Thermal and Electrical Properties of Silica-Mullite-Grqphite Composite Fired at Low Temperature

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Abstract

Silica - mullite powder sieved through 100 mesh, mixed with graphite at certain proportions and placed in a steel mould, then subjected to ≈ 40Mpa .After air- drying for 24 hours the specimen buried in carbon and fired at 1150 ◦C overnight. DC resistance was measured by the method of two probes. The percolation threshold was not sharp , instead it starts from 10.5% graphite ratio up to 21% were it resembles the conductivity of graphite alone . Resistance and reactance analysis were carried out at three frequencies (0.55, 1.5, 5.0) kHz. The specimen was subjected to heating/cooling cycle and the change in DC resistance value (TCR) was found to be less than 1% for each 100◦C rise in temperature.

الصفات الحرارية والكهربائية لمتراكب السيليكا - موللايت - كرافيت المشكل بدرجة حرارية واطئة

الخلاصة:

بعد مزج نسب وزنية محددة من مسحوق السليكا –موللايت عب منخل 100 مش مع الكرافيت ووضع المزيج في قالب من الستيل حيث ضغط الى ما يقارب 40 ميكــا باســكال . أخرجت العينة وتركت لتجف في الهواء 24 ساعة . وضغطت العينة فــي حاويــة حديديــة وغطيت بالكاربون ثم حرقت إلى 1150 م إلى اليوم التالي وتركي لتبرد ضمن برنامج محدد . تم قياس مقاومة التيار المستمر بطريقة السلكين . لم تكن نقطة التحول في التوصلية حادة ولكنها بدءت من النسب الوزنية للكرافيت % 10.5 وإلى حد 21% حيث أصبحت التوصيلية مناضرة لتلك التي للكرافيت لوحدها . أجريت قياسات المقاومة وتحليل الممانعة في ثلاث ترددات (5 , 1.5 ,0.55) كيلو هيرتز . عرضت العينات لدورات التسخين / تبريد وأعيد قراءة التغير فــي المقاومة ووجد انه لا يتجاوز 1% لكل ارتفاع في درجة الحرارة قدرة 100 درجة مؤية.

I. Introduction:

It's familiar to design a single material, which incorporate a combination of properties of two materials into one composite. Accordingly the properties are not available in one material alone, could be retained in the new composite material [(1)] .Ceramic and cement – matrix composites were formulated to give a variety of products including ferroelectric, piezoelectric, semiconductor and magnetic ceramics [(2-4)].

Ceramic, for instance, was quite satisfactory for insulation. Most ceramic materials at room temperature have a volume resistivity value of 10^{12} - 10^{18} ohm- cm [(5)]. But as interest developed in the handling of high frequency currents, more efficient material of new properties are sought.

Materials commonly considered as insulators can break down under high electrical voltages, [1,6)]. It was evident that different grades of carbon modify

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the electrical behavior of cement or ceramic materials [6,7], as well as the mechanical properties [8]. Chung [9] has reviewed the electrical applications of carbon materials (including composites containing carbon). These applications include electrical conduction, electrodes, electromagnetic reflectors, heating, thermoelectricity, sensing, electrical switching, and electronic devices. While Islam [10] etal, related the mechanical and electrical properties with structure of high tension ceramic insulator fired at high temperatures.

There is a fundamental differences between the mechanism of conduction in metals and that of ceramic–like materials although the electrical conduction occurs by the long range migration of either electrons(predominates in metals) or ions (predominates in ceramic like materials) . The temperature dependence of ionic conductivity is usually given by the Arrenhius equation:

$$\sigma = A\exp(-E / RT) \quad \text{………… (1)}$$

Where σ is the specific conductivity, E is the activation energy, R the gas constant and T the absolute temperature. The origin of activation energy was related to the imperfections in the crystals, namely the vacancy concentration and the mobility of ions:

$$\sigma = ne\mu_0 \exp(- E / RT) \quad \text{……….. (2)}$$

Where n is the number of charge carriers, e is their charge, and μ_0 their mobility.

In this work a conductive matrix were composed by incorporating graphite in silica SiO_2 –mullite ($2Al_2O_3.3SiO_2$) [11] to enhance the electrical conductivity. Increasing electrical conductivity in conjunction with other preferred properties of mullite (expansion coefficient of pure mullite from 0- 1000 °C is $5.3x10^{-6}$ °C) enables the implementation of this composite as resistor element for the dissipation of radio frequency powers.

