Dc electrical properties and conduction mechanisms of Al-clay based composite resistors

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We studied the electrical properties of composite resistors fabricated from materials of natural origin based on Al-kaolinite clay mixture. Our electrical measurements and microstructural studies reveal the effect of annealing schedule, insulating particle size and composition on the resistance of the cermet. We measured small values of activation energy of conduction from temperature dependence of resistance and compared these values of activation energy with those obtained from microstructural examinations using electron microscopy. The small activation energy in the range of 0.53–1.24 μeV obtained suggests conduction by direct or quantum mechanical tunneling between conducting grains. All the resistors were observed to show a negative TCR with some possessing TCR as low as 50 ppm/°C in magnitude, which further confirms the tunneling conduction process. The variation of resistivity with the volume fraction of the metallic phase was found to follow a percolative conduction expression of the form $R(X) = R_M(x - x_c)^{-t}$, with the critical exponent t and critical concentration x_c showing a significant dependence on firing temperature. We found that the critical exponent assumed a value of $t = 2.0 \pm 0.8$, which is different from a universal value of 2.0. This was shown to result from tunneling-percolating nature of the cermet.

1. Introduction

Composite resistors or cermets consist of a thorough mixture of an insulative phase and a suitable electrically conductive phase. The electrical properties exhibited by composites, which are unattainable in any of the constituent phases, makes them extremely valuable for use in many applications such as discrete resistors in electronic circuits, pressure sensors in piezoresistive transducers [1] and temperature sensors in devices with self-adjusting power or current cut-outs [2].

The wide spread use, richness in phenomenology and peculiar properties of composite systems, which are not yet completely understood such as metal-insulator transition [3], giant Hall effect [4–6] and colossal magnetoresistance [7–9] have attracted a number of research efforts towards these composites. The available theories describing transport properties of composite systems depend on the composite system under study and the method of studying. The theories include variable range hopping in a narrow band formed by impurity doping of glassy region between conductive particles in thick film systems[10–12], thermally activated tunneling of electrons between conductive particles through insulating barrier containing impurity ions [13–16], fluctuation induced tunneling [17–19], substrate conduction [20, 21] and thermionic emission [22, 23]. Electrical transport properties of composites are largely influenced by the volume fraction of the conductive phase. In describing the influence of volume fraction on electrical properties various statistical approaches were assumed by previous workers [24–28] to relate the structure of cermets to the measured dependence of resistance on conductive-phase concentration or volume fraction. They showed that transport properties exhibited by composite systems can be described in terms of percolation phenomena, which is uniquely defined for composites with a given dimension in space [29].

In this work however, we focused on a cermet or composite system, which differs in material composition, components size and concentration from an island structured metallic film. We paid special attention to the electrical behavior at high metallic or conductive phase concentration (i.e., $x > 50$ wt%). The composite therefore consists of an insulating phase or barrier interspersed between a continuous conducting phase whereby the conducting islands or grains are no longer separated by empty spaces but by a dielectric layer of varying thickness. We examine the effect of annealing schedule, insulating phase particle size and material composition on the room temperature conduction of the composites. We analyze the measured dependence of room temperature resistivity on the conductive phase

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concentration above the threshold of electrical conduction and found that it follows a power law [30]. Measurements of dependence of DC electrical resistance on temperature give a negative TCR and small activation energy of resistance for all the resistors. Based on these measurements and microstructural examinations, the conduction mechanisms in this type of cermet were proposed.

