MECHANISM OF ENTRY OF MATERIAL INTO LIGHT SOURCES FOR SPECTRAL ANALYSIS

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Oxides on the sample cause the breakdown in the gap to be accompanied by the growth of a metal dendrite through the oxide layer. The subsequent main discharge disrupts the dendrite, the surrounding oxide, and the underlying metal. The oxide film affects the entry of material into the arc mainly by localizing the discharge. A barrier layer is produced at the contact between the metal and the oxide, which has a partial rectifying action.

Oxides are produced on metals by the discharge during spectral analysis; oxidation has a marked effect on the entry of material into the plasma [1-8].

It has been shown [9] that metal dendrites are formed between electrodes applied to the oxide on the surface of a metal; these are produced by reduction of the oxide by the space charge near the electrodes [9, 10]. The metallic nature of the dendrite is confirmed by their positive temperature coefficient of resistance [12]. Dendrites may also be formed in the absence of polar liquids [11-13].

Fig. 1. Copper after exposure to a discharge with an oxide layer produced: a) in an ac arc, b)-g) in an electric oven. 1 denotes the oxide and 2 the metal. Magnifications: a)-e) × 40; f) and g) × 50. a) and b) dendrites on surface of oxide; c) end of dendrite with oxide layer broken by striking discharge; d) dendrite produced under the previous conditions on the side of the oxide layer; e) effect of a single arc discharge (anode polarity) on the dendrite of d; f) and g) ruptured oxide layer produced by single arc discharges of f) anode, g) cathode polarities.
The oxides of Cu, Pb, and other metals used in [9-13] were made by heating the pure metals in an electric furnace; the oxides produced by discharges on metals are likely to have the same properties, so the latter may throw some light on the uptake of material by the arc.

We produced oxide layers on the electrodes by using Cu, Pb, Ni, Fe, and brass in arc and spark discharges from a GEU-1 generator (with electronic control).

The striking system of the GEU-1 was used to examine the breakdown of the oxides; starting is provided by an additional section that produces pulses at 25/8 cycles per second. This enabled us to use single high-voltage low-power pulses in these breakdown studies.

We found that metal dendrites were responsible for the breakdown on the surface or in the volume of oxide formed on the electrodes by a discharge or at constant temperature in an electric furnace. Dendrites were also produced when these specimens were used in polar liquids. The electrode material had no appreciable effect on the results either in breakdown or in dendrite production.

Parts a and b of Fig. 1 show copper specimens after breakdown with striking pulses from the GEU-1; the oxide on a was produced in 2 min in an ac arc at 5 a, while that on b was produced by 2 hr in an oven at 800°C. The arrows indicate the dendrites produced by the breakdown. Region 2 of Fig. 1a is part of the electrode unaffected by the arc. Lead, nickel, and iron gave similar dendrites. It is clear that the two methods give oxide films with identical properties; but those made in the oven are more convenient, for they are more uniform and can be made in any thickness. These were therefore the ones usually employed.

All previous workers with oxide films have used electrodes in direct contact with the material; but the arcs used in analysis have one electrode at some distance from the surface during breakdown of the oxide. We have shown that breakdown is accompanied by dendrite growth in this case also.

Figure 1c shows an oxide film pierced by an electrode 1 mm away in air; the arrow shows the end of the dendrite. The light area is unoxidized copper.

The striker thus serves to produce a metal dendrite in the oxide film as well as to ionize the air gap; the main discharge starts when the conducting channel has been formed. The dendrite receives a large power input and is destroyed explosively, the products entering the discharge. This process was confirmed as follows. A striking pulse was used to produce a dendrite (Fig. 1d) at the side of a layer of cuprous oxide 0.4 mm thick in good contact with the base metal. Subsequent striking pulses follow this channel and do not give new dendrites. A single arc pulse was then passed to the dendrite (Fig. 1e); the main discharge developed in the oxide around the dendrite, which destroyed the latter and disrupted the adjacent oxide and underlying metal.

A similar effect occurred when more powerful striking pulses were used; the dendrite produced in the early stage is later burned away and is seen as a burnt-out channel. This is evidently the breakdown mechanism for oxide films exposed to high voltages.

In Fig. 1, parts f and g show that anode polarity at the specimen produces a deep depression with a conical projection at the bottom, whereas cathode polarity produces a shallow pit with erosion products scattered at the sides. The underlying metal showed similar effects when the oxide was removed with 10% sulfuric acid.

It has been reported [1, 2] that most of the material comes directly from the oxides produced by the discharge. We tested this on brass (41% Zn); one specimen was heated in the electric oven for 1.5 hr, while a second was coated with silicone cement, in which scratches were produced after drying, to localize the discharge (mica plates with small holes can be used for the same purpose). These specimens were used in measurements at low voltages (20 uF, 2 A, zero inductance). The intensity of the Zn I 4810 A line was recorded. The counter electrode was a carbon rod turned down to a cone of angle 30° and placed 1.5 mm away. The control specimen was cleaned.

Figure 2 shows that the oxide and cement (curves 3 and 2) gave very similar results. Copper and nickel gave similar results, which show that the oxide film principally localizes the discharge; the steady state is reached more rapidly, and the intensity curve has a sharp peak whose height exceeds.

![Fig. 2. Low-voltage sparking curves for specimens: 1) with clean surfaces; 2) with discharge restricted by a layer of cement; 3) with oxide films.](image-url)