*Bulletin of Electrochemistry 1(1), Jan-Feb 1985, 38-40*

# A SCANNING ELECTRON MICROSCOPIC STUDY OF REFRACTORY COATINGS ON GRAPHITE

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## ABSTRACT

**The surface characteristics of refractory coatings incorporated on graphite by dipping, electroplating and plasma techniques have been evaluated using Scanning Electron Microscope. Fused alumina-sodium silicate, silicon carbide-nickel, fused alumina-nickel, fused alumina and calcined alumina coatings were examined. The coatings obtained by electroplating and plasma were found to be encouraging for further studies.**

## INTRODUCTION

The graphite electrodes used in the arc and other furnaces for the production of electrothermal products are prone to oxidation at temperatures above 400°C, depending on whether the environment is oxidising or reducing. Up to 650°C, the oxidation is penetrative and at higher temperatures, it is diffusion-controlled, primarily taking place at the surface. The reaction is influenced by the frequency of oxygen collisions at the surface above 1200°C. If the surface oxidation is avoided to a considerable extent, the consumption of the electrodes can be minimised thereby effecting great economy in this application by 20-25%. Modifying the surface of the graphite by coating refractory compounds like aluminium oxide or silicon carbide using suitable methods, and employing the coated electrodes in the furnaces, it would be possible to achieve the above aims. The recent trends indicate the growing inclination on the part of the manufacturers to use the coated graphite electrodes in the furnaces. Earlier work on the surface modification of graphite electrodes using different coating techniques has already been reported [1]

In this work, photographs using Scanning Electron Microscope (SEM) were taken on the coated graphite electrodes and the characteristics noted are discussed.

## EXPERIMENTAL

1 cm samples cut out of the 1.2 cm dia and 10 cm long, and the 5 cm dia and 20 cm long coated graphite electrodes prepared as given below, were used for Scanning Electron Microscopic studies:

i) Fused alumina — sodium silicate, dip and diffusion-coated and heated at 1000°C

ii) Silicon carbide-nickel composite electroplated from Watts bath (one sample as such and another heated at 1500°C)

iii) Fused alumina-nickel composite, electroplated from Watts bath (one sample as such and another heated at 2000°C)

iv) Fused alumina, plasma coated

v) Calcined alumina, plasma coated

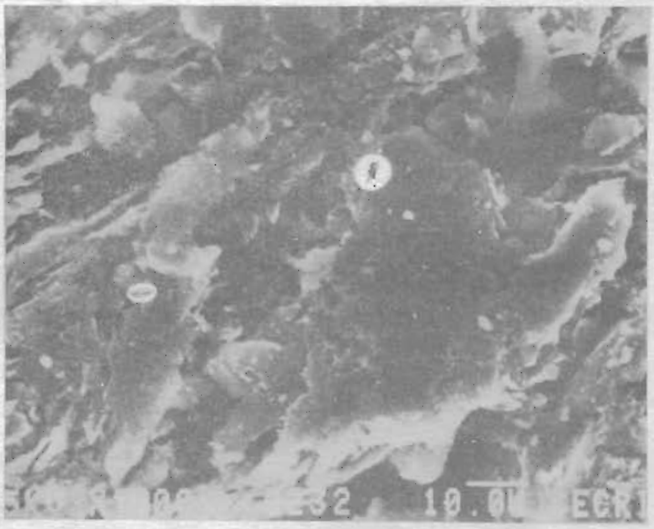
vi) Uncoated graphite as such

Silicon carbide, sodium silicate and the chemicals used for preparing Watts bath were of L.R. grade. Fused alumina was made out of Saurashtra bauxite at this Institute. Calcined alumina (plasma grade) was an imported sample. The graphite electrodes were of indigenous manufacture and of furnace grade.

