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PROCESSING, RESISTIVITY AND MICROSTRUCTURE OF AL-KAOLINITE CLAY-BASED CERMET SYSTEM

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ABSTRACT

Cermets have been fabricated from naturally occurring Al-clay based admixtures. The effect of processing parameters such as firing temperature, firing time and furnace atmosphere on the electrical conductivity and microstructure of the cermets were investigated. Our electrical measurements reveal that the electrical properties vary remarkably with the annealing schedule. The resistance decreases with increasing peak firing temperature T_F, being very rapid at the early stage of firing, i.e between 300 °C and 700 °C. All the cermets have negative temperature coefficient of resistance (TCR) with the magnitude of the TCR dropping from 1220 ppm/°C at peak firing temperature T_F of 200 °C to as low as 50 ppm/°C for T_F =1000 °C. The range of the TCR obtained is comparable to that reported for some thermistors, varistors and other standard resistors. Observations of the microstructure by Scanning Electron Microscope (SEM) showed that increasing the peak firing temperature T_F enhances sintering of the conducting grains. X-ray diffraction (XRD) analysis indicates kaolinite as the major mineral in the clay. An optimum peak firing temperature of 700 °C is recommended for these cermets based on the criteria of low resistivity, low bulk density and stable microstructure of the cermets.

KEYWORDS: Annealing, Composite materials, Electrical conductivity, Electron microscopy, Resistors, Sintering.

1. INTRODUCTION

Cermets are composite systems consisting of a thorough mixture of ceramic and metallic materials. The combined electrical, thermal, and mechanical properties exhibited by these composites, which can not be attained in any of the constituent materials alone, makes them valuable for use in many applications such as, sensors (Prudenziati, 1994), resistors (Morten et. al.,1994, Affronte et. al.,1997), transducers (Sundeen and Buchanan, 2001) electromagnetic shielding (Chung, 2000) and wear resistant materials for cutting tools (Ettmayer et. al., 1995).

One of the important requirements of achieving a good cermet, which is both chemically and mechanically stable, is the thermo-chemical compatibility between the constituent metallic and ceramic phase. In applications where good electrical properties of the cermet are of interest, the ceramic material is usually combined with a suitable electrically conductive metallic phase. Ceramic materials which have been tested and used in this regards include, alumina (Ganapathi et al., 1987, Kobel et al.,2004), carbides (Diletta et. al.,2007), nitrides (Runyan and Gerhardt, 2001), silicates (Pike and Seager, 1977, Prewo et al.,1986) and titanates (You et al,1996, Jardiel et. al.,2007). Owing to its unique binding property and plasticity, naturally occurring clay minerals have since been used as one of the primary components of ceramic products (Burst, 1991). However, its use in electro-conductive cermets where good electrical properties is desired is quite limited. One of the heavily used clay minerals is Kaolinite. It is one of the primary components in the manufacture of electrical porcelain (Murray, 2000). Kaolinite is a 1:1 layered alumino-silicate. One layer of the mineral consists of an alumina octahedral sheet and a silica tetrahedral sheet that share a common plane of oxygen atoms (Benco et. al., 2001). Hydrogen bonding between the hydroxyl ion of the alumina sheet and the tetrahedral oxygen of the silica layer holds the two layers together. The weak nature of the hydrogen bonds allows slip between the layers and enhances the plasticity.

The general fabrication process of ceramic/metal matrix composites consists of compacting the powders of the conducting and insulating constituents together under high pressure and subjecting them to heat treatment (Aghajamian, et al., 1991, Clyne 1996, George and Rack, 2000). These processes initiate solid-state reactions between the constituent materials and bond them together to form a solid compact structure. Thus the final electrical properties depend significantly on the processing conditions. For instance during annealing schedule (such as peak firing temperature, firing time, furnace atmosphere and cooling rate) several transformations and micro-structural changes occur within the materials, which changes the density and chemical composition of the cermets (Bhattacharyya et al. 1978, Kim 1997, Ping et. al. 2001, Alessandrini, et. al., 2002). Thus in order to tailor the electrical properties to meet specific needs, careful selection of the processing parameters such as firing temperature, firing time, furnace atmospheres and compositions of the individual phase is required. In addition, an understanding of interdependence between processing and properties is also necessary. This work set exactly at this point.

