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Session Name: Generators C

SEAM: 28 (1990)

SEAM EDX URL: https://edx.netl.doe.gov/dataset/seam-28

EDX Paper ID: 1444

PERFORMANCE OF CERAMIC ELECTRODES AND INSULATORS IN INDIAN MHD GENERATOR

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ABSTRACT

In the Faraday type of Indian MHD generator, initial power generation experiments using cold metallic electrodes realised low current drain from plasma. Hence ceramic electrodes made of silicon carbide, lanthanum strontium chromite, zirconia ceria with lead electrodes of yttrium barium cuprate or lanthanum strontium chromite were operated in the semihot mode and higher Faraday current was tapped. Preparation of composite ceramic electrodes with zirconia ceria cap directly diffusion bonded to lanthanum strontium chromite lead is also reported. Performance of magnesia insulators in comparison with alumina insulators in plasma and power generation experiments is also discussed.

INTRODUCTION

Indian MHD programme envisages pilot plant experiments to develop subsystem MHD components in the first phase and demonstrate a 200 MWT retrofit MHD in the second phase. Having demonstrated experimental MHD power generation in 5 MWT Indian MHD pilot plant, the present experiments in MHD generator focus on testing of various electrode and insulator materials and their performance evaluation. The D11 MHD generator of pilot plant facility is of linear segmented Faraday design and is intended to study plasma characteristics and materials performance in plasma mode without magnetic field and in power generation mode, using LPG fired, potassium seeded combustion plasma. The electrode wall temperature was increased through design modifications of the electrode module and ceramic electrodes made of silicon carbide, strontium doped lanthanum chromite, ceria doped zirconia cap electrode with lanthanum chromite lead electrode, ceria doped zirconium oxide cap electrode with yttrium barium cuprate lead electrode were tested for power extraction ability. In insulation wall aluminium oxide in sintered form and castable form and magnesium oxide in sintered form were used and their performance was evaluated. Recently composite electrodes have been fabricated by joining zirconium oxide and lanthanum chromite and this passed preliminary thermal shock and d.c. current density tests. The D22 MHD generator is a power extraction channel to operate at high wall temperatures around 2000 K on ceramic to evaluate the composite electrodes. Experiments in D22 will also focus on comparing MgO and BN insulators. This paper describes performance of D11 electrodes and insulators and the preparation of composite electrodes for D22 generator.

ELECTRODE WALL MATERIALS AND PERFORMANCE

The D11 MHD channel has five individual sections after the nozzle and 31 pairs of electrodes are distributed in the first three sections. The electrode module is made up of copper fitted with ceramic inserts and mounted on outer FRP casing plates. The module is shown in Fig.1. The modules were separated from each other by interelectrode aluminium oxide spacer plates. Sintered aluminium oxide with properties in Table 1 provides electrical isolation of electrodes axially to prevent flow of Hall Current. The average segmentation width is 65 mm and thickness 5 mm. The electrode modules are watercooled and circulation of dimeneralised cooling water is effected by inlet - outlet cooling tubes made of stainless steel brazed to the copper base of electrode module. The water cooling tubes serve as current leads also. The electrode module is electroplated with nickel to have better corrosion resistance and impregnated with 100 microns epoxy coating to improve back up electrode insulation. Ceramic electrode inserts are fixed to the electrode grooves with the help of high temperature calcium aluminate cement and these inserts reduce thermal losses and increase average wall temperature.

Preliminary experiments in power generation used water cooled copper electrodes with alumina inserts for the electrode wall. The ratio of copper to ceramic was 50:50 facing the plasma. The temperature of ceramic insert surface was 650 K and copper was 410 K and this turned out to be a cold wall with an associated large near electrode voltage drop and poor current drain. The power generation parameters are shown in Table 2. Post experimental observations revealed severe corrosion of copper electrode surface with the formation of strongly insulating deposit of basic copper sulphate and oxide. The alumina ceramic inserts cracked as a result of seed penetration, condensation and subsquent attack of grain boundaries with loosening of grains (Fig.2) and the disintegration continued under idle conditions after the experiment also. In the subsequent power generation experiment the copper surface was cladded with silver and in order to increase the average wall temperature the copper ceramic ratio was altered to 14:86. The alumina ceramic insert was replaced by rammed calcia stabilised zirconium oxide which has a lower thermal conductivity These modifications (Fig.3) did not improve the current drain and the wall temperature on ceramic was 1050 K and 420 K on copper. The rammed zirconia got sintered well after the Run and the surface erosion was around 2-4 mm.

It is well known that arc mode of current transfer is prevalent on cold walls. As the electrode wall temperature increases, the near electrode voltage drop decreases and the current transfer is through microarcs and diffusion of charged species across plasma electrode interface. At these high wall temperatures, metals oxidize, creep and become unstable. Hence ceramics are preferred as electrode materials, having advantages such as low thermal conductivity to reduce heat losses, moderate electrical conductivity, low thermal expansion to lessen thermal stresses and better chemical stability in MHD atmospheres. In the ongoing electrode development programme, electrodes such as lanthanum chromite, ceria doped zirconia and silicon carbide were taken up for preparation and comparative evaluation in D11 MHD generator in the semihot mode. The design of electrode modules were modified to facilitate charge transfer across plasma ceramic interface as shown in Fig.4.