2. Experimental

Al-clay based composite resistors have been prepared by a compaction method. Aluminum powder of 99.99% purity forms the conducting phase, while a fine physically homogeneous kaolinite clay powder forms the insulating phase. Good properties of aluminum which make it particularly desirable for this application are its high conductivity, light weight and resistant to corrosion through passivation [31] or formation of a thin oxide layer on the surface. In a typical preparation, the aluminum powder was grounded with a laboratory mortar and pestle to remove lumps. The clay material was obtained from a clay deposit and therefore it contains stones and debris. To remove the stones and debris the clay was washed inside a bucket of water so that it formed suspension in the water. The resulting water-clay mixture was then sieved to remove the stones and debris. The water-clay suspension was left for three days so that the clay will form sediment inside the water. The top water was drained off and the clay sediment was then dried in the sun for about a week. The dried clay was then grounded and processed into a fine powder with average particle size of 200 μm. In order to enable the characterization of the resistors in terms of clay particle size, the processed clay powder was further prepared by the use of a six-mesh sieve into six different particle sizes (i.e. 63, 200, 250, 400, 500 and 1000 μm). The aluminum and clay powder were mixed together in a mixer according to different fixed ratios in terms of mass such that the clay occupies 5%, 10%, 15%, 20%, 25%, 30% etc. of the total aluminum-clay mixture. The clay being a phyllosilicate and exhibiting a little plasticity, serves as our binder, binding the conductive particles together. This eliminates the use of separate binders like sodium or lead silicate as used in thick film pastes.

A mechanically operated press capable of exerting a high pressure in excess of 6.9×10^8 N/m^2 was fabricated and used to compress or mould the materials into a cylindrical structure of lengths 5, 10, 15 and 20 mm respectively with a constant diameter of 3 mm. The fabricated resistors were left to air dry in a dust and moisture-free atmosphere, after which a set of ten resistors of the same composition, selected from each length, were put into an electric furnace, fired at 100°C for 30 min, and finally furnace cooled to room temperature. The process was then repeated for other sets of resistors in steps of 100°C up to a maximum of 1000°C. The initial maximum temperature at which each set of resistors was heat-treated and then furnace-cooled to room temperature is designated the annealing temperature or firing temperature T_F.

The DC conductivity or resistivity measurements on this cermet structure were carried out by a two-point probe technique using graphite electrodes and a digital multimeter. Good electrical contact between the graphite electrodes and the ends of the resistors was assured by depositing small drops of conducting silver solutions on the ends of the resistors. All measurements with the exception of TCR measurements were carried out at room temperature.

The dependence of the DC electrical resistance on temperature (i.e. TCR measurements) were carried out in a sandbath between a temperature range of 10 to 100°C. The resistors with electrodes across their ends were heated in a sandbath whose temperature is monitored by a digital thermometer. In this way the resistance and the TCR were measured as the temperature is increased and decreased accordingly.

Microstructural changes in the resistors were investigated using a Scanning Electron Microscope (SEM) of model LEO 1450 situated at OAU Ife, Nigeria. The SEM enabled the characterization of the resistors in terms of composition and microstructural evolutions as the firing temperature increases. It also provides a means of estimating the average conducting particle size.

3. Results and discussion

3.1. Effect of annealing schedule

It is known that annealing schedule (such as the peak firing temperature, firing time, furnace atmosphere and cooling rate) has pronounced effects on the final electrical properties of composite resistors [32]. This is because during annealing several transformations and microstructural changes occur within the materials [33].

Fig. 1 shows the effect of peak firing temperature T_F on resistance for different aluminum-clay ratios using resistors of length 20 mm. The resistance of each resistor was observed to decrease as the firing temperature increases, irrespective of the composition of each resistor. It was observed that at firing temperatures less than 300°C, the resistors have comparatively high resistance. This could be attributed to the fact that sintering has not started and therefore the majority of the aluminum grains are still well separated from one another as shown by the microstructure of 90 wt% Al fired at 300°C in Fig. 7a. The presence of pores in the material could also make it easier for oxygen to diffuse into the material during firing and thereby oxidizing the aluminum grains to form oxide layer on the grains. This oxide layer forms a potential barrier to the conduction electrons in addition to the insulating barrier offered by the clay aggregates. In a structure showing this kind of particle-barrier geometry, electrical conduction can occur by a quantum mechanical tunneling or thermionic emission depending on the thickness and electrical properties of the barrier [34].