We investigate the effect of firing temperature, firing time and furnace atmospheres on the resistivity, TCR and microstructure of Al-kaolinite clay cermet system. Special attention was paid to the

behaviour at high metallic or conductive phase concentration (x › 50 wt%). In this regime the cermet is basically a metal matrix composite differing in material composition, component size and concentration from an island structured metallic film. We characterize the cermets using electrical measurements, microstructural examination and X-ray diffraction analysis. Our measurements and analysis reveals the effect of processing parameters on this cermet. An optimum peak firing temperature for the cermets was established based on the criteria of low density and stability.

2. Experimental procedure.

Al- kaolinite clay based cermets have been prepared by a compaction method. A pulverized 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 makes it particularly desirable for this application are its high conductivity, light weight and resistant to corrosion through passivation (Evans, 1968) or formation of a thin oxide layer on the surface.

The clay material was obtained from a kaolinite clay deposit at Ilorin (8^o 30' N, 4^o 33' E), Nigeria. The clay was washed inside a basin of distilled water so that it formed suspension in the water. The resulting water-clay suspension was then sieved to remove rocky lumps. The suspension was left for three days so that the clay forms sediment inside the water. After sedimentation the top water was drained off and the clay sediment was then dried, grounded and processed into a fine powder with average particle size of 50 μm. The aluminum and clay powder were then mixed together in a rotatory mixer according to different fixed ratios in terms of mass with the clay occupying 5%, 10%, 15%,20%, 25%, and 30% of the total aluminum-clay mixture.

A mechanically operated molding press capable of exerting a high pressure in excess of 6.9×10^8 N/m^2 was fabricated and used to mould the materials into a cylindrical structure of lengths 5 mm, 10 mm, 15 mm, and 20 mm respectively with a constant diameter of 3 mm. The fabricated cermets were dried in a vacuum, after which a set of ten cermets of the same composition, selected from each length, were put into an electric furnace, fired at 100 °C for 30 minutes, and finally furnace cooled to room temperature. The process was then repeated for other sets of cermets in steps of 100 °C up to a maximum of 1000 °C. The initial maximum temperature at which each set of cermets was heat treated and then furnace cooled to room temperature is designated the maximum firing temperature, T_F. Immediately after annealing at the desired temperature and furnace cooling to room temperature, each of the cermets was weighed on a Santaurius 20 electrical weighing balance and their corresponding bulk densities determined.

The DC conductivity or resistivity measurements on these cermets 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 cermets was assured by depositing small drops of conducting silver paste 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 (TCR measurements) were carried out in a sand bath between a temperature range of 10 °C to 100 °C. The cermets with electrodes across their ends were heated in a sand bath 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) Model LEO 1450. The SEM enabled the characterization of the cermets in terms of composition, grain sizes and microstructural evolutions as the firing temperature increases.

Compositional analysis of the cermets at each firing temperature was done with a Philips PW 1050/25 X-ray diffractometer using CuKα radiation in the region between 10 and 80^o at a speed of 1.2° per minute and a step size of 0.02°.

3. Results and Discussion.

3.1. Electrical Characterization

Figure 1 shows the effect of peak firing temperature TF on the resistance of the cermets with different aluminum-clay ratios. The resistance decreases with increase in the peak firing temperature, with the decrease being rapid for cermets containing higher concentrations of clay. A comparatively high resistance is also observed at firing temperatures below 300 °C, for cermets with higher concentration of clay. During this stage (TF ‹ 300 °C) the majority of the aluminum grains are still well separated from one another by pores and the clay aggregates. This is clearly shown by the presence of pores in the microstructure of 90 wt% Al cermet fired at 300 °C shown in Fig. 2(a). The presence of the clay aggregates and the inter-grain gap observed at this stage act as a tunneling barrier width to the conduction electrons (Ayodele and Akomolafe, 2005). This barrier width inhibits the tunneling of electrons from grain to grain and thus giving rise to the high resistivity observed.

