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Energy spectra of electrons field emitted from a broad area composite cathode of tantalum carbide

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Details are given of the field electron emission (FEE) characteristics of a cold cathode consisting of a multi-array of tantalum carbide needles prepared from a directionally solidified eutectic. It is shown that, whilst these needles have similar dimensions, only a small fraction of these potential sources actually contribute to the total emission current. From electron spectroscopy studies it has been established that the characteristic half-width of the emission from individual areas is about ~ 260 meV and that the emission mechanism is based on a semiconductor regime. The Fowler–Nordheim (F–N) plots of the total emission from the cathode and that from small emitter areas are both linear over a wide field range.

1. Introduction

Broad area electron emitting cathode devices operating in the thermal mode have been well established for many years and used in cathode-ray tube and microwave transmitting devices. Operation of these cathodes in the field emission (FE) mode, using a high voltage to extract electrons directly from a sharp point (tungsten or carbon fibre) has only been investigated in detail using single point emitters of the type found in electron microscopes. Attempts to increase the total current extracted from the cathode in the FE mode by increasing the number of single emitting fibres have not been successful due to fabrication problems, although electron lithography and the film deposition techniques as used by Spindt [1] at SRI appear promising. These thin film fabrication techniques are expensive and hence materials having a fibrous composite structure are of potential interest.

Operation of cathodes in the field mode (cold cathodes) has been the subject of several reviews [2–5]. Distinct advantages can be obtained by operating in the field mode, the principal ones being 1. absence of a heater simplifies the tube technology, 2. absence of a heater gives "instant start", i.e. warming-up or induction period is eliminated, 3. no heater burn-out problems, and 4. materials tend to be more robust at lower temperatures.

Experimental studies of potential field emitter materials have centred on tungsten [6], lanthanum hexaboride [7, 8], carbon fibres [9, 10], the carbides of titanium [11] and tantalum [6, 7]. It is apparent that, where systematic comparisons exist, the carbides and borides are more resistant than metals to ion bombardment damage inherent to operation in the field mode [6, 8]. Provided that the field emitter is made of these materials with suitable physical properties (low work function, low vapour pressure, high thermal and electrical conductivity) there is a case for believing that their performance in the field mode will be at least equal to that of established thermal emitters.

Earlier experiments on carbides, summarized briefly here in Table I, but in greater detail in [12–14], confirm that a high current density can

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TABLE I

Fibre material	Current (A)	Current density (A cm^{-2})	Pressure (millibar)	Duration (h)
TaC	200×10^{-6}	0.08	4×10^{-9}	1200 +
VC	80×10^{-6}	0.5	5×10^{-7}	1000 +
NbC	120×10^{-6}	0.0035	5×10^{-7}	1000 +

be obtained when a high voltage is applied in a diode configuration under demanding conditions for prolonged periods. These results were obtained using the fibre composite materials produced by directional solidification of suitable eutectics and etched to produce the type of structures shown in Fig. 1. This material consists of tantalum carbide fibres in a nickel chromium matrix with fibre diameter of approximately 1 μm.

These directionally solidified eutectic (DSE) materials (often referred to as DSE composites) have been developed principally as high temperature corrosion resistant alloys for use in gas turbin blades for jet engines. Many of the materials that have been produced however contain fibres of refractory metal carbides. It is likely therefore that some of these alloys with the appropriate fibre structures can be employed for other purposes such as a broad area cathode with the electron emission occurring from the individual fibres.

The fibres as grown in the eutectic are oriented with respect to the matrix in which they are formed and emerge as single crystals. Although an examination of the bulk properties of the materials of the same nominal compositions as the fibre gives an indication of the fibre properties, no detailed determinations have been made of the fibres as grown in the eutectics. Few criteria exist for the selection of suitable carbides and little is known of the fundamental factors influencing electron emission; even basic information on parameters such as work function, are sparse.