Between firing temperatures of 300–700°C, the resistance reduces drastically, this is because sintering has started, some structural defects have been gradually annihilated and porosity is being reduced. All these lead to coalescence of the aluminum grains forming a

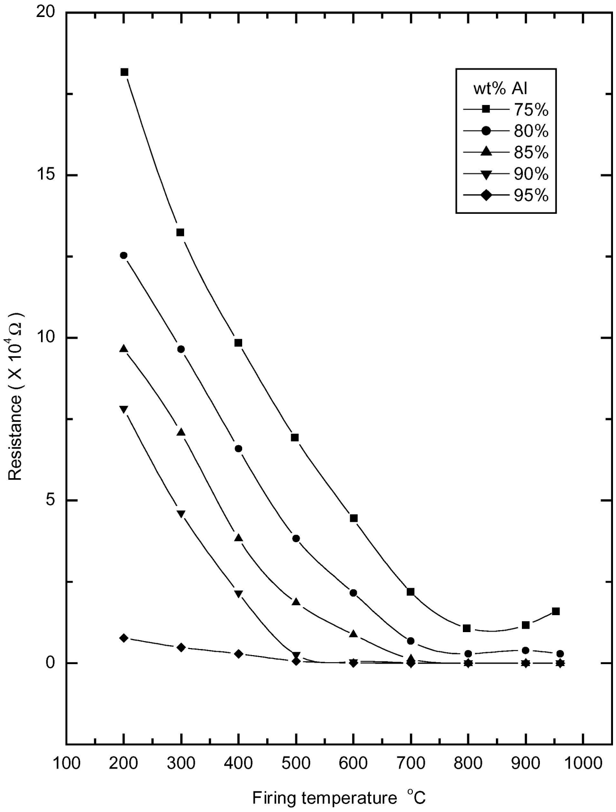

Figure 1 Variation of resistance with firing temperature.

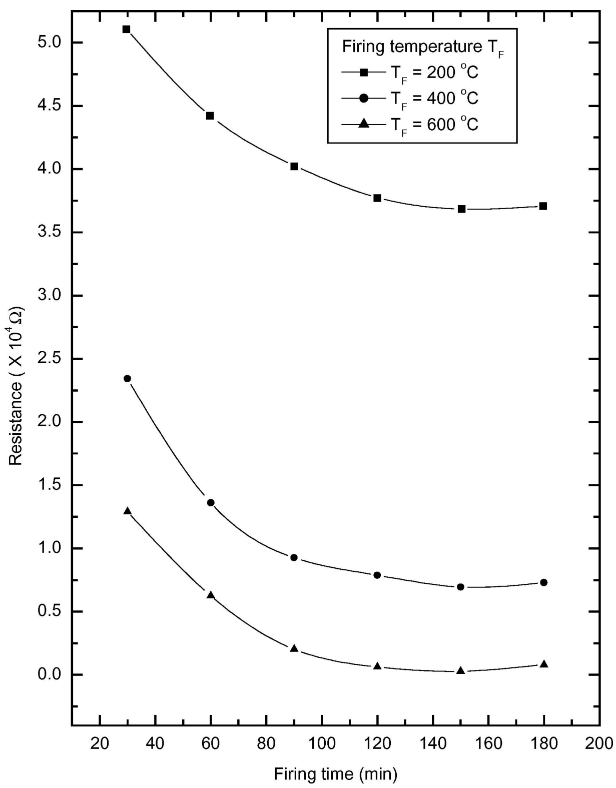

Figure 2 Effect of firing time on resistance for 90 wt% Al cermets.

combination of continuous metallic conduction path and sintered junctions through the cermet structure as shown by the microstructure of the 90 wt% Al fired at $T_F = 600°C$ in Fig. 7b. These facilitate easy conduction of electrons through the structure and also explains why the graph seems to level off at $T_F > 800°C$.

Annealing also has the effect of increasing the aggregate grain size or causing grain growth during sintering through agglomeration of the particles to form clusters [35, 36]. This is clearly evident by comparing Figs 7a–c. This increase in grain size reduces the activation energy necessary to transfer electrons from one cluster or grain to another, which in turn reduces the resistance in agreement with the observed results.

Fig. 2 shows the effect of firing time on resistance. The resistance falls very rapidly at the early stage of firing. Afterwards, the decrease proceeds at a much slower rate and eventually level off. The sharp and rapid drop in resistance is due to burning off of the organic matters in the clay aggregates, initiation of sintering and annihilation of some defects. The leveling off of the graphs can be attributed to the completion of these processes and the chemical reactions which take place in the material especially oxidation of the metal grains [33].