2. Experimental

2.1: Materials

Silica- mullite powder purchased from the construction research centre, Ministry of industry (Jadiriyah, Baghdad). Grinded, sieved through 100 mesh. Used without further treatments. It was prepared by the method of heating kaolinite in the following sequence:

Kaolinite $Al_2Si_2O_5(OH)_4$ undergo dehydration to produce disordered metakaolinite $Al_2Si_2O_7$

, upon continuous heating the latter converted to defect aluminum – silicon spinel $Al_2Si_2O_{12}$, which is sometimes also referred to as gamma alumina type structure .Further calcinations to ≈ 1050 ° C the spinel phase nucleates to mullite $3Al_2O_3.2SiO_2$ and highly crystalline cristobolite SiO_2:

Step 1 (575 °C):

$2Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 4\ H_2O$

Step2 (925°C):

$2Al_2Si_2O_7 \rightarrow Si_3 Al_4O_{12} + SiO_2$

Step3 (1050 °C)

$3Si_3 Al_4O_{12} \rightarrow 2Si_2 Al_{12}O_{13} + SiO_2$

Boric acid, BDH technical grade.

Sodium nitrite, BDH technical grade.

Carbon black, BDH technical grade.

Graphite, synthetic powder (7782-42-5) product of Aldrich.

2.2: Fabrication of specimen:

Carbon steel (No.285) used for the construction of the mould shown in figure 1.The internal surface of the cylinder as well as the inside rod were grinded to a roughness of (Ra .001 µm). The grinding as well as the standard clearance dimensions were proved to be essential in extruding the specimen from the mould. The mould was equipped with a safety outside cover.

Materials were weighted in (100 ±0.01) g proportions using Mettler Toledo balance (model BD202). Each 100g contains from 4-25% graphite, in addition to 5 g from each boric acid and sodium nitrite, made up to 100% by silica- mullite. Ten grams of distilled water were added, and the paste – like admixture was manually and thoroughly mixed in a porcelain mortar for at least 30 minutes.

Each time, the whole proportion was loaded inside the cylinder of the mould, and then other parts were assembled. It was subjected to constant pressure (20-40 Mpa), using manual hydraulic press (50 tons) which exerts the pressure from the top against the fixed base. Each press lasted for one hour, after the elapse of that time; the specimen was removed from the mould (with caution to avoid the destruction of the specimen's ends) and left for air – drying for 24 hours.

The dry specimen then placed in a steel cylinder (L250 x I.D 50) mm filled with carbon black. Carbon black should cover the centered specimen for at least 5 mm; otherwise, specimen not very well centered might loss their formulated graphite. Steel container containing the specimen equipped with a punched cover (φ ≈1 mm) was placed in a furnace (Carbolite FX 300) and fired at 900- 1150°C overnight. Then, the power switched off and the door open, the specimen left inside for cooling another12 hours.

After cooling inside the fixture the specimen removed, cleaned, and their outside ends (10 mm) being fitted with a nichrome wire as terminals .All specimens were preconditioned by passing high currents for at least 30 minutes. Specimens that over heated (≈120 °C) were excluded from the resistance measurements. Specimens were hollow cylinders of (L150x O.D 25) mm. The cavity inside was of (L 150x O.D 10) mm.

2.3. Testing:

2.3.1. DC resistance measurements:

Electrical resistance measurements were accomplished by connecting the ends of the specimens to two separate wires connected through nichrome wire. The connections insure full contact of the whole outer surface of the terminals. A fluk digital millimeter (model 75) was used.

2.3.2. Reactance measurements

The current passing through pure inductor is lagging behind the applied alternating voltage in an angle of 90°, and the maximum current value equal the maximum voltage divided by induction impedance:

$$\mathbf{I_{max} = V_{max} \backslash X_L} \quad \text{……. (1)}$$

I_{max}: Maximum current, V_{max}: Applied voltage, X_L: inductance

The current passing through pure capacitor will lead the applied alternating voltage in an angle of 90°, and the maximum current value equal the maximum voltage divided by the capacitance impedance:

$$\mathbf{I_{max} = V_{max} \backslash (1/ Xc) = V_{max}/ (1 / 2\pi fc)} \quad \text{… (2)}$$

When f: frequency, c: capacitance. However if:

(X_L – X_c) positive i.e. X_L> Xc: the circuit will be inductive.

(X_L – X_c) negative i.e X_L< Xc: the circuit will be capacitive.

($X_L - X_c$) zero i.e. X_L= Xc: the circuits will be pure resistor, which the mullite – carbon mixture should satisfy.

The ratio of voltage to current represents the impedance (z) and measured by ohm, which is formed of two components the real component (the resistance) and the imaginary part (the reactance) for such measurements and analysis impedance analyzer (HP 4191 A) was used at 0.55, 1.0, and 5.0 kHz.

