Effect of Annealing on DC Charge transport in Copper-Clay Cermets

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Abstract: The influence of the annealing schedule on direct current charge transport of Copper-Clay based cermets is reported here. The cermets are cylindrical rods of constant 3.0mm diameter and varying lengths ranging between 5.0 mm and 25 mm. The cermets were fabricated by employing a compaction method that uses a mould at a constant pressure of 6.9×10^{8} N/m^2 on various Cu-Clay compositions ranging between 70 and 95 vol.% Cu. The cermets were subjected to varying peak annealing temperatures ranging between 100 and 1000 ^{0}C and for annealing time t_f ranging from 30 minutes to 180 minutes before being furnace-cooled to room temperature. Results showed that the annealing schedule greatly affects the resistivity, size-effect and Temperature coefficient of Resistance (TCR). The electrical properties showed that sintering is complete irrespective of the annealing temperature between 300 and 1000 ^{o}C when the annealing time t_f exceeds 120 minutes. [Journal of American Science 2010;6(6):210-216]. (ISSN: 1545-1003).

Key words: Cermet; Annealing; Composite; Clay; Size Effect

1.0 Introduction:

A close control of the electrical properties of thick-film resistors is of primary importance in the development of passive network for hybrid microelectronics. It is well known that ohmic values and temperature coefficients of resistance (TCR) are correlated to the firing parameters (time and temperature) used in ink-processing (Harper, 1974, Hoffman and Popowich, 1971) so that a close control of the firing cycle is essential for reliable properties of thick film resistors.

Due to the very complex nature of clay materials, there had been few studies reported in characterizing qualitatively and quantitatively the electrical properties of cermets produced from a suitable metal powder and clay. Various investigators such as Wimmer et al (1974), Mizsei and Lantto (1991), Prudenziati et al (1991), Prudenziati and Acquab (1994), Morten et al (1994), Akomolafe and Oladipo (1996), Afronte et al (1997), Kuzy (1997) and Stein et al (1997) have sought to explain the factors contributing to the complex behaviour exhibited by thick film resistor systems. Some of these properties exhibited include temperature coefficient of resistance (TCR), size effects, ohmic and non-ohmic resistances, piezoelectric and pyroelectric effects, thermally induced variations, etc.

Below a certain volume fraction of metal in the composite defined as the critical threshold ϕ_c, the composite behaves as an insulator while above this composition it becomes an electrical conductor. The material so produced is known as cermet.

A steady-state model for the resistivity of composites is presented, based on the idea that the resistance offered by a composite is the resultant of large number of resistors combined in series and parallel. There are three separate contributions to the resulting resistance namely, constriction resistance at the contacts, tunnelling resistance at the contacts, and intrinsic filler resistance through each particle, with tunnelling resistance generally dominating the overall magnitude of the overall resistance (Ruschau et al, 1992).

This paper reports the effect of heat treatment on the electrical properties of copper-clay cermets. The clay used is obtained from Ilorin, Kwara State in Nigeria.

2.0 Experimental Procedure:

A mechanically operated high-pressure press capable of compressive force in excess of $5\times10^3\ N$ was fabricated for this experiment. The press is capable of producing one resistor at a time with the resistors having selected lengths between 5 mm to 25 mm but of a constant diameter of 3 mm.

The composite resistor is made up of conducting, insulating, and binding elements with attached terminals. The conducting element used for fabricating the cermet resistors is copper powder of about 99.95% purity. This was ground to a fine powder so as to remove lumps using a mortar and pestle. The insulating and binding elements were clay powder to which a few drops of sodium silicate was added as binder. The clay samples were obtained from Ilorin. They were carefully selected for a homogeneous physical property and then, dried and processed to a fine powder of an average particle size of 250 μm. Graphite rods were used as the terminals of the Cu-clay composite resistors produced because the fired cermets were not solderable.

In the course of this research work, use of Cu-clay composite by volume ratio rather than by mass ratio was selected so that it will be easy to compare the result with similar experiments performed irrespective of the density of the conducting and insulating material used.