However, the observed results can also be explained in terms of tunneling process. At the early stage of firing (about 30 min) the metal grains have not been completely oxidized and the oxide barriers, where they are already formed are so thin that they do not have much effect on the conduction process. Only processes mentioned above are modulating the conduction process. But as the firing time gets longer (i.e about 90 min or higher) sintering would have stopped, organic matters in the clay aggregates must have been burnt off, defects annihilated and most of the grains must have been completely oxidized and covered with thick oxide layer thereby making the resistance to tend towards a steady value due entirely to tunneling.

3.2. Temperature dependence of resistance

We have also measured the temperature dependence of electrical conduction between the temperature range of 10°C to 100°C. We observed an exponential like decrease in resistance with an increase in temperature. This is as expected in this kind of composite and this behavior is shown in Fig. 3. The resistance-temperature relationship shown by the composite suggests that electrical conduction takes place by tunneling of charge carriers between conducting grains through the insulating layer. In order to generate charge carriers, electrons have to be removed from one grain before tunneling to an adjacent grain. The energy required for this is the charging energy E_c which can be expressed as [13]:

$$E_c = \frac{e^2}{4\pi\varepsilon\varepsilon_o r k(r, s)} \quad (1)$$

where r is the radius of the grains, s is the gap between the grains, ε is the dielectric constant of the insulating phase and $k(r, s)$ is a function which depends on the shape and arrangement of the grains.

We estimated the activation energy E_A of conduction by fitting the obtained resistance data with the Arhenius equation of the form

$$R = R_o \exp\left(\frac{E_A}{kT}\right) \quad (2)$$

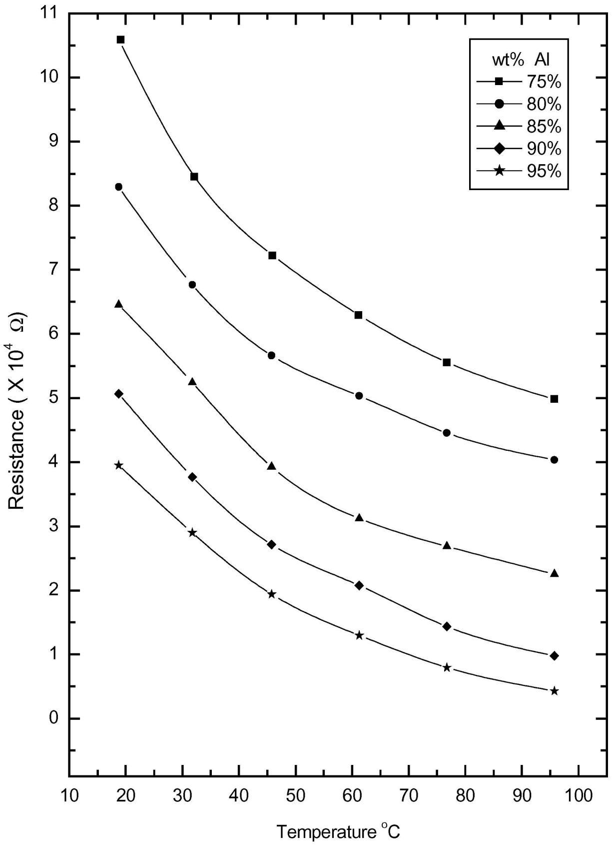

Figure 3 Variation of resistance with temperature for materials fired at $T_F = 200°C$.