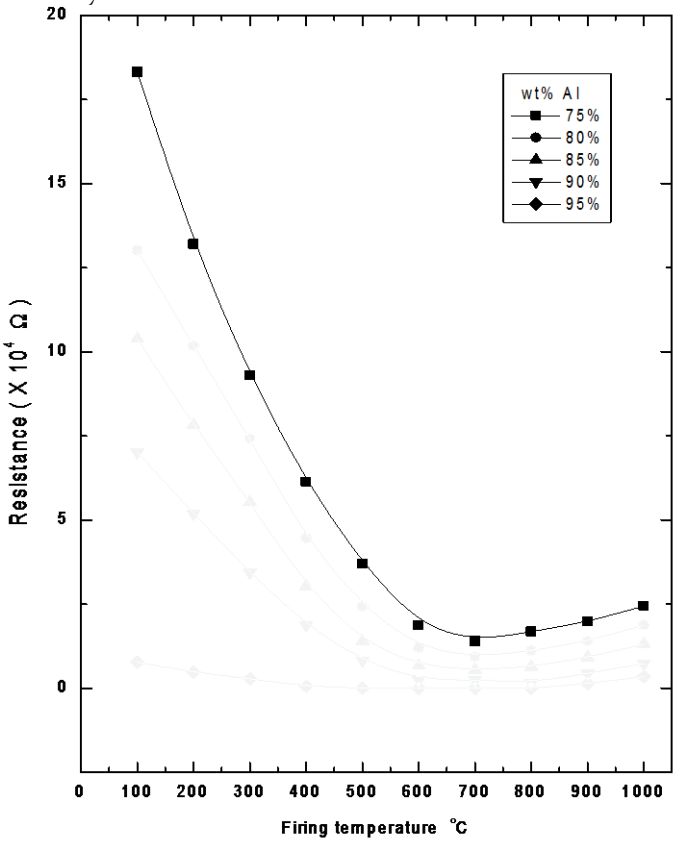
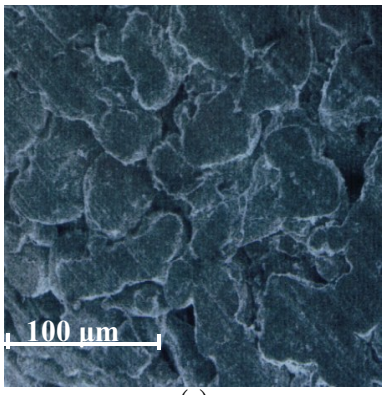


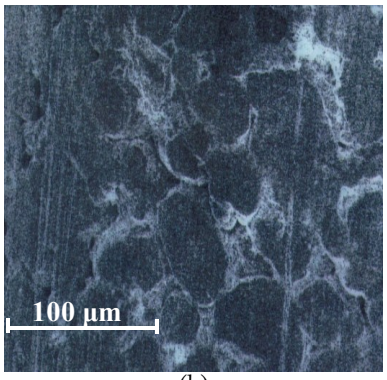
Figure 1. Variation of Resistance with Firing time for Resistors of length L = 20 mm.

Between firing temperatures of 300 °C and 700 °C, the resistance reduces drastically, this is because sintering has started, some structural defects are gradually annihilated and porosity reduced. All these are expected to lead to coalescence of the

aluminum grains, forming a 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. 2(b). These facilitate easy conduction of electrons through the structure. One effect of annealing during sintering at this stage is increasing the aggregate grain size through agglomerations of the Al grains to form clusters (Biesterbos, 1974). This is clearly evident by comparing Figures 2(a), 2(b) and 2(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.



(a)



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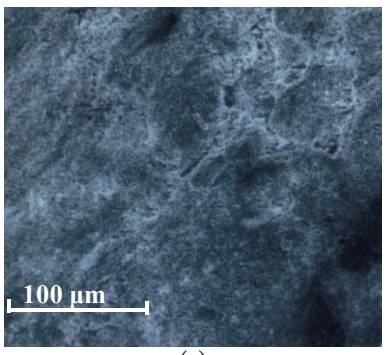

(c)

Figure 2. Evolution of microstructure of the resistors (90 wt% Al) fired at (a) 300 ° (b) 600 °C (c) 900 °C.

Above 700 °C , we observed a slight increase in the resistivity. At this firing temperature the aluminum grains are now well coalesced and sintered. The organic matters bounded to the surface of the clay mineral have been burnt out at this stage. The slight increase in resistivity at this stage may be an effect of the furnace atmosphere (Zongrung and Chung, 2005). These effects may include chemical reactions, which take place within the materials as a result of complete oxidation of the aluminum grains by the furnace gases.

We plot in Fig. 3, the effect of annealing temperature for cermets of length 5 mm. There is not much difference in the pattern of resistance variation when compared to cermets of length 20 mm shown in Fig. 1. The only difference is the extent or degree to which the resistivity rises when TF is higher than 700 oC. For the 5 mm cermets the resistivity above 700 °C seems to be higher than that of cermets of length 20 mm. This is an inverse effect, which can be attributed to the fact that diffusion of furnace gases into the materials is faster and easier for the shorter cermets and hence the shorter cermets attain a higher level of oxidation faster than the longer ones. Thus above 700 °C, the resistivity of the shorter resistors is comparatively higher than the longer ones. This effect is similar to what was observed by previous works in a closely related cermet system (Prudentziati et. al. 1991).