Strontium doped lanthanum chromite corresponding to La 0.84 Sr 0.16 CrO_3 was prepared by ceramic process as described elsewhere (1). X-ray diffraction reveals orthorhombic perovskite phase and SEM showed (Fig.5) recrystallised uniform structure with well developed lanthanum chromite crystal grains of size around 3 microns. Intergranular porosity helps to improve therml shock resistance. DC conductivity profile as in Fig.6 shows constancy of conductivity above 300 deg. C. The cylindrical pellets were electroded on the rear surface with silver, fired at 800 deg. C and fixed in the electrode module as shown in Fig.7. Calcia stabilised zirconium oxide was packed around to provide structural integrity to lanthanum chromite and maintain a hot surface near the lanthanum chromite core and thus avoid a steep temperature fall adjacently.

Ceria doped zirconium oxide has good electronic conductivity. However below 800 deg. C resistivity of zirconia is so high that it ceases to be a good current transfer electrode. So a lead electrode is necessary to take up conduction between 50 m/o zirconium oxide - 50 m/o CeO_2 cap electrode and back up copper module. La 0.84 Sr 0.16 CrO_3 and yttrium barium cuprate ($Y_1Ba_2Cu_3O_7$) were experimented as backup lead electrodes. The material preparation is reported elsewhere (2). Establishing an electrically contacted joint between cap electrode and lead electrode is an ongoing development activity. Platinum foil sintered interface, platinum paste applied and fired interface, platinum powder mixed with La(Sr)CrO_3, $Y_1B_2Cu_3O_7$ silver powders as an interface and direct brazing alloys were tried between cap electrode and lead electrode. It has not been decisively established yet as to which one is a better interface. Experiments in MHD generator used platinum silver interface applied as a paste between zirconia ceria cap electrode and lanthanum chromite, yttrium barium cuprate lead electrodes and cofired at 900 deg. C. Silicon carbide electrodes operate as heating elements in furnaces upto 1600 deg. C with protective coating and without a coating upto 1400 deg. C. They have good electron emission capabilities and have resistivities around 1 ohm cm at 1500 deg. C. These electrodes were fitted in the electrode module similar to lanthanum chromite electrode described earlier. The experimental power generation parameters given in Table 3 and Figs.8&9 show open circuit Faraday voltage and short circuit Faraday current for all the electrodes including ceramic fitted electrodes and water cooled copper electrodes present in the electrode wall. High Faraday currents were drawn for silicon carbide electrodes, zirconia ceria electrode and lanthanum chromite electrode. Higher Faraday currents were drawn for silicon carbide electrodes. Maximum wall temperature at 3 mm below zirconia castable was 1590 K. Post Run observations (Fig.10) showed that all the above electrodes were found to be intact with electrical continuity and No physical damages except for the one with yttrium barium cuprate lead electrode in which zirconia ceria electrode had capped out (Fig.11) indicating interfacial bond failure due to thermal incompatibilities. The silicon carbide electrode had oxidised and blistered surface and room temperature electrical resistivity had almost doubled possibly due to attack of silicate bond by potassium seed.

Recent work on joining zirconia ceria and lanthanum chromite by solid state sintering to form a directly diffusion bonded composite hot electrode, has yielded good results. 25 to 50 mole % zirconia - 50 to 75 mole % ceria with and without 2 mole % tantalum oxide was the cap electrode. La 0.84 Sr 0.16 CrO3 was the lead electrode. Initial experiments on having an intermediate graded interface comprising different compositions of lanthanum strontium chromite and zirconia ceria yielded poor results (Fig.12). The cap electrode composition lead electrode composition and interface composition were pressed uniaxially in one shot in a steel die and sintered at 1600 deg. C. Inclusion of an interface led to delamination failures mainly due to differential shrinkage problem during sintering. Shrinkage match appeared to be more important than thermal expansion match. Shrinkage match was done by prefiring zirconia ceria powder and lanthanum strontium chromite powder in air, ground and the usual ceramic process was continued. The delamination at the interface was eliminated by this method. The composite electrodes are shown in Fig.13 These electrodes were subjected to thermal shock between room temperatures and 1550 deg. C without failure. The interfacial microstructure having lanthanum strontium chromite crystals and zirconia grains are shown in Fig.14. These direct diffusion bonded composite electrodes will be fitted in electrode modules as shown in Fig.15. These electrodes will be tested for power extraction ability, near electrode voltage drop, wall temperature attainable, etc. in D22 MHD generator in the forthcoming Run.