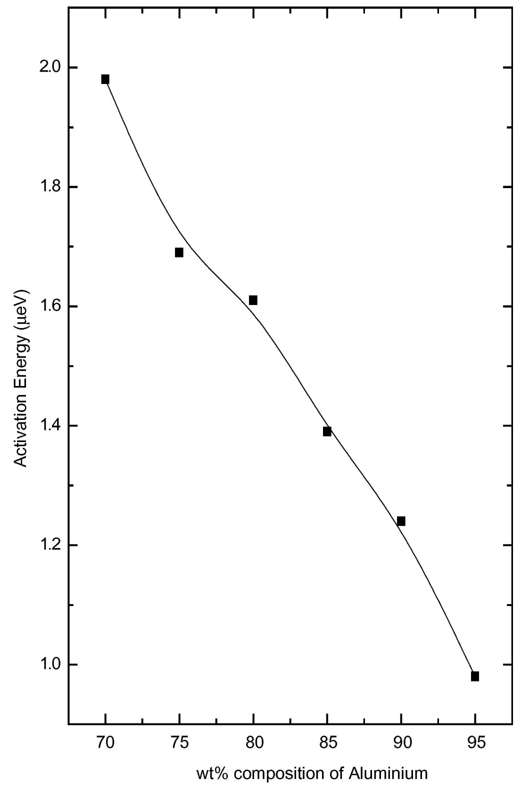

Figure 4 Plot of activation energy Vs. wt% composition of Al for materials fired at 200°C.

where T is the temperature in Kelvin, k is the Boltzmann's constant and R_o is a pre-exponential factor depending on the mobility of the charge carriers.

We also calculated the activation energy using Eq. (1) given that $E_A = E_c/2$ [37]. The grain size r and inter-grain gap s are estimated from the microstructure of the resistors while for this kind of cermet, $k(r, s)$ is taken to be ~1.98 [38] and ε is ~2.6 [39–41]. The calculated and measured values of the activation energy with the respective values of grain size r and inter-grain gap s are shown in Table I.

The two values of activation energy are readily comparable showing that conduction is an activated process involving the tunneling of the electrons through an insulating potential barrier formed by the oxide layer on the grains and the clay aggregates. However, the small activation energies obtained also suggest that conduction does take place by direct or quantum mechanical tunneling of the electrons.

Thus we may conclude that at room temperature conduction is by direct or quantum mechanical tunneling, while at high temperatures conduction is activated as well as by direct tunneling.

The activation energy according to Equation 1 depends inversely on the macroscopic dielectric constant of the insulating barrier. An increase in dielectric constant would therefore result in a reduction of the effective activation energy. This dielectric constant should increase with increase in concentration of the aluminum, because increasing the density of metallic oxide particles brings about proximity of highly polarizable metal particles [13] as well as increasing the concentration of the interfacial oxide layer, which also forms part of the tunneling barrier. Therefore the activation energy should decrease with increase in the aluminum concentration, this is in agreement with our experimental results as shown in Fig. 4.

All the resistors were found to have or possess a negative TCR, which is consistent with the proposition that conduction is an activated process. We observed that the TCR decreases with increase in the firing temperature with the magnitude of the TCR decreasing from about 1220 ppm/°C at firing temperature of 200°C to 100 ppm/°C for T_F of 900°C. This can be attributed to sintering and coalescence of the metal grains as the firing temperature increases. This reduces the tunneling distance between the grains thus making the conduction to be mainly through the metallic path or backbone. This makes the material to be metallic in nature with the TCR tending towards a positive value.

3.3. Effect of clay particle size

The resistance through the cermet can be considered to be the result of a series of large number of resistors combined in series and parallel with each particle and particle-particle contact contributing to the bulk or total resistance [42]. Three contributions to the bulk or total resistance of the cermets are: constriction resistance associated with the constriction of electron flow through the small area where two conducting particles meet [42], tunneling resistance associated with the insulating layer coating the conducting particle and intrinsic grain resistance through each particle. The constriction resistance and tunneling resistance of the

TABLE I Values of activation energy, grain size, inter-grain gap, critical exponent t and critical concentration

Firing temp. T_F °C	Measured activation energy for 90 wt%Al (μeV)	Calculated activation energy for 90 wt%Al (μeV)	Critical exponent t	Critical concentration x_c	Average grain size r (μm)	Average Inter-grain Gap s (Å)
200	1.24	1.97	2.1	0.630	71	300
300	1.17	1.68	2.3	0.628	83	290
400	0.98	1.52	2.6	0.626	92	260
500	0.91	1.39	2.7	0.621	100	255
600	0.83	1.28	2.8	0.620	109	240
700	0.53	1.16	3.0	0.616	120	200
800	–	–	1.7	0608	–	–
900	–	–	1.9	0.600	–	–

