High temperature materials for magnetohydrodynamic channels

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Abstract. The development of suitable materials for use in MHD generator is one of the most challenging areas. The very high temperatures (~ 2700 K) coupled with the highly corrosive seed-laden atmosphere limit the choice of materials in contact with the plasma to just a few ceramic oxides. These materials in contact with the high temperature plasmas in MHD generator are simultaneously subjected to stresses of mechanical, thermal, chemical and electromagnetic nature. The development and suitability of the different potential electrode and insulator materials such as lanthanum chromite, zirconia-based materials, alumina, magnesia etc. are reviewed with particular reference to the MHD channel materials programme in the MHD Project at BARC.

The operating experience with alumina-based ceramics and other materials under MHD operating conditions is also detailed. This includes the specifications, processing, bonding of the ceramic materials, the test programme and evaluation. Also presented are some of the novel processing techniques like plasma spraying and their application in the development of MHD materials. The advantages and limitations of each of these materials and their principal mode of degradation while in service are also discussed.

Keywords. Coal-fired MHD generator; high temperature electrode; insulator materials; metal-ceramic joint; slag ceramic interaction

1. Introduction

Magnetohydrodynamic power generation (MHD) is a branch of fluid mechanics dealing with the flow of an electrically-conducting fluid (plasma) in the presence of a magnetic field. The same principles of electromagnetic induction, utilised in conventional rotary generating machine, are applied to conducting fluids flowing through a magnetic field. An MHD generator essentially combines the functions of the steam turbine and electrical generator of a conventional system. In the MHD generator, the thermal energy of the plasma is directly converted into electrical energy—hence the MHD power generation is termed as the direct energy conversion process. As a consequence of high temperature direct conversion operation, the power plants incorporating MHD generators are potentially more efficient than conventional turbine power plants.

The development of MHD generator involves the magnetic system, inverter and channel. The MHD channel which forms the heart of the MHD installation, operates under extreme conditions of temperature, thermal flux, velocity of plasma, magnetic and electric fields. Hence, the design, fabrication and assembly are complex tasks. In principle, a modular structure is preferred. The modular construction, though complex, increases the electrical reliability of channel by prescribing finite potential breaks between various elements.

The materials used in contact with the plasma have to be stable at high temperatures, withstand seed attack and thermal shock, retain their refractoriness, electrical resistivity and mechanical strength during operation and have the capacity of being fabricated to required shapes. These requirements, therefore, impose stringent conditions on the purity of the material, the fabrication techniques and quality control of various

processes. As on today, the development of suitable material for channel applications remains an open problem. This problem is being attacked in many ways. Some of the approaches being followed to find suitable answers to the problem are: (i) the development of new technologies and processes; (ii) the development of new materials, and (iii) development of new engineering concepts using standard materials.

2. Materials and techniques

The refractory materials, generally in contact with plasma in the MHD channel serve as electrodes, electrical insulators or as thermal insulators (figure 1). Even though efforts in several countries have been devoted to their development, ideally suitable materials to work in contact with plasma have not been found. Over a period of years significant progress has been made but much more work remains in the field.

The primary constraint of material durability has forced the designers to compromise with less optimum designs of the channel or to think of alternatives like frequent duct changeover. Recent interest in coal-fired MHD plants has introduced additional problems of electrochemical interaction of slag with the channel materials. The slag coating affects both the performance of the generator and the durability of the channel materials. A schematic representation of slag-coated channel wall is shown in figure 2.

The refractory materials in general should have the following desirable properties:

(a) *Thermal properties*: The materials must have adequate thermal conductivity to transmit the high heat fluxes from plasmas at temperatures over 2500 K. They should also resist the thermal shock conditions caused by large temperature gradients under operating conditions as well as during start-up and shut down.

(b) *Electrical properties*: The electrical resistivity of electrodes should be less than 1 ohm-cm and should withstand current densities of 1–2 A/cm². They should also

Figure 1. Schematic of Faraday MHD channel.

Figure 2. Schematic of slag-coated channel wall showing variation in chemistry and properties through the wall.

possess good electron emission characteristics. The insulators should have resistivities greater than 100 ohm-cm and a dielectric breakdown strength greater than 4 kV/mm at elevated temperatures.

(c) *Chemical properties:* The material should withstand seed and coal slag attack and should be stable under oxygen partial pressures of 10^{-2} – 10^{-3} atmospheres. In general materials of low vapour pressures and high melting points are required. When different materials are used, they should be chemically compatible with each other.

(d) *Mechanical properties:* Sufficient to withstand the effect of high power density fluid without significant creep deformation.

2.1 Materials for clean fuel MHD channel

Today high purity Al_2O_3 and MgO appear to be popular as insulator materials. These materials exhibit good chemical and structural stability and high electrical resistivities of the order of 10^2 – 10^5 ohm-cm at 1973 K. Between the two, MgO is preferred because of resistance to seed attack. Sato and Kazukawa (1980) have tested more than 65 kinds of refractories (ceramics, spinel and pure single oxide ceramics) for alkali corrosion using K_2SO_4 – K_2CO_3 and K_2SO_4 melts. The results indicate MgO and ZrO_2 – CeO_2 have strong corrosion resistance whereas Al_2O_3 showed good results only in K_2SO_4 melts. Combination of MgO and Al_2O_3 are also being evaluated as insulator materials.