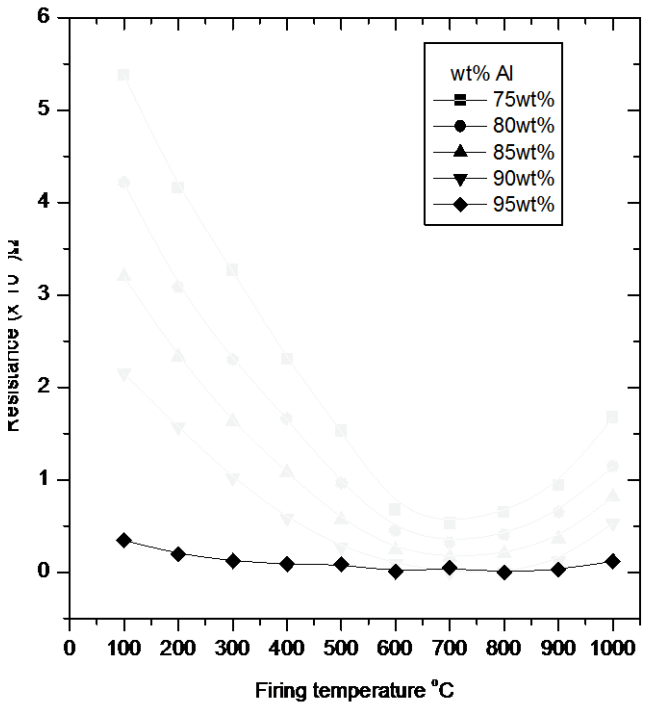

Figure 3. Variation of Resistance with Firing time for Resistors of length L = 5 mm.

The variation of bulk density of the cermets with firing temperature is shown in Fig. 4. The bulk density of the cermets decreases with the increasing firing temperature, attaining a minimum at T_F = 700 °C and slightly increasing above T_F = 700 °C. The drop in bulk density at the early stage of annealing is due to burning off of the organic matters in the clay aggregates, sintering and shrinkage in cermets bulk size as earlier suggested. The slight increase in bulk density of the cermets when fired above T_F = 700 °C also confirms our earlier suggestion that complete oxidation of the conducting grains occurs at this stage. The presence of thick oxide layers on the conducting grains at this stage might account for this slight increase in bulk density.

The above results shows that the optimum annealing temperature of the cermets can be taken as 700 °C as indicated by the low resistivity and bulk density observed at this firing temperature.

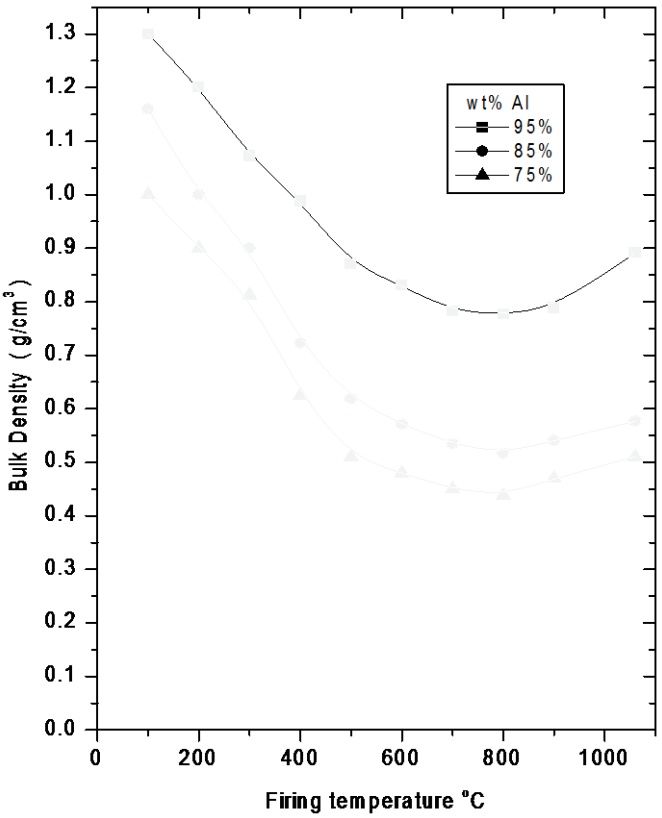

Figure 4. Variation of the cermet's bulk density with firing temperature

The effect of firing time on the resistance of the cermets was studied as reported in Fig. 5. The resistance is observed to fall off rapidly at the early stages of firing. Afterwards, the decrease proceeds at a much slower rate and eventually levels off. The leveling off of the graphs can be attributed to the completion of the processes and the chemical reactions, which take place at each firing temrature. The rate of fall however depends on the peak firing temperature T_F. The lower the value of T_F, the longer it takes for the cermets to attain a fairly constant value. This is because the processes, which affect resistance change, proceed at different rates, being faster at higher T_F.