2.3.3. Temperature measurements:

Samples were held horizontally by standing over two alumina cylindrical ceramic pieces (L50xφ25) mm. The temperature recorded by insertion to about 50 mm K- type thermocouple in the cavity within the specimen without touching the sides. Digital read-out temperature reader (model HP 2168A) was used to record the rise in temperature during operation. Neither cooling nor insulation was applied on the specimen during the recording of the temperature. The TCR values were measured at two different temperatures according to the formula:

$$\mathbf{TCR = (\Omega_h - \Omega_l) / [\Omega_l (T_h - T_l)] \times 10^6} \quad \text{.....(3)}$$

TCR: Thermal change of resistance. ppm / ˚C

Ω_h: Resistance at high temperature. Ohm

Ω_l: resistance at lower temperature. Ohm

T_h: Higher temperature. ˚C

T_l: lower temperature. ˚C

3. Results and discussions:

Figure (2) shows the resistance of silica - mullite- graphite composite as a function of graphite content. As graphite content increased only 1% (from 4.5% to5.5 %) the resistance was reduced to about 10%. In accordance with Chung(12), conductive filler can enhance the conductivity of the composite even when the volume fraction is below percolation threshold (after this threshold the whole material acts as a conductor). A substantial decrease of resistance occurs at graphite percent of 10.5% followed by a further steady decrease up to the percent of ≈ 21%, which resembles the resistance of graphite alone.

The results revealed that neither boric acid nor sodium nitrite contribute in the whole volume resistance, but, both acting as binder, although boric acid form boric oxide B_2O_3 or $B_{0.67}O$, has a weaker structure than SiO_2, since Bi^{+3} can surrounded itself with only three oxygen atoms in the triangular coordination . Boric oxide has low softening point and a high expansion coefficient which is preferred properties in this composite.

Figure (3) shows that applied pressures from (20 – 40) Mpa have no pronounced effects on the measured resistance values of specimens after firing, instead the resistance values pounced about their starting value at 20 Mpa . It was expected that increasing the applied pressures will bring about the graphite particulates to come close and eventually the resistance will drop as a function of pressure. With graphite such expectation is not valid

Even uniformly sized materials cannot pack into a solid body without presence of considerable porosity. The ceramic like composites has low thermal diffusitivity; more heating should be added or removed from the silica- mullite body to change the temperature. It's quite evident that conductivity is high in materials of metallic bonds, because electrons are very efficient carriers of thermal as well as electrical energy. Most of the heat transfer through a porous solid has accomplished by the solid part of the body (up to70%) while the other transfer mechanisms (the heat carried by the gas in the pores, convection in the pores, radiation across the pores) contribute in the remaining (30%) [5], figure (4) shows the rise of temperature of the specimen with the increasing of the applied power. Therefore it's quite recommended for such dissipation media to be equipped with an efficient heat sink as well as cooling fans to overcome excessive heat generated during operation of high radiofrequency power. However, the variation of resistance values were found to be around 1% for each rise of 100 C in temperature, despite the lack of cooling techniques in the present setting . DC resistance retained its recorded value and show very limited variation during operation or storage for 6 months.

Table (1) shows the reactance and the resistance of three samples compared with a commercial resistor (Allen Bradley 100Ω ± 20%) measured at three frequencies (0.55, 1.0and 5.0) kHz. The present composite shows that the reactance is lower than that of the commercial specimen at 550 Hz by ≈ 1%.

Although the deviation was not substantial but its not fully reasoned. However it could be related to two causes:

Either the presence of iron or other metallic contaminants in the raw material acting as pure conductors. Valance electrons in metals are not anchored to any specific atom, thus their energy permits them to move among the atoms in all directions with equal velocity, the sequences of such movements are fully illustrated in equations of section 2.3.2.

Or due to the effects induced by exerting the pressure only from the top. The conduction in this case depends largely on the packing of graphite particulates and their orientation. The orientation is quite effective since graphite has different properties in different directions, this assumption may well supported by the fact that the percolation threshold is quite sharp for other composites [6] . However the microstructure and the mechanical properties will be discussed thoroughly in the forthcoming paper.

4. Conclusions

The resistance of silica-mullite-graphite composite was greatly modified by the graphite ratio. The percolation point is not sharp at this setting; however the composite resembles the conductivity of the graphite at higher percentages. The static pressures exerted on the top of the specimen from 20 -40 Mpa have no pronounced effects on the resistance. Neither boric acid nor sodium nitrite has clear effects on the final resistance of the specimens fired at ≈1100 ˚C. heating / cooling cycle showed a variation in the resistance not more than 1% for each rise in temperature of 100 ˚C. The reactance even lower than that of a commercial product.

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Table 1: Resistance and reactance of three specimens compared with commercial type.