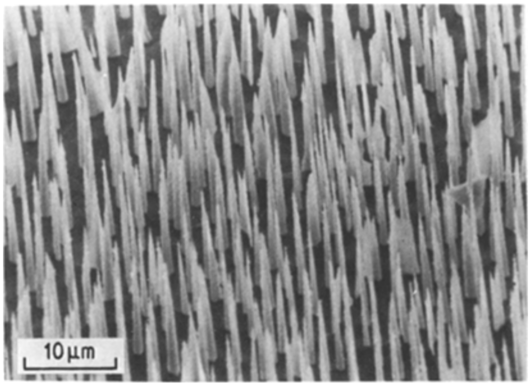

Figure 1 A scanning electron micrograph showing the needle structure which is characteristic of the surface of the TaC cathode.

The present work is concerned with the measurement of the energy spectra of electrons field emitted from a TaC cathode. Apart from the practical value of knowing the energy spread of electrons emitted from this type of source, such measurements are of great value in providing fundamental information about the electron emission mechanism, as discussed in Section 4. As far as we are aware, no previous attempt has been made to measure the energy spread from these eutectic materials.

An additional benefit that can be gained by using the measurements of energy spread is that the areas of the cathode which are emitting can be detected with a limited aperture spectrometer. It is uncertain from the diode measurements performed previously whether each individual fibre emits a low electron current or if a smaller number of fibres operate at higher currents.

2. Materials selected and fabrication

A detailed description of the fabrication method for DSE composites will not be given here since more comprehensive descriptions are given elsewhere [15]. Briefly the techniques of direction solidification of eutectic systems is achieved by moving the crucible containing the molten refractory carbide components and the metal matrix through a temperature gradient towards lower temperatures in such a manner as to maintain a planar boundary dividing the parent liquid and the solid formed from it. The reaction at the eutectic temperature is

$$\text{Liquid cooling} \rightarrow \text{Solid } \alpha + \text{Solid } \beta.$$

The constraint on the system imposed by sweeping out the liquid with a plane front (unidirectional solidification) can give plates or needles of α in a β matrix. In the case of needles the morphology requisite for a needle array is present. Selected etching can expose the tips of the α needles: in Fig. 1 the α needles are represented by TaC and the β matrix by Ni/Cr.

It is necessary to locate alloy systems in which carbides and borides form eutectic systems with metals. A literature search [12] has located numerous systems which appear suitable. A short-listing of candidate materials was based on the following critera for refractory metal needles: 1. high melting point (~ 2000 K), 2. low vapour pressure, 3. mechanical robustness, 4. low sputter yield, 5. electrical conductivity (moderate values sufficient), 6. chemical inertness (permitting selective etching of metallic matrix), and 7. low work function. The limited data available made it necessary to use mainly criterion 1 together with some calculations of the relative thermodynamic stability of the candidate materials under postulated field conditions [12]. From the final short list, TaC was a prime candidate. The properties of the metallic matrix are less significant apart from the requirements that it forms a eutectic system with the refractory metal carbide, has a low vapour pressure and can be etched preferentially to expose the fibre structure.

All results on energy spread reported here refer to the TaC needles in a nickel–chromium matrix.

3. Experimental methods

3.1. Diode tests on tantalum carbide

Prior to testing in the electron spectrometer, the sample of tantalum carbide, 8 mm in diameter, was evaluated in an experimental diode to confirm that electrons were emitted and that the Fowler–Nordheim [16] (F–N) relationship was obeyed. The F–N plot will produce a straight line if electron emission is caused by the field emission process.

The sample of TaC shown in Fig. 1 was prepared by electrochemically etching the nickel–chromium matrix away to expose the TaC fibres. The experimental details of the test diode are described elsewhere [13, 14]. The principal components however are a stainless steel chamber pumped with a polyphenol ether based oil diffusion pump and a facility to change the anode to cathode separation without exposing the cathode to the atmosphere. An electron bombardment filament within the chamber was used to outgas the cathode up to a temperature of 500° C prior to testing.

Two F–N plots obtained at 1 and 2.2 mm, anode to cathode separations are shown in Fig. 2, at a chamber pressure of 5 x 10^{-7} torr.