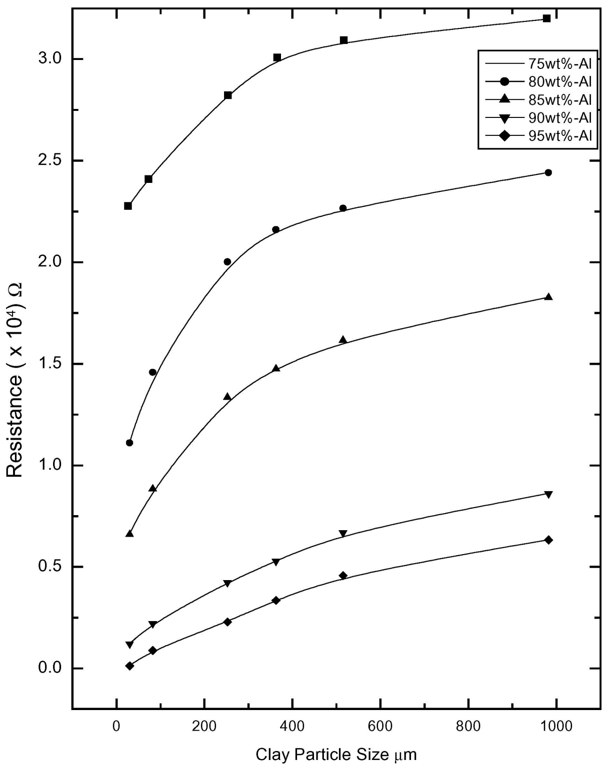

Figure 5 Variation of resistance with clay particle size for materials fired at 400°C.

particle-particle contacts are known to depend on the conducting particle size [42, 43]. We anticipated that changes in the insulating particle size or clay particle size would also affect the constriction resistance, the tunneling resistance and eventually the cermet's resistance. This is because this would affect significantly the compactness of the cermet material, transmission of pressure, vacancies and grain boundaries. We therefore measure the effect of variation in clay particle size on the cermets' resistance

Fig. 5 shows the effect of clay particle size on resistance. The resistance was observed to increase nonlinearly with increase in clay particle size. This could be attributed to the following reasons:

1. Larger clay particle size would reduce compacting pressure generated within the resistor. This results in more structural defects such as vacancies and fractures, since the bond between the clay particle and the conductive element would not be that strong again.

2. Larger clay particle size would increase the separation between aluminum grains, and therefore increasing the electron tunneling barrier width, which in turn increases the resistance.

3. Larger clay particle size increases the porosity of the cermet thereby enhancing the easy diffusion of gases especially oxygen into the cermet structure. This increases the oxidation of the grains, the tunneling resistance of the conductive particle-particle contacts and eventually the bulk resistance of the material.

A reduction in compacting pressure due to increase in clay particle size, may also reduce the contact spot area between the conducting particles [42] which leads to increase in the constriction resistance between grains and eventual increase in the total or bulk resistance.

3.4. Percolative behavior

Variation of resistance of a composite material with the volume fraction or concentration of the conducting phase is an important characteristic of a composite system, since it describes how easily the system can be controlled.

In this cermet we observed an increase in resistance with increase in insulating phase concentration as shown in Fig. 6. The increase is due primarily to increasing barrier width or separation between the aluminum grains. At a certain value of the volume fraction of the conducting phase called the percolation threshold, the resistance steeply decreases. Ponomarenko [44] and Sherman [45] defined it as a minimal concentration or volume fraction of the conducting phase at which a continuous macroscopic length first appears in the system.

We examine the percolation characteristics of the cermet by fitting our resistivity data to Equation 3 using Least square method.

$$R(x) = R_M(x - x_C)^{-t} \quad (3)$$

where R_M is the resistivity of the metallic or conducting phase, constant for a given system, x_c is the percolation threshold and t is a critical exponent. Table I show the values of the critical exponent t and critical concentration x_c obtained by Least square method, whereby x_c and t are adjusted until a best fit curve is obtained.

