode with an accompanying field enhancing effect.

the vacuum as occurs in purpose fabricated MIM electron sources (22).

The three essential requisites of this model are (a) that the MIM structure should initially 'block' the exchange of charge as the external field is applied to the surface, so that the potential of the flake rises with respect to the substrate electrode; (b) that there is a geometrical enhancement of the field appearing across the junction resulting from the flake being effectively at the potential existing at, perhaps, a micron above the electrode surface (for the configuration illustrated in Fig. 5, the field across the 100 Å thick insulating layer could be many times larger than that existing across it without the flake), and (c) that the thickness of the overlying flake should be $\leq 1000 \text{ Å}$ so that the majority of the hot electrons are able to escape to the vacuum (22). The first requirement of a 'blocking' contact is apparently confirmed by the experimental evidence of Fig. 1, where the carbon particles appear to be charged, and therefore presumably electrically insulated from the substrate. This same evidence also suggests that the geometrical configuration of at least some of the particles could fulfil the second and third requirements. Thus it appears that the necessary conditions could well exist to promote a MIM hot-electron emission mechanism.

In conclusion, two further examples of indirect evidence supporting this model should be cited. Firstly, the anode probe technique of Athwal and Latham (13) for locating emission sites on broad-area electrodes frequently identified sites by X-ray spectroscopy as consisting of particles containing such metallic elements as aluminium and silver (19). These general findings have been recently confirmed by a similar experiment employing an Auger, rather than X-ray, analysis facility (23). Secondly, when a test electrode pair suffers a flash-over it is generally found that the electron emission is subsequently very much higher at a given field: the reason for this is dramatically illustrated in Figure 6, which shows the 'before' and 'after' emission site maps (9,15). On finally examining the surface of the cathode, it was found to be decorated by numerous particles of anode material; in this case stainless steel. It was therefore concluded that the proliferation of emission sites displayed in Figure 6b was a consequence of the creation of MIM structures by metal being 'splashed' from the anode onto suitable insulating regions of the cathode surface. Indeed, the degradation of the insulating properties of a vacuum gap due to the presence of metallic particles is well known (24).

Fig. 6 Emission site maps (9,15) recorded at a constant field of 12 MVm^{-1} 'before' and 'after' a flash-over event between a 15 mm diameter copper cathode and a stainless steel anode. The proliferation of sites is thought to be associated with the 'splashing' of metal droplets of anode material onto the cathode surface.

From the technological point of view, the above findings have two important implications. Firstly, they indicate that the carbon concentrations which are known to exist at grain boundaries on broad-area electrodes (25) could be possible sources of field emission currents, and hence ultimately a limiting factor on the performance of high voltage electrodes. Secondly, brief mention should be made of a recent study associated with the electron loading of superconducting RF cavities (26), in which artificial carbon sites have been used to simulate effects of naturally occurring field emission sites.

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References

1. F.S. Baker, A.R. Holber and J. Williams, *Nature*, **239**, 96-97, 1972.
2. C. Lea, *J. Phys. D., Appl. Phys.*, **6**, 1105-1114, 1973.
3. R.V. Latham and D.A. Wilson, *J. Phys. E., Sci. Instrum.*, **15**, 1083-92, 1982.
4. R.V. Latham and D.A. Wilson, *J. Phys. D, Appl. Phys.* **16**, 455-63, 1983.
5. G.F. Erikson and P.N. Mace, *Rev. Sci. Instrum.*, **54**, 586-90, 1983.
6. R.E. Hurley, Private communication, 1978.
7. K.H. Bayliss, R.V. Latham, F. Jones and D.J. Mellor, *Vacuum*, to be published 1984.
8. R.E. Hurley, *J. Phys. D, Appl. Phys.* **12**, 2229-2245, 1979.
9. K.H. Bayliss, Ph. D. Thesis, University of Aston, Birmingham, U.K., 1984.
10. B. Jüttner, *Physica*, **114B+C**, 255-61, 1982.
11. R.V. Latham, *IEEE Trans. Elec. Insul.* **EI-18**, 194-203, 1983.
12. R.V. Latham, Private communication, CERN, May 1983.
13. C.S. Athwal and R.V. Latham, *Physica*, **104C**, 46-49, 1981.
14. N.K. Allen, C.S. Athwal and R.V. Latham, *Vacuum*, **32**, 325-332, 1982.
15. K.H. Bayliss and R.V. Latham, submitted for publication 1984.
16. N. Hilleret, Private communication, CERN, March 1983.
17. C.S. Athwal and R.V. Latham, *J. Phys. D, Appl. Phys.*, **17**, 1029-1043, 1984.
18. C.S. Athwal and R.V. Latham, *Physica*, **104C**, 189-95, 1981.
19. R.V. Latham, *High Voltage Vacuum Insulation: The Physical Basis*, Academic Press, London and New York, 1981.
20. R.V. Latham, *Vacuum*, **32**, 137-140, 1982.
21. I.L. Spain, *Chemistry and Physics of Carbon*, Vol. 16, pp.119-304, Mariel Dekker, New York and Basel, 1981.
22. Yu B. Yavkelevitch, *Vacuum*, **30**, 97-107, 1980.
23. O. Fischer and P. Niedermann, Private communication, University of Geneva, May 1984.
24. J.J. Maley, *J. Vac. Sci. Technol.*, **11**, 892-895, 1974.
25. A. Septier, *Proc. Workshop on RF Superconductivity*, Karlsruhe, 1980, pp. 56-76.
26. C.S. Athwal and W. Weingarten, *Int. CERN Report*, 1984.