The copper and clay powders were mixed together in five different fixed ratios. The ratios were obtained in terms of volume such that clay occupied 5 %, 10 %, 15 %, 20 % and 25 % of the total Cu-clay powder mixture.

A constant pressure of $(6.9 \pm 0.05) \times 10^8$ N/m ^{2} was exerted to produce each resistor in the mould. Several resistors of varying lengths as mentioned above were produced for each cermet composition. These resistors were air-dried for several days. The resistors were put in a furnace regulated to 100 ^{o}C and fired at this temperature for two hours. It was observed that change of cermet resistance with annealing temperature becomes insignificant as the annealing time exceeds 120 minutes as observed in Fig. 5 when the annealing temperature exceeds 300 ^{o}C.

The resistors were then furnace–cooled to room temperature and the resistance and length measured. The average of several measurements was then recorded for the resistance of each selected lengths. This procedure was repeated for all the resistors, which were fired in steps of 100 ^{o}C up to a maximum of 1000 ^{o}C.

3.0 Results and Discussion:

Data on sheet resistivity and TCR changes due to variation in firing thermal cycle of resistors have been reported (Ayodele and Akomolafe,2005) but poor information in available on the phenomenon responsible for these changes in electrical properties.

In compacted composites, it is well established that, for a given composition, the electrical properties strongly depend on grain size, morphology and applied pressure (Thornmerel et al, 2002). Three major models have been developed previously to make predictions on the electrical behaviour of ideal composites.

i.) The effective medium approximation,
ii.) Percolation theory and
iii.) The micro-structural approach.

The properties of composite system are understood in terms of percolation phenomena, when a sufficient amount of conductive filler is loaded into an insulator matrix, the composite transforms from an insulator into a conductor as a result of continuous linkages of filler particles. As the volume fraction of filler increases, the probability of continuity increases until the critical volume fraction beyond which the electrical conduction is high and becomes, comparable to the conducting filler material.

Effective-media theory attempts to quantify the resistance of these systems, based on the idea that contribution of each phase to the conductivity depend not only on the relative amount of the phase present but also on the degree of conductivity offered by the phase. A number of effective-media equations have been derived to model the shape of this curve (Ruschau et al, 1992, Kirkpatric, 1973 and McLachlan et al, 1990). While these equations can successfully mimic this shape, they are not useful in describing the magnitude of the electrical resistivity of the composite. In this work, attempts were made to study variation of resistance with annealing temperatures, variation of resistance with annealing time and variation of TCR with annealing temperature.

Variation of Resistance with annealing temperature

The effect of the variation of resistance with annealing temperature T_f was studied. It was observed that the variation of resistance with firing temperature generally exhibits a trough-like form as shown in Fig. 1 which shows the variation of resistance with annealing temperatures for a resistor of length l =10 mm.

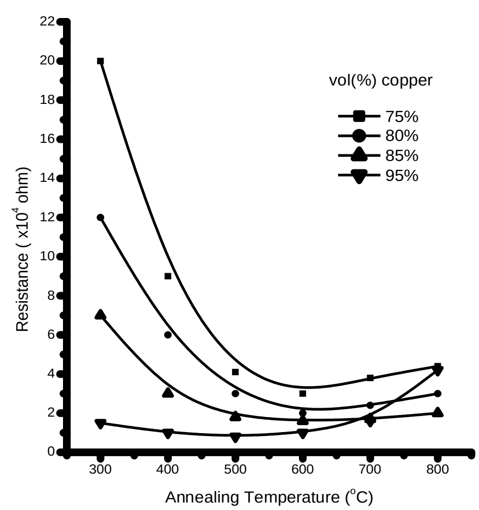

Fig. 1 Variation of resistance with annealing temperature (l = 10 mm)

Figure 2 shows the relationship between the cermets resistance, clay particle size and the annealing temperature. It can be seen that the curve produced is also trough-like in form. Clay of higher particle sizes generally produce resistors of higher resistivities than those made from the smaller particle sizes.