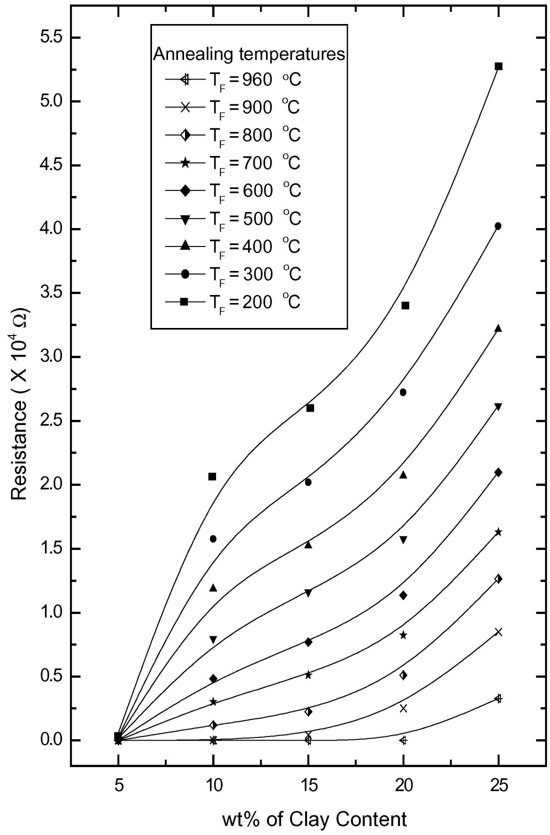

Figure 6 Variation of resistance with wt% clay content.

From Table I we observe that the critical exponent *t* shows a slight dependence on the firing temperature. We also observe that the values assume a non-universal value since the universal value of 2.0 is generally accepted for a 3-Dimensional system [46]. The results obtained suggest that this cermet can be essentially regarded as a tunneling–percolation systems in which tunneling through the oxide layer occurs only between nearest neighbors in a percolating network of tunneling bonds consistent with the tunneling-percolating model of Balberg [24, 47] and Grimaldi *et al*. [48].

The change in the critical exponent with the firing temperature may be due to changes in the particle size and the distributions of the inter-particle distance or width as the annealing temperature increases. The process of sintering, agglomeration of the particles and growth in conducting particle size, which are observed to increase with the annealing temperature are gradual processes characterized by formation of narrow necks along contact between adjacent particles, grain boundaries within each neck and interstices. These processes contribute to fluctuations in the tunneling width or distance, which eventually result in a divergent distribution of tunneling conductance proposed to be the cause of non-universality [48]. This proposition however becomes clearly evident above 800°C, when the process of sintering has been completed, the critical exponent changes again to a universal value of ∼1.9.