INSULATION WALL MATERIALS AND PERFORMANCE

The insulation wall materials should not short the axial and transverse electric fields and ceramic materials such as aluminium oxide, magnesium oxide and boron nitride having high electrical resistivity and low thermal conductivity to reduce wall heat losses are suitable. Since aluminium oxide technology is well established in this country, early experimental run used sintered hexagonal alumina plates (Fig.16) electroless nickel plated and brazed to water cooled copper pins. In the power generation mode these alumina plates were uprooted due to braze failures. It was also realised that in this arrangement failure of even one plate allows localised heating of the nearby joints due to contact of plasma gas and successive removal of them. Hence alumina brazed pins were replaced by ceramic filled peg walls. The D11 channel insulation wall has water cooled hexagonal copper pegs built into mosaic with ceramic insulation material filled in the copper peg. The individual pegs are mounted on a SS 304 plate with common water cooling passages and fixed to an outer FRP casing. The plasma sprayed pegs were filled with ceramic castables. This castable surface got eroded to a depth of 4 - 5 mm at the centre. It was decided to use sintered magnesium oxide as it has resistance to potassium seed and sintered version has higher erosion resistance than castable version.

Magnesium oxide was precipitated from hydrated basic magnesium carbonate and wet milled with 1 W/O aluminium oxide to serve as a sintering aid. The mixture was calcined at 1400 deg. C to obtain coarse tough grains. This powder was granulated with PVA binder and pressed uniaxially into discs and sintered at 1500 deg. C for 4 hours. XRD showed spinel cubic phase and samples were fractured and observed under SEM. The material had well faceted 10 micron grains free from cracks and other defects except for pores left for thermal shock resistance (Fig.17). The electrical resitivity measurements showed an order of magnitude superiority of MgO over aluminium oxide.

MgO pellets were filled in copper pegs using high temperature adhesives (ceramabond 571 liquid filled with fused MgO fines, Aremco, USA). They were assembled in the insulating wall of high heat flux portion of the channel. These discs completed three experimental runs with a total of 115 hours. The properties of MgO discs and run parameters are given below:

Density	: 2.63 gms/cc
Porosity	: 26%
Resistivity at 800 deg.C	: 5.85 MΩcm
Grain size	: 10 microns
Plasma temperature	: 2800 K
Heat flux through insulation wall	: 3.7-4.2MW/sq.m
MgO surface temperature	: 1240 K
No. of hours of operation in the power/plasma mode	: 115 hrs.30 mts

After the run the pellets were examined in a stereo microscope X 50 and was found to be free from post run macro defects such as cracks, loosening of grains, etc. The resistivity was measured again and was found to be around 5.5 micron cm at 800 deg. C deviating little from prerun values.

D 22 MHD generator uses a plate wall type of insulation module separated by rectangular Mgo plates (50 x 40 x 5 mm) and plates would be filled with zirconium oxide castables to reduce heat losses. It is proposed to test these modules along with BN and compare the performance at surface temperatures as high as 1700 K on MgO.

CONCLUSIONS

(1) Lanthanum strontium chromite, silicon carbide, zirconia ceria leaded with lanthanum strontium chromite served as semihot electrodes for D11 Indian MHD generator.

(2) Novel ceramic composite electrodes with zirconia ceria cap electrode directly diffusion bonded to lanthanum strontium chromite lead electrode have been prepared for D22 MHD generator to operate at 2000 K on the ceramic wall.

(3) Magnesium oxide worked well on the insulator wall for 115 hours in the power generation and plasma mode.

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(2) Balachandran R., Ram Mohan N. & Thiagarajan K. - Studies on YBa2Cu3O7-x ceramic superconductor - BHEL Journal, Vol 9, No. 1, 1988.

ACKNOWLEDGEMENTS

The authors thank Dr. S.A. Arunachalam, Head, MHD Centre and Prof. S. Sivan, Regional Engineering College for helpful discussions during the work. Technical association in the preparation of samples by Mr. Y. Johnkutty is acknowledged. This work was carried out as part of MHD programme development funded by Department of Non Conventional Energy Sources, Government of India. Permission by BHEL Management to present the paper is gratefully acknowledged.

TABLE 1

PROPERTIES OF SINTERED ALUMINA

Phase	: Alpha alumina
Chemical composition (wt. %)	
Al_2O_3	: 99.0
SiO_2	: 0.42
Fe_2O_3	: 0.04
$Na_2O + K_2O$	: 0.24
TiO_2	: 0.10
Density (gm/cc)	: 3.5 - 3.6
Total porosity (%)	: 10 - 12
Electrical resistivity (1000 K)	: 0.32×10^6 ohm cm
Breakdown voltage	: 2.25 KV/mm

TABLE 2

POWER GENERATION RUN PARAMETERS

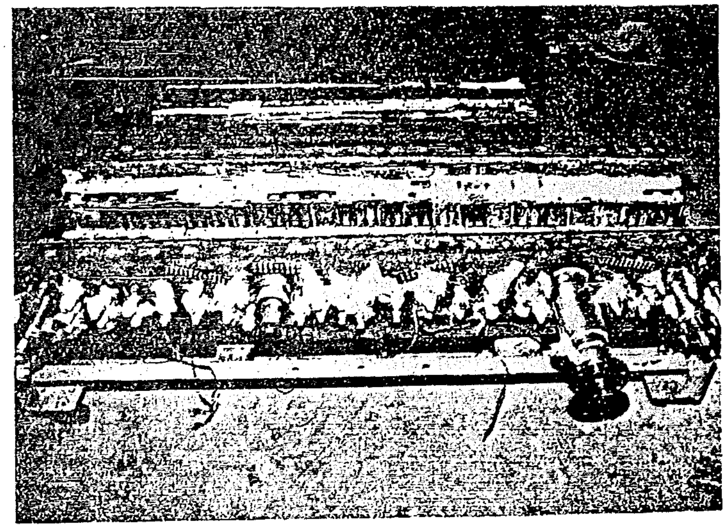
(Channel using copper electrodes with alumina ceramic inserts)