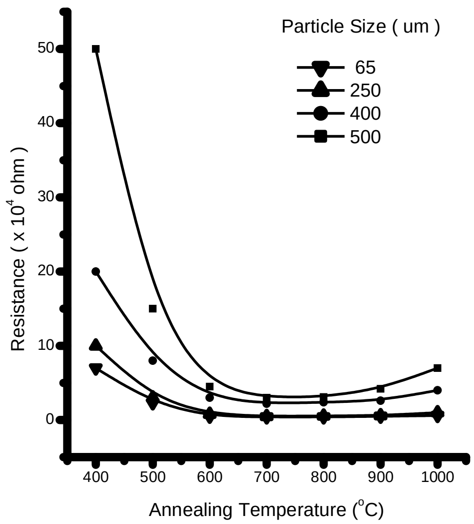

Fig. 2 Variation of resistance with annealing temperature (l = 25 mm)

For all the resistance studied, the resistance of the composite resistor containing 95 %(vol.) Cu was found to be lowest at all annealing temperatures for all the resistor length considered. It is expected that the particle size of the insulator phase would affect significantly the compactness of the cermets material, transmission of pressure, vacancies, grain boundaries of the cermet material (Akomolafe and Oladipo, 1996). This should in turn affect the final electrical property of the cermets material. The resistance/resistivity of the copper-clay cermets resistor were observed to increase non-linearly with the clay particle size for all the annealing temperatures considered; this variation is shown in Fig 3, which show the variation of resistance with average clay particle size at various firing temperatures.

Fig. 4 shows the variation of cermets resistance R with clay content for a resistor length of 10 mm and for various annealing temperatures. The graph shows an exponential increase in resistance with increasing clay powder concentrations at all firing temperatures.

Ligabue (1984) and Ruffi (1984) observed that factors which affect the final resistance of a cermets resistor depend on the nature of the glassy matrix and the substrate, reactions of the conductive grains with the matrix, sintering and ripening of the grains and glass, and partial crystallization of glass.

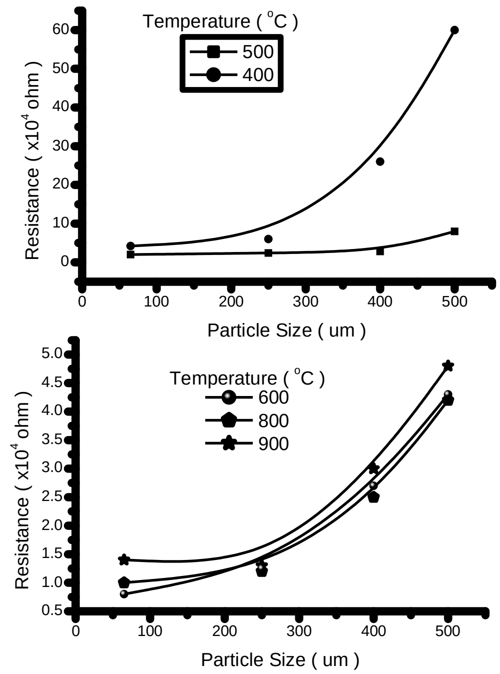

Fig. 3 Variation of resistance with clay particle size (l = 15 mm)

The variation of resistance R with peak annealing temperature T_f exhibits a trough-like form, which was observed to become more pronounced with increasing clay concentration. The comparatively high resistivity occurring for T_f < 400 ^{o}C could be attributed to the incomplete sintering of the copper-clay composite mixture as a result of the low T_f.

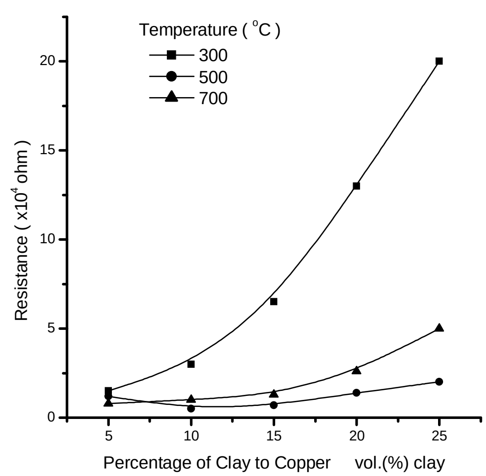

Fig. 4 Variation of resistance with clay content (l = 10 mm)

However, the high resistivity occurring for cermets fired at $T_f > 700\ ^oC$ is most likely the result of furnace atmosphere oxidation effect. Observation of the resistors under a low power optical microscope shows that the outer shell of the cermets contains end materials structurally different from those of the inner core. This may be responsible for the variation of resistivity of the resistors with length.