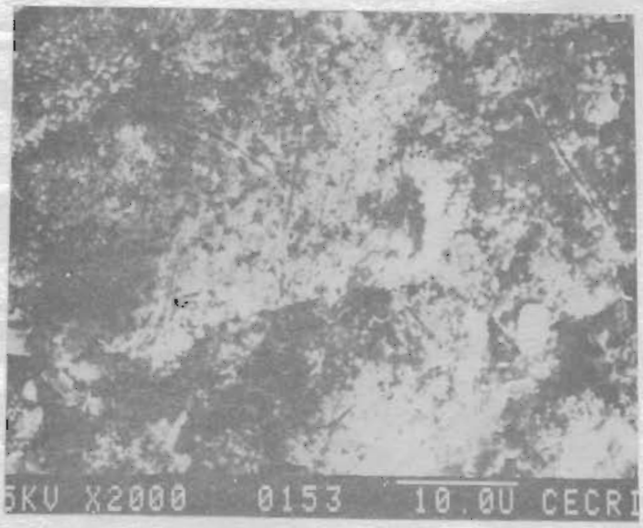
## RESULTS AND DISCUSSION

The SEM photographs are presented in figures 1 and 2. Table I

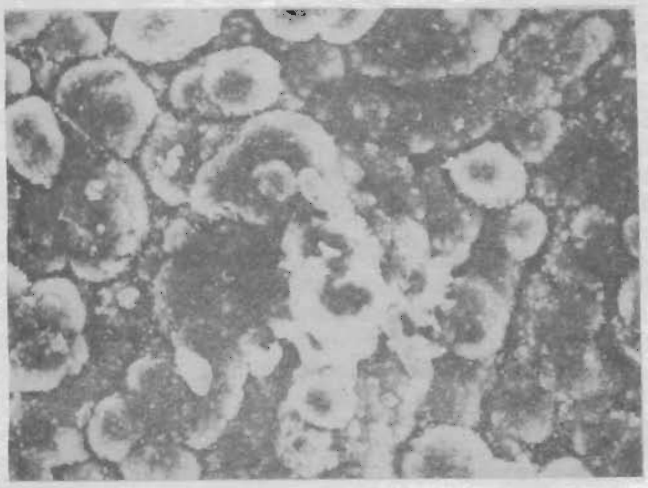
**Fig. 1 :** ***SEM MICROPHOTOGRAPHS OF ELECTROPLATED AND DIFFUSION COATINGS***



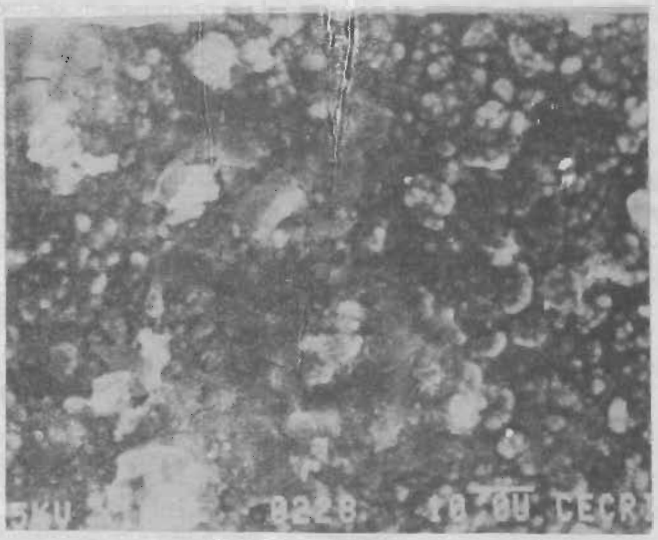
*232. Uncoated graphite*



*153. Silicon carbide-Nickel coated as such*



151. Silicon carbide-Nickel coated and heated at 1500°C

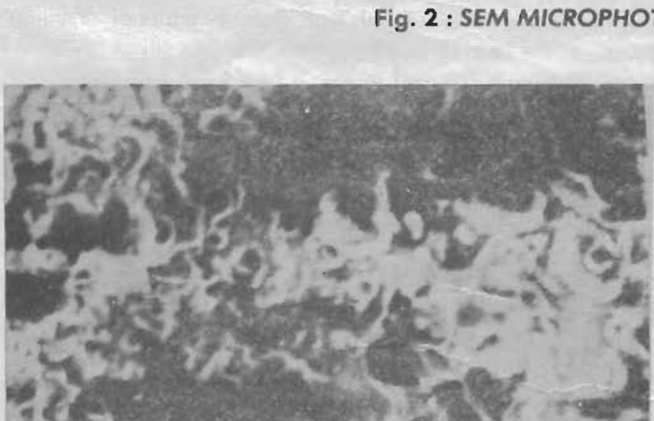


228. Fused alumina-Nickel coated as such

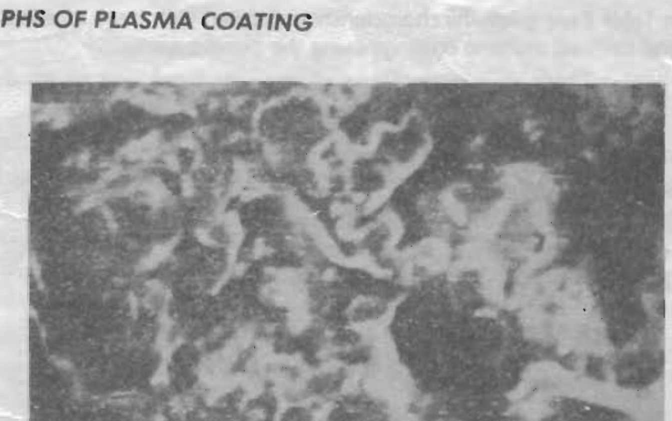
230. Fused Alumina-Nickel Coated and heated at 2000°C

152. Fused Alumina-Sodium Silicate as such

**Fig. 2 : SEM MICROPHOTOGRAPHS OF PLASMA COATING**



234. Fused Alumina as such



235. Calcined Alumina as such

gives the characteristics of SEM photographs of uncoated graphite and electroplated composite coatings of silicon carbide-nickel and fused alumina-nickel.