Mass flow rate of combustion products	: 1 kg/sec
Thermal input (main combustor)	: 5.0 MW
Preheat temperature of oxidiser	: 810°C
Percentage oxygen enrichment	: 43%
Plasma temperature	: 2810 K
Plasma conductivity	: 12 mho/m
Magnetic field applied	: 2 Tesla
Total duration of power run	: 2 hours
Open circuit Faraday voltage per electrode pair	: 95 V
Short circuit Faraday current per electrode pair	: 2.7 amps
Average power	: 3 KW

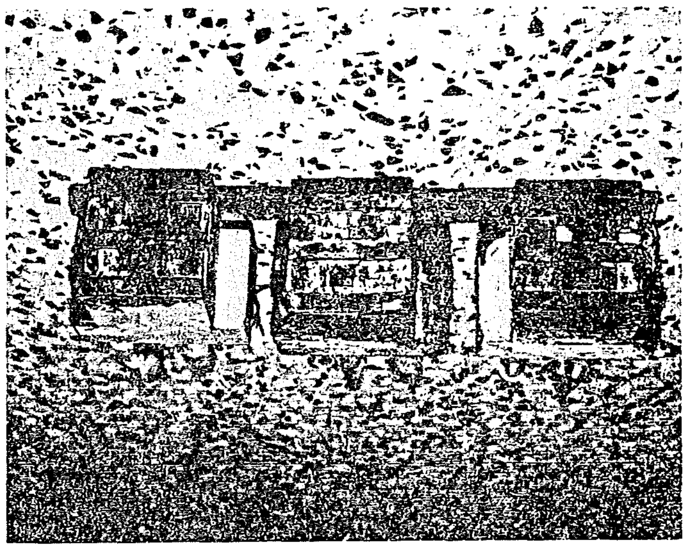
TABLE 3

EXPERIMENTAL POWER GENERATION PARAMETERS

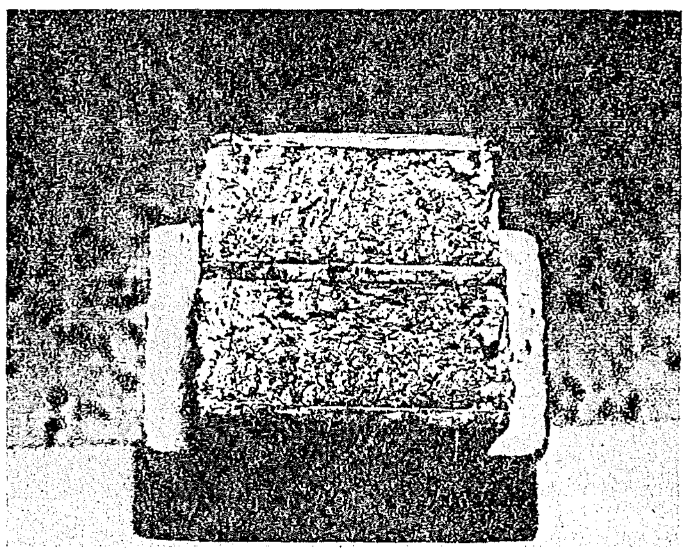
Plasma temperature	: 2860 K
Hot oxidiser temperature	: 1300 K
Plasma electrical conductivity	: 8 mho/m
Magnetic field	: 1 - 2 Tesla
Combustion product mass flow rate	: 1.1 kg/sec
Thermal input to main combustor	: 4.8 MW