According to Ziman (1960) using the free election theory, the resistivity may be obtained in terms of the carrier mean free path such that

$$\rho = \frac{(3/8)^3 h}{q^2 n^{2/3} \lambda} \qquad 1.$$

where, h is the Plancks constant, λ is the carrier mean path and q is the charge of the electron. It is expected that narrowing the conduction path will reduce λ and thus increase the resistivity ρ. This explains the increase in resistance of the composite resistors with increasing annealing temperatures at annealing temperatures exceeding 700 ^oC.

Variation of resistance with annealing time

The average resistivities of the cermets were found to decrease for all cermet concentration with annealing time. This decrease in resistivity approaches a constant level as the annealing time t_f becomes greater than 120 minutes. Observation shows that the rate of sintering increased with increase in the annealing temperature as shown in Fig. 5 which shows that complete sintering takes place at all annealing temperatures considered between 300 and 1000 ^0C for $t_f \geq 120$ min.

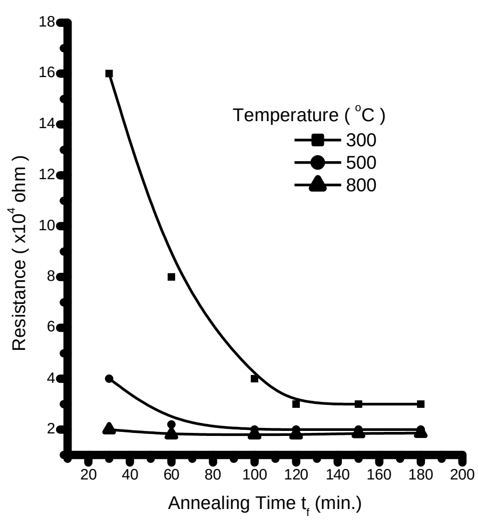

Fig. 5 Variation of Resistance with Annealing time (l = 10 mm., and 80% (vol.) Cu)

The change in resistivity obviously shows that re-arrangement of the internal structure of the cermets had taken place. This re-arrangement may have caused conductive grains to fuse in the cermet probably due to the composite being subjected to elevated temperatures. Other factors which may be responsible for the lower resistivity with increasing annealing temperature is the reduction in insulative phase by decomposition of carbonates and evaporation of the insulative phase. It is also possible that diffusion of copper ions into the insulative phase takes place hence, lowering the overall resistivity of the cermet.

Variation of Size-Effect with annealing temperatures

The variation of resistor length on the normalized resistance R_s is known as size effect. In this case, the normalized resistance as used by Akomolafe and Oladipo (1996) is

$$R_s = \frac{R_n}{R_{n(25\ mm)}} \qquad 2.$$

where,

R_n = Resistance of a given length of a resistor and

$R_{n(25\ mm)}$ = Resistance of the maximum length of Cermet resistor.

The effect of resistor length on the normalized sheet resistance is shown in fig. 6 for three copper concentrations of 95 %, 85 % and 75 %(vol.) . It was observed that direct size effect (namely, a lower effective sheet resistance for short resistors) is exhibited for composite resistors irrespective of the annealing temperature.

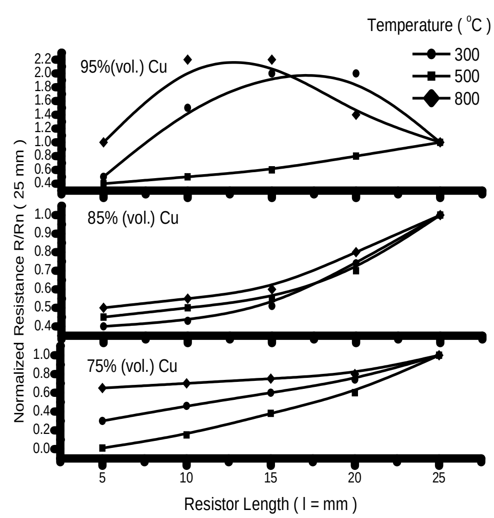

Fig. 6 Variation of Cermets Resistance with Resistor Length

This is apparent in Fig. 1 at copper concentrations of 85% and 75% (vol.) fired at T_f = 300 ^oC, 500 ^oC and 700 ^oC.