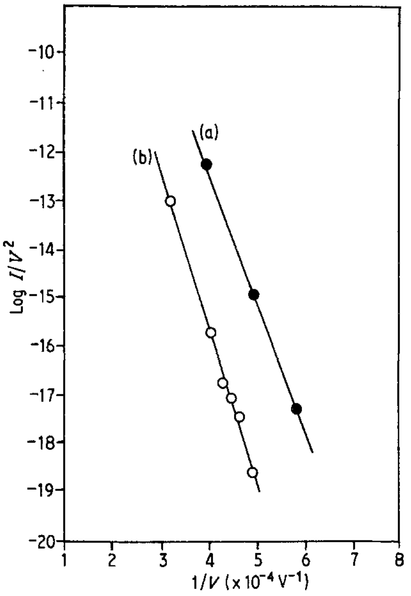

Figure 2 F–N plots of the total emission drawn from the TaC source at anode-to-cathode separations of (a) 1.0 mm and (b) 2.2 mm.

3.2. Electron energy spectra

A high resolution electron spectrometer was used to study the field emission characteristics of the multi-array specimen of TaC tips shown in Fig. 1. The design and performance of this instrument when used with single micropoint emitters have been described elsewhere [17]. In addition Allen and Latham [18] have reported on its adaption for studying the emission properties of the microscopically localized sites found on broad-area electrodes; i.e. the operational mode employed for the present investigation. Referring to Fig. 3, the spectrometer is a 180° hemispherical deflection type which as a design resolution of ~ 30 meV operating under ultra high vacuum (UHV) conditions of ~ 5 x 10^{-11} torr. To analyse the emission from broad area specimens, a comprehensive manipulator stage is incorporated which allows the specimen cathode "C" to be scanned in front of a probe hole "P" of a polished planar anode "A" whilst maintaining a parallel preset, inter-electrode gap. By applying a sufficiently high voltage between the specimen and anode, i.e. such that a prebreakdown electron current of ~ 1 μA flows between them, and scanning the specimen in a raster pattern, it is possible to locate

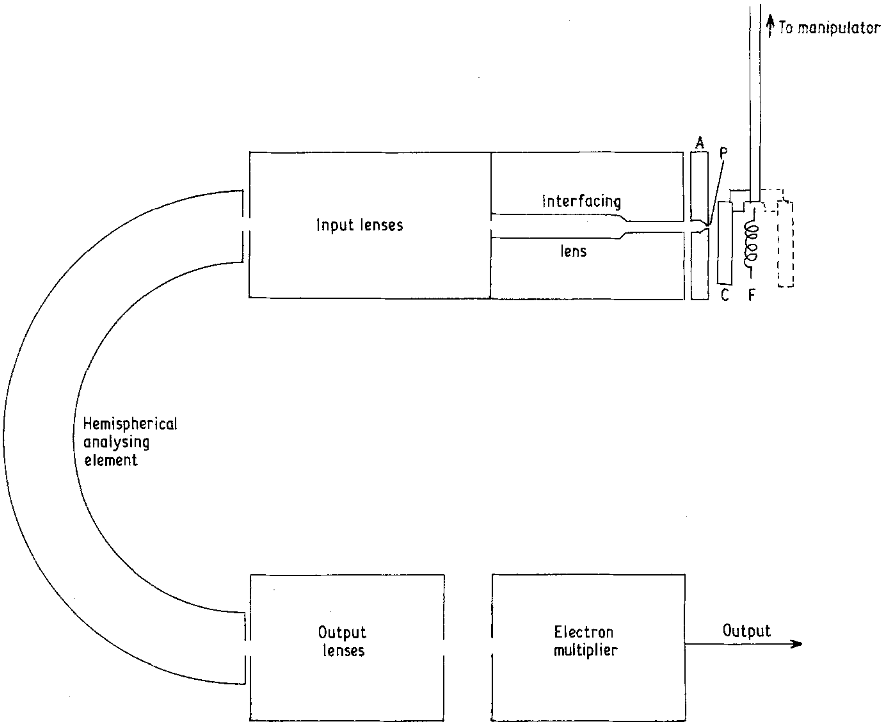

Figure 3 Schematic lay-out of the electron spectrometer facility [17, 18].

the individual emission centres on the electron optical axis.