Specimen	550 kHz		1.0 kHz		5.0 kHz	
	Ω	J	Ω	J	Ω	J
Commercial Type	80	0.9	80	1.8	80	2.5
1	81.1	0.8	81.1	1.4	81.1	2.0
2	74	0.85	74	1.4	74	1.9
3	75.5	0.8	75.5	1.4	75.5	2.3

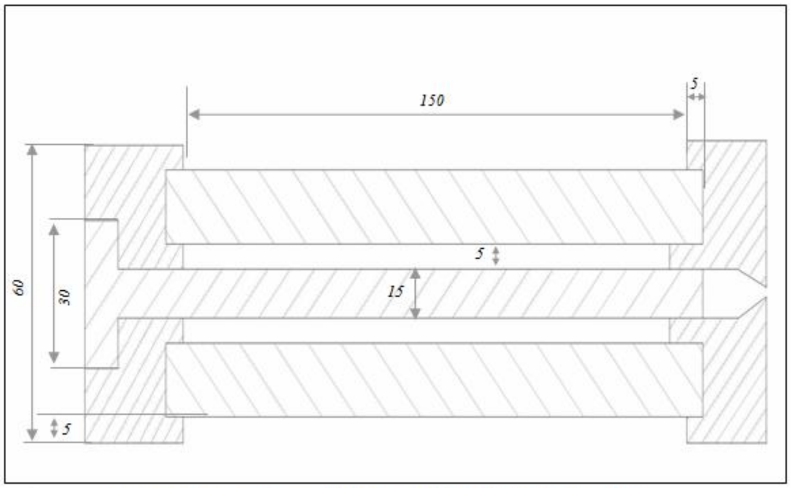

Figure 1 : Cross section view of the steel mould dimension are in mm.

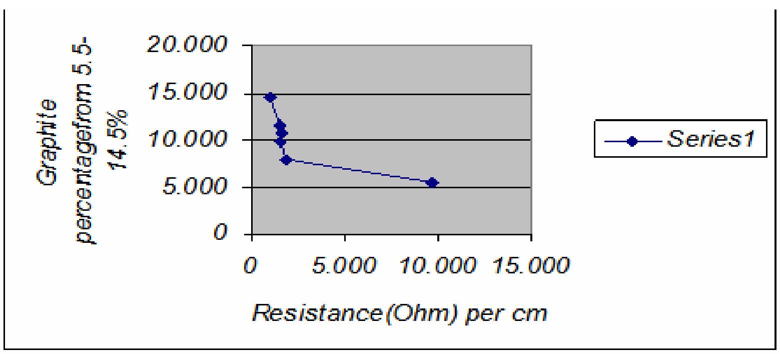

Figure (2) Variation of resistance with added graphite ratio for specimen pressed 40

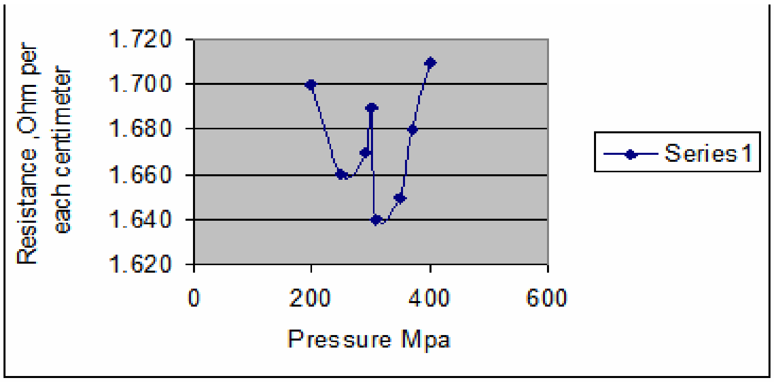

Figure (3) Effect of increasing pressure (20-40) Mpa on the measured resistance

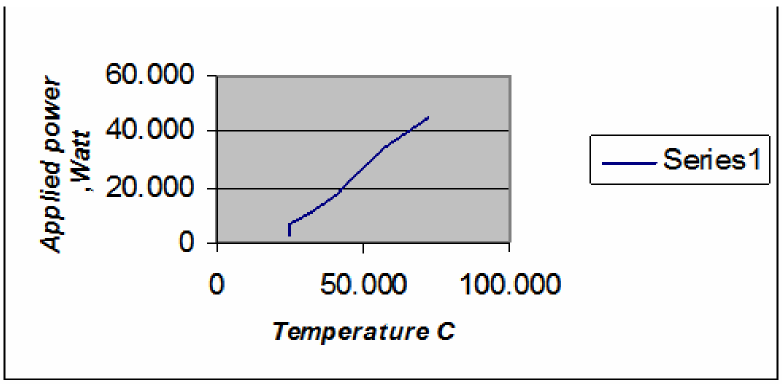

Figure (4) Temperature rise as a function of applied power on the specimen. Operation