Ususally, a material exhibiting size effect will present either a direct size effect or an inverse size effect but certainly not both occurring in the same material. However, as a result of annealing, an anomalous size effect was observed for the 95%(vol.) copper-clay cermets annealed at T_f = 300 ^oC and 700 ^oC in that we showed that the same cermet resistors exhibited both direct and inverse size effects depending on its length. It is known that size effects in resistive phase are due to a change in shape when the length varies and/or a change in resistivity along the layer associated with a compositional change.

When the effective sheet resistance for short resistors is higher than that for longer resistors, a material is said to exhibit inverse effect: otherwise, it exhibits direct effect. Prudenziati et al (1991), Morten et al (1991), Hrovat et al (1986) and Akomolafe (1995) have reported these effects in various works.

The variation of cermet resistivity with change in resistor length observed in our cermets could be greatly influenced by a change of resistivity along the path of conduction rather than a change in thickness of the cermets along its length due to the in-homogeneity of the cermet composition along its length. According to Akomolafe and Oladipo(1995), the in-homogeneity in the composition of the cermets along its length and chemical reaction of terminations has been found to affect the size effect of cermets. It was concluded that the graphite terminal could not have caused any significant change in the size effect observed in the cermets because the termination were not attached to the cermet during annealing but only during the process of measurement such that significant diffusion or chemical reaction could not have taken place as to affect the overall size effect.

It was observed that all cermets of copper concentration less than 95 % (vol.) irrespective of their length exhibited a direct effect i.e. shorter resistors have lower resistance. The direct size effect observed may be due to a "Pinch-off-effect" analogous to that which occurs in the conduction channel in FETs. Thus as the length of the cermets increases significantly, chemical reaction which result in compounds of higher resistivities along the axial depth into the resistors increases thus producing a very narrow conduction channel. This causes the longer resistors to exhibit higher resistance i.e. direct size effect is exhibited.

The anomalous size effect observed is due to the transition of the cermet resistor from one exhibiting a direct size effect to one exhibiting an inverse size effect. It can be inferred from the rate of change of cermets resistance with annealing temperature that rapid chemical reactions take place within the resistors at two ranges of temperatures (Fig. 1 and Fig. 2.) i.e. between 300 ^oC and 400 ^oC and when annealing temperature becomes greater than 700 ^oC i.e. at the two high slopes of the trough. The direct size effect dominates throughout in the cermet except when the copper concentration exceeds 95% when the inverse size effect dominates the direct size effect. The inverse effect observed may be as a result of the diffusion of furnace gases into the cermets whose rate reduced because of the hard shell formed round the core of the cermets, thus diffusion of gases through the terminal surface alone becomes significant. Chemical reaction from these terminal surfaces causes the resistance at the ends of the cermets to increase significantly. This increase in resistance is not a function of the cermets length and seems to maintain a fairly constant value. Hence an inverse size effect results i.e. shorter resistance having higher resistance takes effect.

Variation of TCR with annealing temperature

Plots of the variation of cermets resistance with cermets temperatures ranging between 20 ^oC and 100 ^oC were obtained for cermets resistor annealed at T_f=400, 600, 800 and 1000 ^oC. The temperature coefficient of resistance was observed to be negative for all the copper-clay cermet studied. Results of the cermets TCR measured at 30 ^oC is presented in Fig. 7. The result showed that increasing annealing temperatures reduced the magnitude of the TCR as presented in Fig. 7.