The voltage–current characteristics and electron energy spectrum of the emission centre can then be measured. It should also be noted that an important property of this type of instrument, that will be referred to later when discussing the interpretation of spectral data, is the ability to identify the position of the Fermi level of the substrate cathode on any given spectrum [17]. Other features of the facility include alternative *in situ* specimen cleaning treatments: firstly, the specimen cathode "C" and anode "A" can be outgassed by electron bombardment using the filament "F", and secondly, the specimen surface can be argon-ion etched using a spherical-source

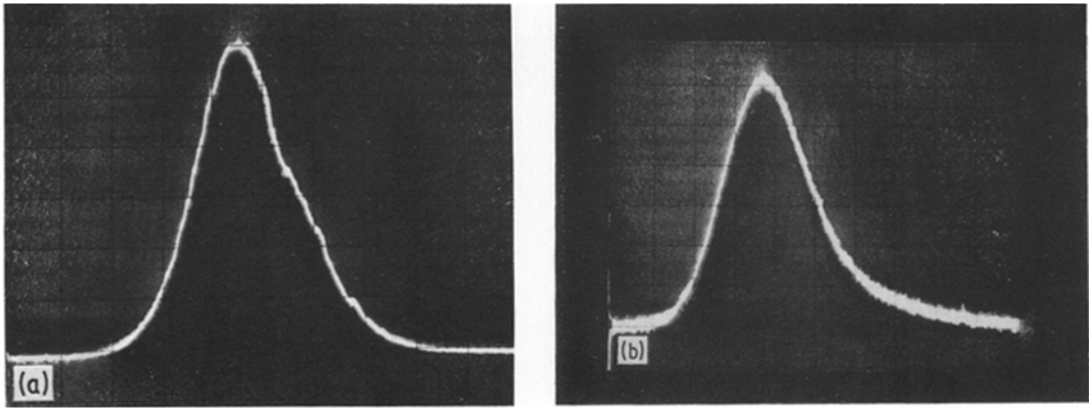

Figure 4 Energy spectra for the two types of emission site found on the TaC cathode: energy is decreasing from left to right. (i) Spectrum of site A: 2 V scan from 6.59 to 8.59 V, with the Fermi level located at 6.26 V, which is off the picture. (ii) Spectrum of site C: 1 V scan from 6.26 to 7.26 V, with the Fermi level (marked by a vertical line) located at 6.26 V.

gun directed at ~30° with respect to electron optic axis (not shown in Fig. 3). Outgassing of the specimen is usually carried out at 50 W for ~5 min to bring the surface to dull red heat; the anode requires the same power for ~3 min to bring it to a similar condition. For ion etching a relatively mild treatment is used, typically involving a 4 kV, 30 to 50 μA beam for 10 min.

4. Results

The first interesting finding to emerge from an initial examination of the emission current distribution from the out-gassed TaC specimen set to a 0.5 mm gap, was that for an applied voltage of ~3.5 kV, there were only three distinct emission sites (A, B and C) on the surface; i.e. despite its multi-point structure (see Fig. 1). For site A, the electron energy spectrum had the form shown in Fig. 4a and is characterized by having a broad half-width (~0.44 eV), a shallow high energy slope and, of particular significance, is displaced in energy by over a volt below the Fermi level. In fact, this "spectral shift" is conventionally quantified as the energy difference between the Fermi level in the bulk of the specimen (which is known from a prior calibration to occur at a particular position on the energy scan) and the energy value corresponding to a point 75% up the high energy edge slope of the spectrum. For a "free-electron" metal, Young and Kuyatt [19] have shown that these two points will coincide and so the degree of spectral shift gives a measure of the deviation of the emission source from free-electron behaviour. The magnitude of this type of shift is also frequently dependent on the emission conditions and can be presented either as a function of the applied field ($\propto$ the applied voltage, V) or total emission current as shown in Fig. 5.

A subsequent analysis of site B showed it to have broadly similar characteristics to those of A and will not therefore be considered in more detail. However, the third site C exhibited quite different behaviour. From a comparison of its spectrum shown in Fig. 4b with that obtained from site A (Fig. 4a), it is immediately apparent that this second emission process has the important distinction of having an exceptionally narrow half-width of ~260 mV: also, its smaller shift of 310 mV was found to be independent of field and emission current. A comparison of the corresponding voltage–current characteristics of sites A and C is given by the Fowler–Nordheim plots of Fig. 6. From their linearity, it appears that both processes follow a "metallic" emission law despite their "non-metallic" type of emission spectra; on such a model, their difference in slope would be interpreted in terms of emitters having differing local field enhancement factors β and/or work functions. These observations will be considered further in the discussion of this paper.