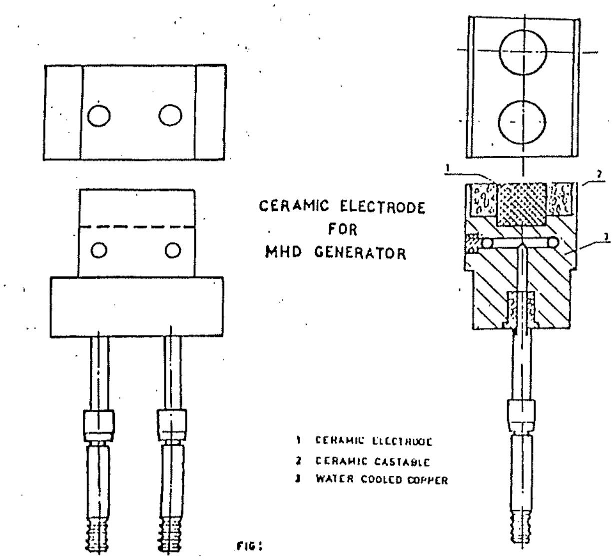
F 1. ELECTRODE MODULE IN D11 GENERATOR



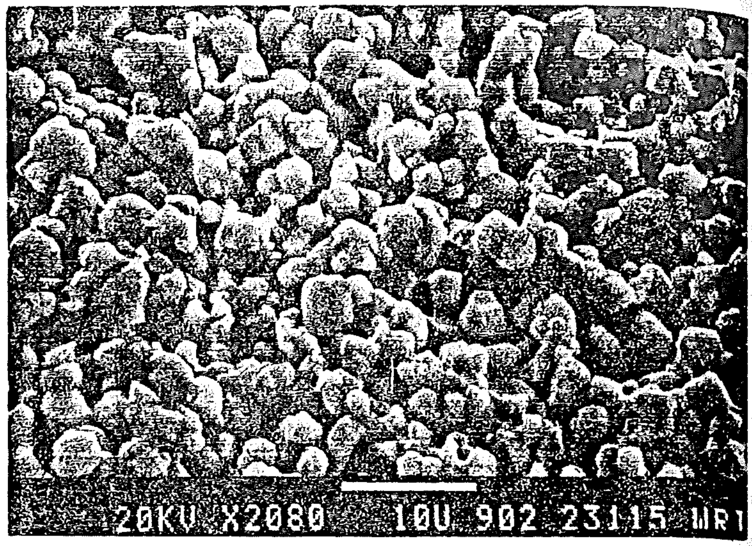
F 2. CRACKED ALUMINA INSERTS AFTER POWER RUN



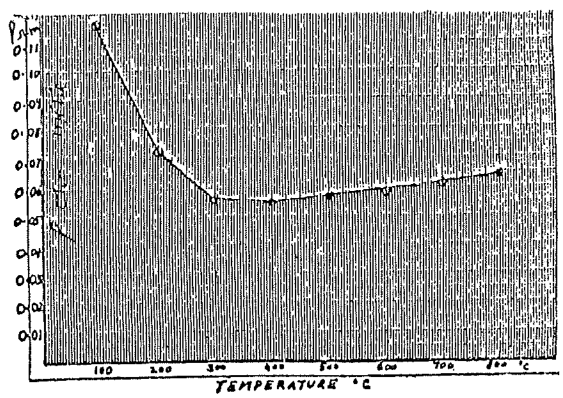
F 3. ELECTRODE MODULE WITH ZIRCONIA CASTABLE AFTER POWER RUN



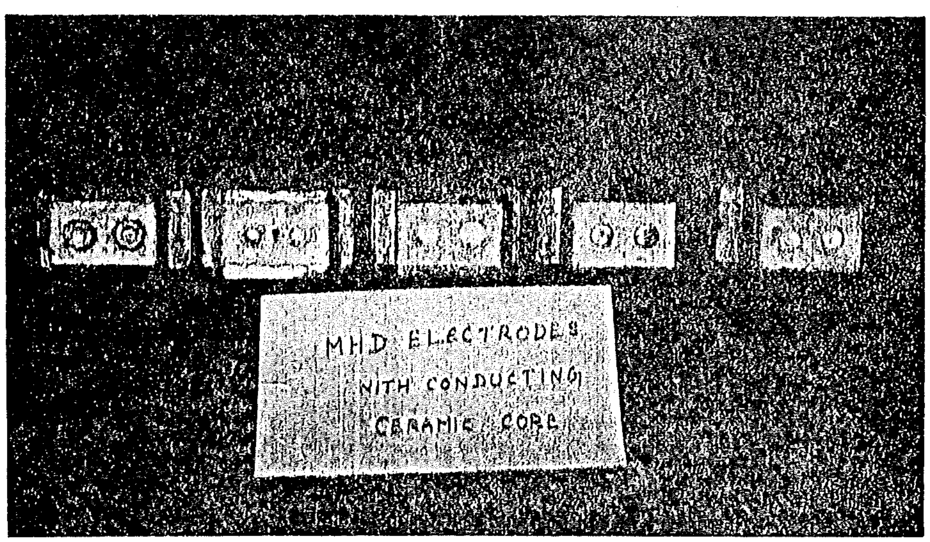
F. 4. CERAMIC ELECTRODE FOR MHD GENERATOR



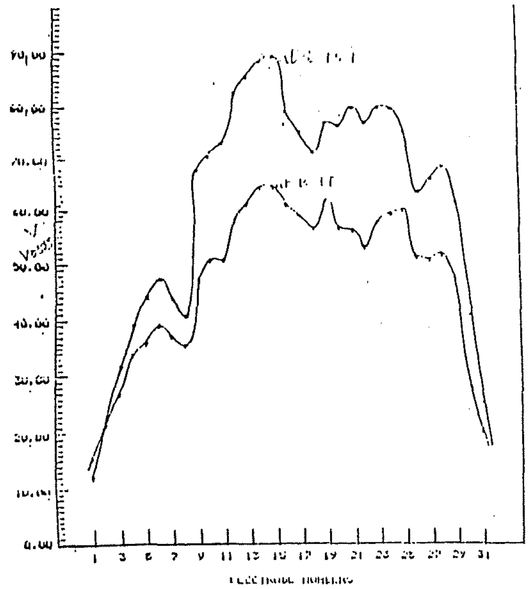
F. 5. SEM OF LANTHANUM STRONTIUM CHROMITE