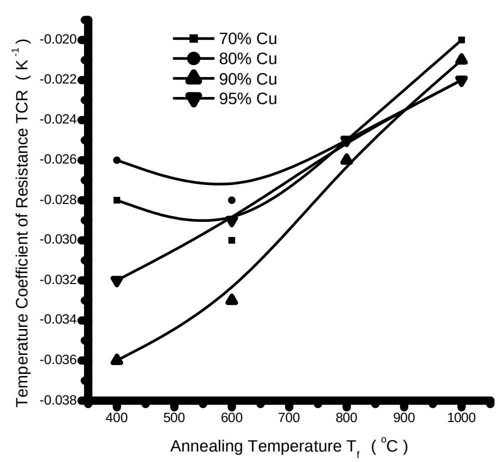

Fig. 7 Variation of TCR with annealing Temperature measured at 28 ^oC

The effects of the peak annealing temperature on the TCR and the rate of change of TCR of Cu-clay cermets are observed in figs. 7 and 8 respectively. It is expected that the TCR of a cermets will increase and tend toward positive values as the metallic content increase (since metals posses positive TCR).

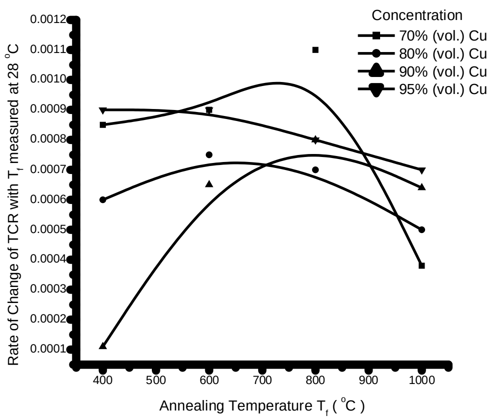

Fig. 8 Variation $\left.\frac{d(TCR)}{dT_f}\right|_{T=28\,^{o}C}$ of at 28 °C with Annealing Temperature T_f

However, fig. 7, which presents the result of the variation of TCR measured at 28 °C with copper concentration, shows that the TCR still remains negative with increase in the metallic content. The disagreement between the expected result and that obtained here show that even when the concentration of copper is 95 %, the cermet is still far from what can be modelled by the free election theory. It has been shown by Ruffi (1984) and Akomolafe (1995) that the mechanism of conduction in cermets in mainly due to tunnelling of electrons.

The basic assumption is that the cermets composition is made up of conducting grains embedded in a glassy matrix and these conductive grains can be pictured as a multi-valued resistor network through which charge carriers move by percolative tunnelling. This model assumes that the resistance of the resistor network is electrically equivalent to a thick film resistor where each resistor is insulated by a very thin dielectric layer through which electrons flow by tunnelling and by thermally activated ionic diffusion.

According to this model above, higher cermets temperatures will produce lower resistivity in the cermets because electrons will acquire higher energies, which will increase the probability of tunnelling through the insulating barrier.

The effect of the annealing temperature on the rate of change of TCR (Fig. 8) show that the magnitude of the rate of change of TCR decreased with increase in annealing temperature except for cermets with 95%(vol.) copper content. The variation of the derivative of TCR

$$\gamma = \left.\frac{d(TCR)}{dT_f}\right|_{T=28\ ^{o}C} \qquad 3.$$

with the annealing temperature (eqn. 3) expresses how sensitive the cermets is when used at room temperature as a thermistor. The result is presented as a function of the annealing temperature. It shows that maximum sensitivity of cermets resistance to temperature (at room temperature) is obtained for cermets annealed between 600 and 800 °C for 70%(vol.) copper cermets.

The explanations for this behaviour in terms of the annealing schedule is not yet clear and effort is still on to obtain the relationship between the annealing temperature and the TCR of copper-clay cermets.

4.0 Conclusion:

Copper-clay based cermets of varying copper content and length have been fabricated using a constant pressure of about 6.897×10^{8} $Nm^{-2.}$ The fabricated resistors were all of average diameter 3mm and were made of various length ranging between 5 mm and 25 mm in steps of 5 mm.

Experimental results show that annealing greatly affects the overall electrical properties such as the resistivity, TCR and size effect phenomenon. The rate of change of resistance with annealing time become insignificant when the annealing time T_f exceeds 120 min., the overall resistivity of the cermets was found to exhibit a trough-like form; High resistivity occurring at the low annealing temperature and the high end of the peak annealing temperature T_f.

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