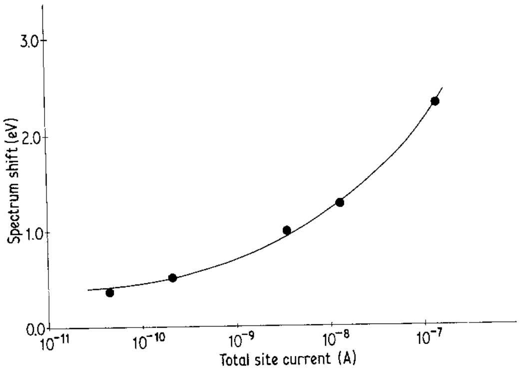

Figure 5 The variation in the shift of the spectrum from site A with its emission current.

Following this first series of measurements, the specimen surface was finally argon-ion etched for 2 h using a 40 μA, 4 kV beam. On re-examination, several new emission sites appeared, replacing those studied earlier. Unfortunately, many of these were very close to the edge of the specimen where the highly non-uniform field conditions prevented their emission from being focused into

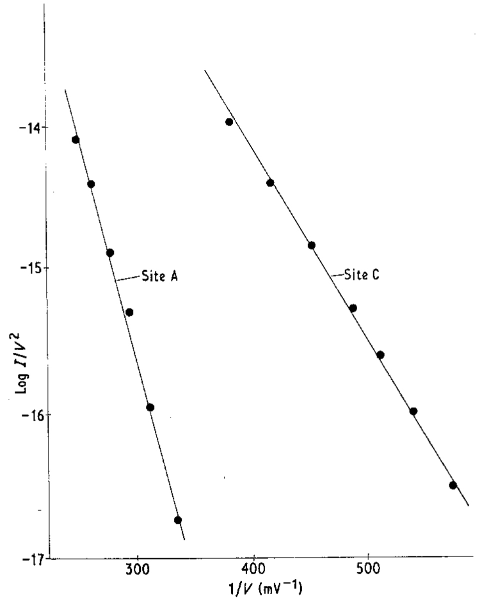

Figure 6 F–N plots of the emission characteristics of sites A and C.

the spectrometer. It is however significant that those that could be focused were found to have very similar emission characteristics to those of the original site C, i.e. with a narrow half-width (Fig. 4b) and exhibiting no shift with field or emission current.

5. Discussion

The phenomenon of spectral-shift is commonly observed in studies with laboratory fabricated semiconducting emission sources [20–22]. In most cases the shift is independent of field and current and is conventionally interpreted as reflecting a property of the emission process itself, such as would occur if electrons were to tunnel into the vacuum from localized surface states. From the general comparison of the spectra obtained from this type of study with those obtained in the present investigation, it can be reasonably concluded that the spectrum obtained from site C (Fig. 4b) is consistent with it being derived from a sharp semiconducting emitter: the narrow half-width further suggests that the emitting surface is relatively free of contamination. The fact that argon-ion etching creates further emitters of this type, presumably by a sharpening process, can also be seen as strongly supporting the conclusion that the spectrum of Fig. 4b may be taken as representative of the protruding TaC microtips shown in Fig. 1.

Variable-shift spectra, such as shown in Fig 4a, can sometimes be plausibly explained in terms of the resistivity of the material concerned, whereby a significant voltage drop can develop along the emitter between bulk metal cathode mounting and the actual point of emission. However, in the present case, the non-linearity of Fig. 5 clearly indicates that the shift has resulted from a more complicated mechanism than a simple ohmic effect. The singularity of this type of site suggests it originates from a microregime that is atypical of the cathode surface; one possiblility would be a contaminating dust particle since such features are known to field emit strongly [23].

The location of localized emission sites when scanning the specimen surface confirms that the emission is not uniform and that only a few needles emit at any one time. This non-uniformity in electron emission may be aggravated by the fact that the needle geometry tested for this particular TaC eutectic is not physically uniform and needles of different diameters and tip radii are present. Further tests using other eutectics with different physical geometries and more regular interface spacing and tip radii would be beneficial.

Acknowledgement

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