Table I : SEM studies on electroplated composite silicon carbide-nickel and fused alumina-nickel coatings on graphite

| SEM Photograph No. | Magnification (X) | Type of coating | Characteristics | Remarks |
|---|---|---|---|---|
| 232 | 1000 | Uncoated graphite | Flaky particles with pores in between them | For comparison |
| 153 | 2000 | Silicon carbide-nickel coated, as such | Silicon carbide and nickel particles visible | good coverage |
| 151 | 2000 | Same as above, heated at 1500°C | Melting of nickel has taken place. Silicon carbide particles are spread uniformly over graphite | -do- |
| 228 | 1000 | Fused alumina-nickel coated, as such | Nickel clusters and fused alumina particles are observed. | -do- |
| 230 | 1000 | Same as above, heated at 2000°C | Melting of nickel has taken place. Flakes containing fused alumina particles visible. | — |
| 152 | 2000 | Fused alumina-Sodium silicate dip coated, as such | Good coverage of sodium silicate with cracks and impurity particles | — |

In Table II are given the characteristics obtained with fused alumina and calcined alumina coatings using the plasma spray.

Table II : SEM studies on fused alumina and calcined alumina plasma-coatings on graphite

| SEM Photograph No. | Magnification (X) | Type of coating | Characteristics | Remarks |
|---|---|---|---|---|
| 234 | 500 | Fused alumina, as such | Fusion of particles, (white) seen. Black portions are pores | Application at high temperatures yet to be made. |
| 235 | 500 | Calcined alumina, as such | Same as above but fusion per unit area is 'small' | -do-<br>Alumina powder is imported one (plasma grade) |

Graphite, as such (No 232 — figure 1) is flaky in structure with a scaly form and contains pores which are irregular in shape and unconnected for the most part, being black in colour in the SEM photograph, graphite is usually porous to the extent of 18 to 32%.

Silicon carbide-nickel electroplated composite coatings (Nos. 153 and 151 — figure 1): As silicon carbide and nickel are good conductors of electricity, a smooth, uniform and homogenous composite deposit containing white particles (nickel) and black particles (silicon carbide) [2] has been obtained (No. 153). On heating to 1500°C (No. 151), nickel alone gets melted and it forms an eutectic with graphite at 1.9% carbon content above 1315°C, leaving silicon carbide particles uniformly over the surface. At 1000°C in air, oxidation sets in and a thin film of $SiO_2$ formed protects the carbide beneath it. Silicon carbide adheres to the substrate as it forms covalent bonds with carbon in graphite.

Fused alumina-nickel electroplated composite coatings (Nos. 228 and 229 — figure 1) : While nickel is conducting and fused alumina non-conducting, a uniform and rough deposit comprising agglomerates of nickel with fused alumina particles [2] is observed (No. 228). On heating to above 1000°C, the nickel melts, forms an eutectic with graphite, as stated earlier and also forms a solid solution with alumina just above the melting range. Flake graphite containing white alumina particles is seen in the picture. The oxidation is diffusion-controlled at high temperatures and can take place at the outside surface only. No change has been noted in the diameter of the graphite electrode both before and after heating to high temperatures.

Sodium silicate-fused alumina diffusion coating (No. 152 — figure 1) : The graphite substrate is fully covered with the oxide glass and small impurity particles but the coating contains cracks, due to the presence of alkali metal ions which reduce cross-linkages between $SiO_2$, $Al_2O_3$ and oxygen atoms, thereby reducing the softening temperature from around 1545°C to 655°C, viz. the $NaO_2$-$SiO_2$ softening temperature.

The alkali metal-oxygen bond is low, thus leading to internal and external strain resulting in the cracking of the glass.

Fused alumina/calcined alumina plasma coatings (No. 234 and 235 — figure 2) : In the plasma spray, both the alumina compounds are molten before solidification and the high conductivity substrate quenches the molten coatings rapidly, limiting flow and the coating density. The sprayed coatings are porous because it is not possible to eliminate all the fissures and joints between the particles [3]. Only low viscosity material will form denser coating and the flow is inhibited with high viscosity material, resulting in pores. In the case of fused alumina, the viscosity is found to be lower than with calcined alumina, hence the coating density is high, which is not so with the other sample.

*Acknowledgement* : The authors thank the Spectroelectrochemistry and the Scanning Electron Microscopy groups for all the assistance given for taking the SEM photographs. They also express their sincere thanks to the welding Research Institute, BHEL, Tiruchi for help in plasma coating.

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