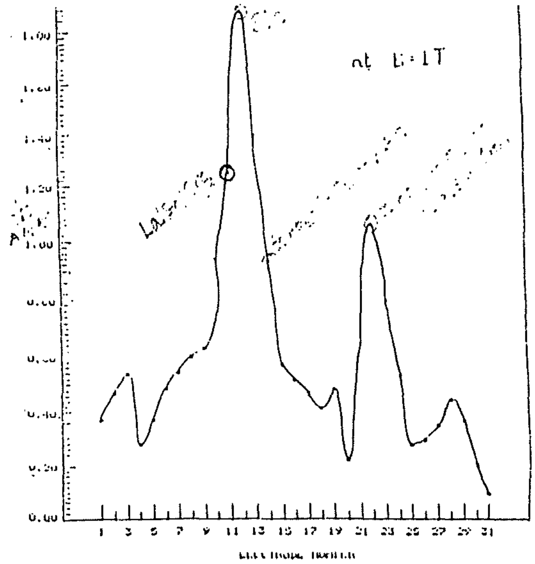


F. 6. DC CONDUCTIVITY PROFILE OF LANTHANUM STRONTIUM CHROMITE

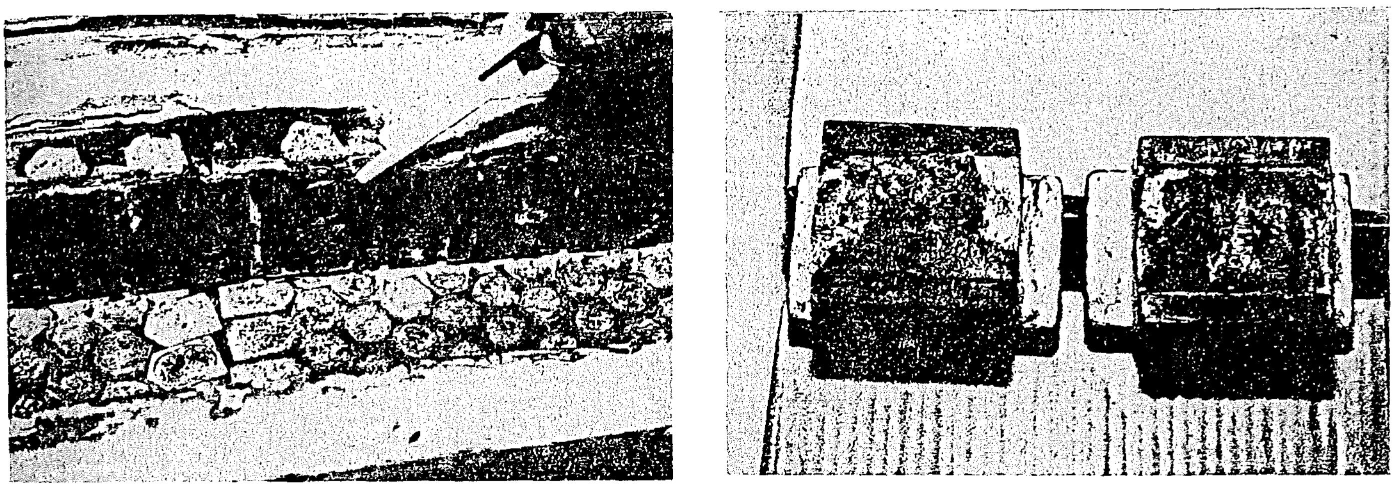


F. 7. LANTHANUM STRONTIUM CHROMITE, SIC, ZIRCONIA CERIA ASSEMBLED ELECTRODE MODULES

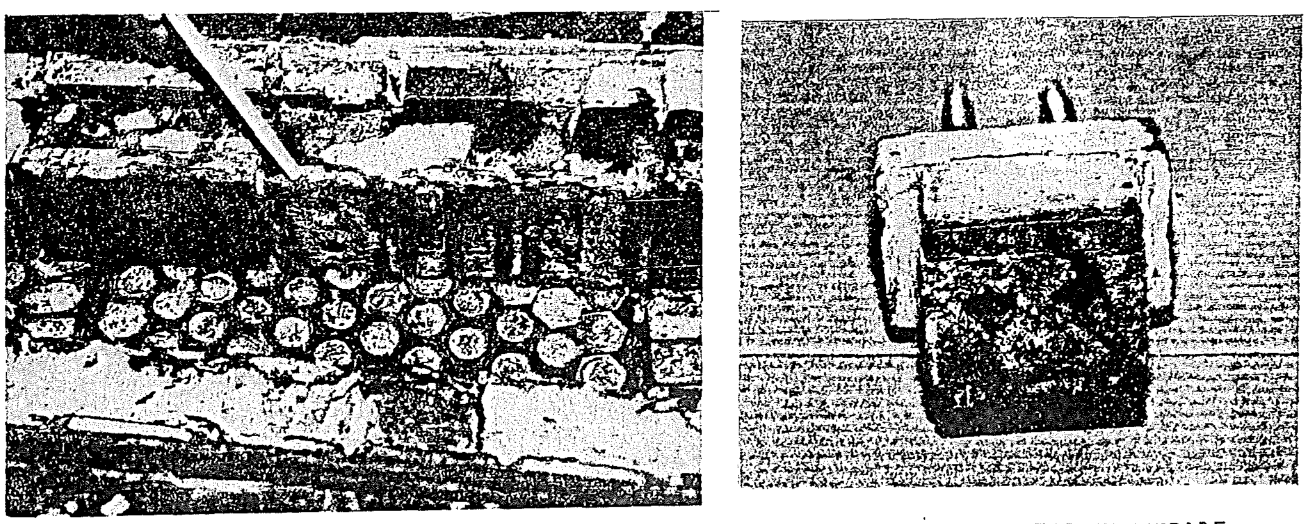




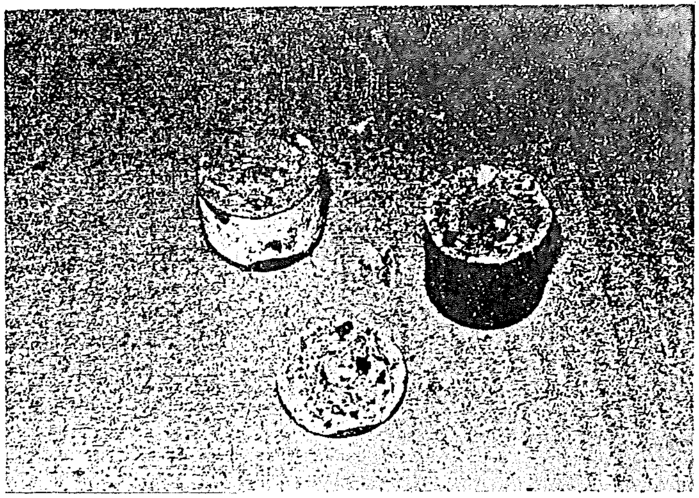
F. 8 & 9 FARADAY VOLTAGE AND FARADAY CURRENT OF ELECTRODES IN POWER RUN