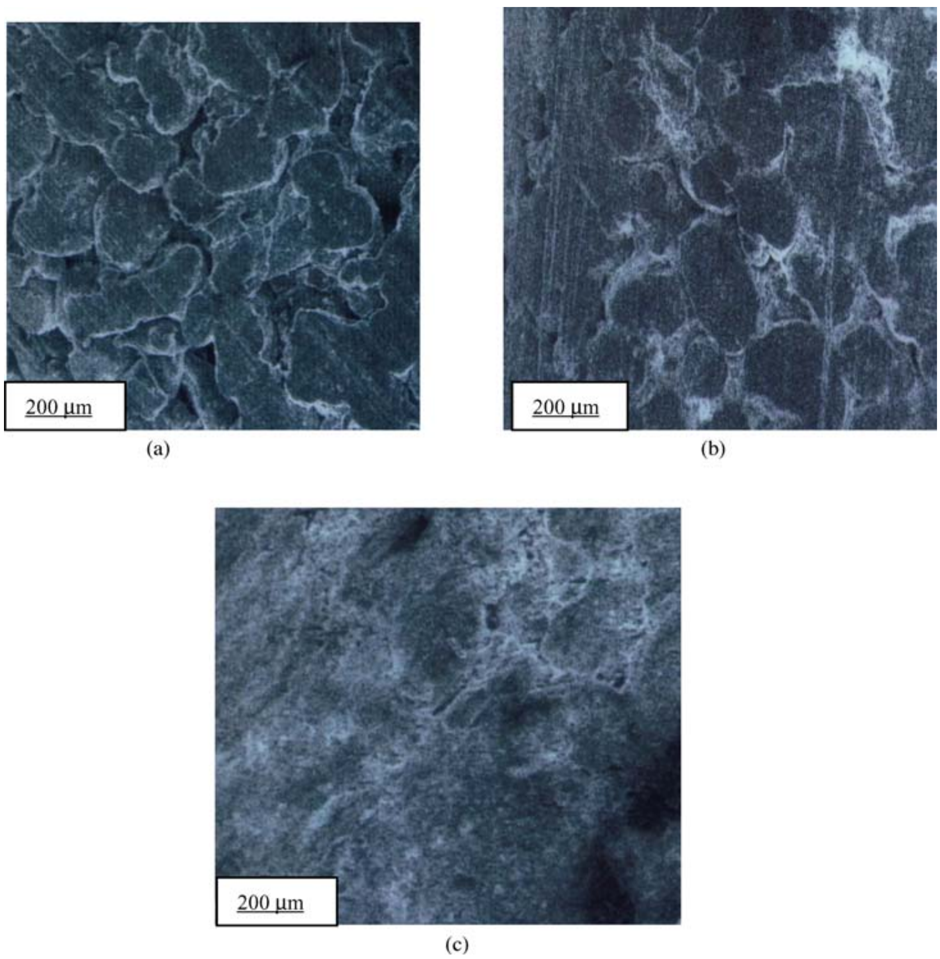

Figure 7 Evolution of microstructure of the resistors (90 wt% Al) fired at (a) 300°C, (b) 600°C and (c) 900°C.

We also note that the percolation threshold decreases with increasing firing temperature. This is because higher firing temperature enhances or aids agglomerations of the particles to form clusters or continuous conducting path in the structure, thereby reducing the concentration of the conducting phase necessary to achieve percolation. The high value of the critical concentration obtained which is different from the Scher and Zallen [49] criterion for a 3-Dimensional network is however, not quite surprising. This is because the case we considered is closely related to that described by Balberg and Binenbaum [50] in which they showed that in a continuum system of conducting particles made up of spherical spheres of hard core radius b with soft penetrable skin layer (e.g. oxide layer in our case) preventing physical contact or "automatic contact" between them the critical concentration would deviate from Scher and Zallen [49] value and would tend to a higher value of 0.64 depending on the thickness of the layer and the hard core radius. These values of the critical concentration are also closer to what Thommerel *et al.* [51] observed while working on Al/PPS composite.

3.5. Microstructural studies

The micrographs obtained from scanning electron microscope reveal details of the arrangement of the grains as the materials is subjected to heat treatment. These are shown in Figs 7a–c.

The microstructure at the early stage of firing (at 300°C) is shown in Fig. 7a.

At this stage the microstructure is characterized by the presence of distinct aluminum grains, which are well separated from one another by pores, and white patches of clay aggregates or thin oxide layers. This might be due to the fact that sintering of the grains has not started fully. The average particle size estimated at this stage is about 70 μm. Further increase in the annealing temperature results in the sintering and agglomeration of the particles, reduction in porosity and formation of highly compacted structure. This is evident in Fig. 7b the microstructure of the same composition fired at 600°C. The estimated grain size at this stage is about 92 μm.

However, above 900°C the grains become highly agglomerated forming a continuous conducting or metallic path through the structure and becoming almost impossible to isolate distinct grains, islands or clusters and thus making it difficult to estimate the grain size at this stage. This microstructure is shown in Fig. 7c. The conduction mechanism at this stage is basically percolation of the electrons through the metallic backbone as indicated by the low resistance values obtained and a value of $\sim$1.9 obtained for the critical exponent t (as shown in Table I) at this stage.

4. Conclusion

We have studied the electrical properties of Al-clay based composite resistors. Experimental results and microstrucrural examinations show that the electrical resistance varies remarkably with annealing schedule, aluminum content, clay particle size and temperature. We explained these variations on the basis of tunneling barrier model of conduction, as suggested by the agreement between the small activation energy in the range of 0.53–1.24 μeV obtained by measurements and calculation. These observations and propositions are shown to be consistent with those proposed and observed by other workers on a closely related cermet system. The dependence of cermet's resistance on the metallic or conductive phase concentration was explained in terms of percolation theory with the critical exponent $t = 2.0 \pm 0.8$ and percolation threshold x_c showing a marked dependence on the microstructure of the cermets.

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