In BARC, the alumina modules made from castables, plasma spraying and sintered blocks have been tested extensively by oxy-acetylene flame testing facility. Copper-ceramic module used has been shown in figure 3 and the results tabulated in table 1. The technique of joining metal (copper) to ceramic has also been developed and dealt in § 2.3. The performance of sintered alumina pieces (around 10% porosity) of different shapes in Indian MHD generator test-section (figure 4) has been satisfactorily tested in Soviet U-02 facility in Moscow during May 1980. The total test duration was 64 hours and included electrophysical tests and life tests under applied electrical fields. The results of detailed analysis on the materials used in the channel have shown that improvements should be made on ceramic materials. This will consist of better purity of starting materials, improved processing techniques and more optimal properties like porosity, grain structure and thermal shock resistance (Rohatgi and Shishkov 1981).

For electrodes, apart from metal and their alloys (Hurby *et al* 1980), oxides of zirconia and lanthanum chromite have been investigated extensively. Zirconia

Figure 3. Schematic of copper-ceramic module for flame test.

Table 1. Summary of results of flame testing of materials

Material	Supplier	Total Porosity (%)	Heat flux (MW/m ²)	Maximum surface temperature (K)	Remarks
Alumina castable peg wall	M/s ACC Bombay	45	0.6–0.8	1783	No cracks were observed. Seed penetration was observed throughout the sample.
Sprayed alumina peg wall	BARC	12	0.75–1.1	1873	No cracks were observed. Seed attack was observed.
Sintered hexagonal block soldered to copper	M/s ACC Bombay	10	0.8–1.1	1950	In some samples fine cracks were observed after the test. Seed attack was observed.
Sintered circular block soldered to copper	BHEL R and D Corporate Hyderabad (Trial samples)	3–4	0.7–1.6	1593	Cracks were observed after the test.

stabilized with CeO and Y₂O₃ have yielded encouraging results up to 1700 K. However, the low thermal and electrical conductivity and ionic conduction of zirconia are some of the objectionable features of this material. More than 50 % electronic conduction have been already achieved with CeO doped zirconia. Further, the study indicates that a composition of 80 % CeO₂–18 % ZrO₂–2 % Ta₂O₅ is a better candidate for MHD electrode material (Hosler and Frederikse 1975) as it combines all the good features in one compound mostly, high conductivity, nearly 100 % electronic conduction, single phase structure and chemical stability up to 1900 K. Lanthanum chromite (LaCrO₃) has an excellent electrical conductivity but at higher temperature loss of chromium results in degradation of material due to attack by water and seed (Sata and Kasukawa 1980). Nevertheless because of high electronic conduction, this material has a long interest on generator electrode material. Over a period of years many attempts have

Figure 4. First Indian MHD channel, tested in U-02 facility of Moscow.

been made to improve the properties of this material. Suppression of chromium evaporation in LaCrO_3 by substitution with magnesia have been successfully attempted in BARC by George *et al* (1976). The material designated as LC 20 M exhibits good sintering characteristics in single firing at 1650 K with a porosity of less than 10% and grain size of 3–8 μm . The electrical resistivity was around 0.2 ohm-cm with a very low temperature coefficient. The sample withstands current density of the order of 20 Amp/cm² for long duration. The thermionic work function $W_p = 2.75$ mV and Richardson constant, $A_R = 0.11 \text{ A cm}^{-2} \text{ K}^{-2}$ were suitable for MHD electrode applications by Pai *et al* (1980). The resistivity of different potential electrode materials (Schneider *et al* 1979) for MHD use is shown in figure 5.

2.2 Materials for coal fired MHD channel

The properties of slag and slag coated materials have been the subject of investigations in recent years. Effects of slag on MHD generator performance have been studied by Bogdenske *et al* (1975). Very good results have been reported for stainless steel electrodes (operating approximately at 900 K) with moving slag on them. However, difficulties were experienced with suitable insulations between the electrodes and through the side walls in the Faraday generator (figure 6). Use of metal as electrodes (cold wall mode) also exhibits some serious instabilities in the current transfer and to the poor electrical conductivity of solid slag. Migration of oxygen through the slag layer under the influence of the electrical field also causes oxidation of the anodes. To minimise the possible deleterious reactions and degradation of the electrode system, Mason *et al* (1975) have identified $\text{FeAl}_2\text{O}_4\text{--Fe}_3\text{O}_4$ spinel (figure 7) as a potential electrode for open cycle coal fired MHD cycles. This spinel-alumina electrode module offers a number of distinct advantages like: (i) completely electronic conductivity; (ii) absence of resistive reaction layer at the electrode face; (iii) diffusion of iron into

Figure 5. Resistivity of potential electrode materials.

Figure 6. Schematic of arc-slag interaction on cold stainless steel electrode (900 at steel surface).

the alumina; (iv) grading of spinel layer as indicated in figure 7 will minimise the driving force for inter-diffusion with alumina at the hot and of the module adjacent to the slag.