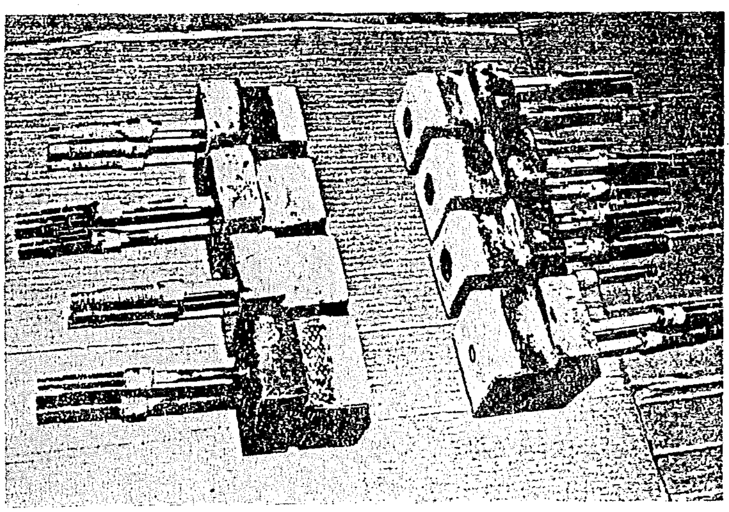
F. 10. LANTHANUM CHROMITE AND ZIRCONIA ELECTRODES INTACT AFTER POWER RUN



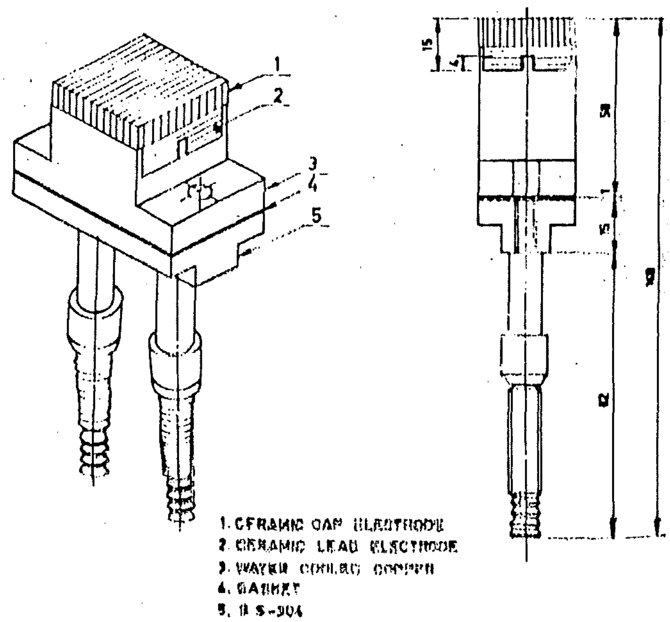
F. 11. PULL OUT OF ZIRCONIA CERIA WITH YTTRIUM BARIUM CUPRATE LEAD ELECTRODE



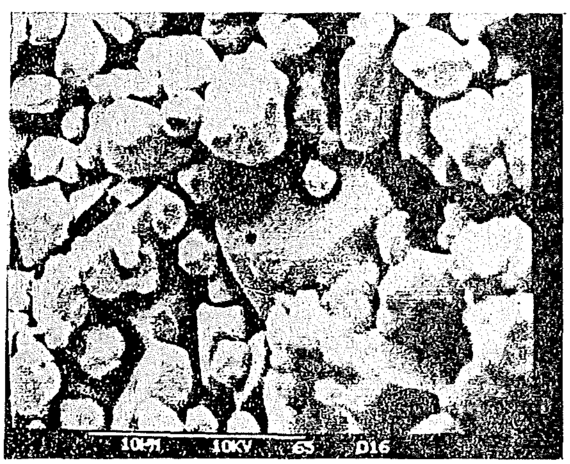
F. 12. DELAMINATION IN INTERFACED COMPOSITE



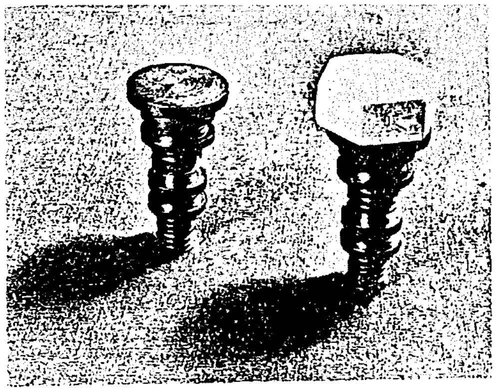
F. 13. COMPOSITE ELECTRODES ASSEMBLY



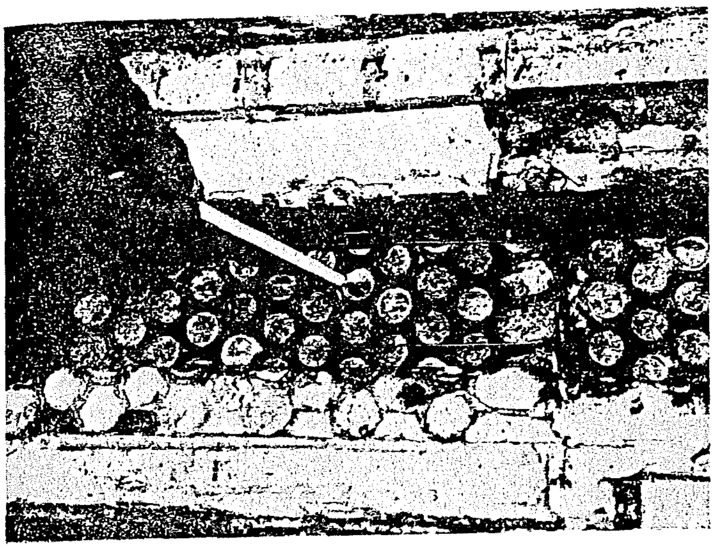
F. 15. COMPOSITE ELECTRODE FOR D22 GENERATOR



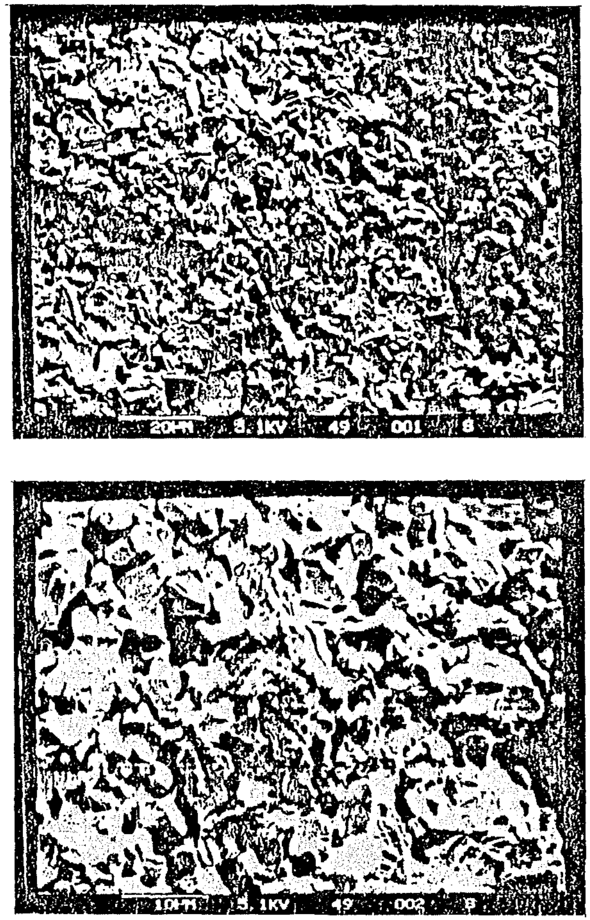
F. 14. MICROSTRUCTURE OF INTERFACE



F. 16. ALUMINA PLATES BRAZED TO COPPER PINS



F. 18. MAGNESIA AFTER 115 HOURS OPERATION
IN THE GENERATOR



F. 17. SEM OF MAGNESIUM OXIDE