In BARC, the degradation kinetics of ceramics [Al_2O_3 and Calcia stabilised zirconia (CSZ)] by slag reaction has been studied by making ceramic-slag couples and analysing their reaction (Karthikeyan *et al* 1982). The slag powder was prepared by conditioning the fly ash of coal from Bihar fields. The reaction couples were prepared by plasma spray technique. In the study it has been found that the main degradation reaction of alumina is the dissolution of alumina into the slag whereas in CSZ the degradation is mainly due to the depletion of calcia from CSZ resulting in the formation of thermally unstable monoclinic zirconia. The growth of calcia depletion and enrichment zones is shown in figures 8 and 9.

Figure 7. Schematic of spinel ($FeAl_2O_4-Fe_3O_4$) electrode.

Figure 8. Growth of calcia depletion zone in CSZ.

2.3 Ceramic-metal joints

In Faraday MHD generator, joining of ceramic to water-cooled copper plays a vital role. For maintaining the designed heat flux of the channel and surface temperature of ceramic it is essential to join ceramic to metal with good thermal conductance and

Figure 9. Growth of calcia enrichment zone in slag.

adequate joint strength. The technique of uniform metallic coating to porous alumina ceramic (10% porosity) by electroless method (figure 10) has been successfully developed by Totlani *et al* (1979) in BARC. The technique is essentially a chemical method of deposition constituting bath of metal ion (nickel), suitable complexing agent and a reducing agent. The ceramic surface to be metallised is made catalytic towards reduction of metal ions by rinsing in stannous chloride solution followed by a rinse in a dilute palladium chloride solution. The bonding by such method is purely mechanical interlocking. The metallic coating obtained by this method has better solderability and excellent wear resistance characteristics. The main features of the technique are: (a) No diffusion of metal species in the pores of ceramic, hence does not alter the properties of ceramic. (b) Gives stronger bond. (c) Much cheaper and easy process compared to other techniques.

3. Conclusions

In summary, the development of MHD channel as a power generating device is primarily dependent on the development of suitable ceramic materials that can withstand for long duration in the hostile MHD environment. Some of the new materials have showed excellent promise and have lasted for several hundreds of hours of operation. Table 2 shows the essential current status of this development and the potential candidates for future power channels. The Indian MHD programme is to identify the specialised selective areas for further research in the choice of material and processing techniques.

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Figure 10. Secondary electron image (SEI) of nickel-alumina junction.

Table 2a. Test result on various MHD electrode materials

Materials	Test facility	Clean or slag	Temperature (°C)	Time (hr)	Maximum current density (A/cm ²)	Observations (by investigator)
1. ZrO ₂ -11% CeO ₂ (hot pressured)	Poznan (4 MW)	Clean	—	—	—	Burned out at 1680°C; current to be limited to 0.8 A/cm ²
2. 88ZrO ₂ :12Y ₂ O ₃ 50ZrO ₂ :50CeO ₂ 25ZrO ₂ :75CeO ₂ 80CeO ₂ :18ZrO ₂ :2Ta ₂ O ₅	U-02 (US-USSR Joint Test) Phase I	Clean	1720	127	0-1.25	Strong seed penetration CeO ₂ -loss
3. Hercynite (FeAl ₂ O ₄ .Fe ₃ O ₄)	U-02 (US-USSR Joint Test) (Phase II)	Clean	1650	100	0-0.8	Hercynite melted
4. 3MgAl ₂ O ₃ .1Fe ₃ O ₄ (1 mm thick)	AVCO	Slag	1400-1500 (slag surface)	5	—	Most MAFF dissolved. Good continuous slag layer.
5. Cermet (LaCrO ₃ +40% Cr+3% Pd)	U-25	Clean	1500-1700	100	—	Little damage
6. SiC	Westing house	Slag	—	10	—	Oxidation, seed reaction erosion 0.3 mm/hr
7. Copper	AVCO-Mark VI	Clean and slag	200	20	—	Little damage, strong arcing
8. Copper	U-02 (Indo-Soviet Joint Test)	Clean	200	65	—	Little damage, varied from small arcing to strong arcing

Table 2b. Test result on various MHD insulator materials

Materials	Test facility	Clean or slag	Temp. (°C)	Time (hr)	Observations (by investigator)
MgO (98% T.D.)	Westing house	Slag	1600	—	Appreciable damage
MgO (90% T.D.)	U-02 and U-25	Clean	1800	100-300	Good thermal stable, little seed attack
MgO (83% T.D.)	U-02 (US-USSR Test)	Clean	1700	127	Strong seed penetration
MgO-Spinel (90%) (Modular)	U-02 and U-25	Clean	1800	100-300	Better than MgO for Small heat fluxes
Al ₂ O ₃	Poznan	Clean	2000	3	Performed reasonably, partial melting
Al ₂ O ₃ (10% T.D.)	U-02 (Indo-Soviet Joint Test)	Clean	—	65	Alumina peeled off after 9 hrs. of testing, interelectrode alumina performed satisfactorily

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