Figure 6 shows the variation of the cermet's resistance with temperature. The slope of each curve is directly proportional to the temperature coefficient of resistance (TCR). All the resistors were observed to show a negative TCR with magnitude of the TCR showing a dependence on the firing temperature. Figure 7 shows the plot of the calculated TCR against the firing temperature. The magnitude of the TCR decreases with increase in the peak firing temperature. The TCR of the cermets is primarily controlled by the contact between the conducting particles. An increase in the firing temperature would result in sintering and coalescence of the aluminum grains which reduces the electron tunneling distance between the grains thus making the conduction mechanisms to be mainly through metallic path formed by the sintered aluminum grains. This in turn makes the material to be metallic in nature with the TCR tending towards a more positive value as shown in Fig. 7.

Another interesting observation from Fig. 7 is that the TCR increases with decrease in Al concentration. This may be due to the fact that the decrease in aluminum concentration reduces the number of electrons available for conduction; this reduces the activation energy of conduction, which in turn reduces the TCR of the cermet (Lai et. al., 2001).

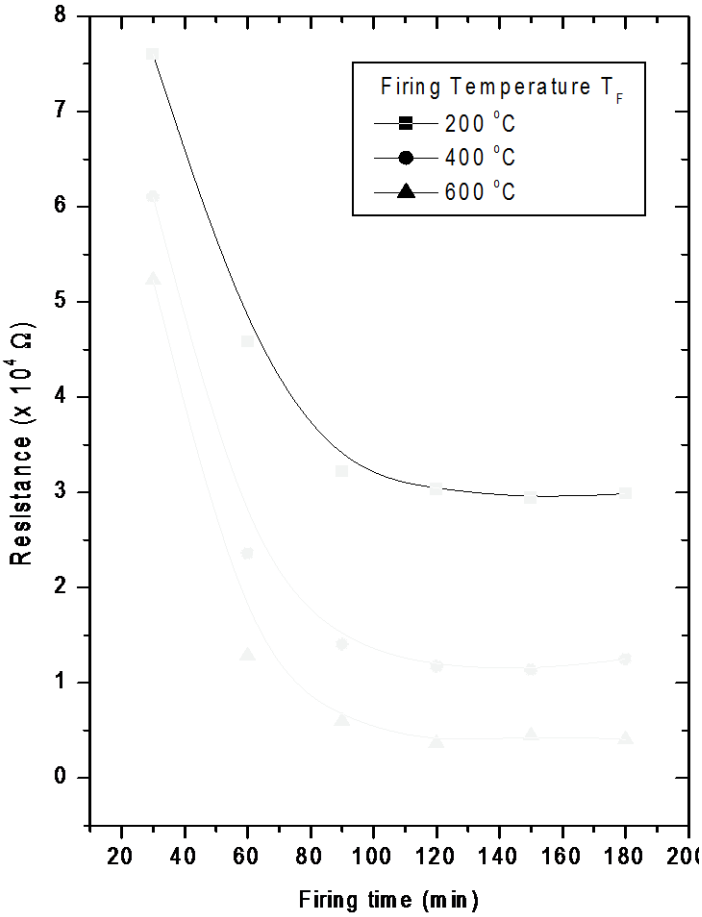

Figure 5. Effect of firing time on Resistance for Cermets with 80 wt% Al.

The low value of the TCR (i.e 50 ppm/oC) obtained at TF = 1000 oC shows that the cermets could find applications in analog sensor and control circuits where small variation in the resistance with temperature is usually desired (Crosbie et. al., 1998). On the other hand the high values of TCR obtained at low firing temperatures, which is comparable to those of carbon composition resistors, could also be of interest as thermistors in temperature sensing applications (Goodman, 1977).

3.2. Microstructural and X-ray diffraction analysis

The microstructure at the early stage of firing (T_F = 300 °C) is shown in Fig. 2(a). 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 may not have started fully. The average particle size estimated at this stage is about 70 μm. Further increase in the peak firing temperature results in the sintering and agglomeration of the particles, reduction in porosity and formation of highly compacted structure. This is evident in Fig. 2(b) the microstructure of the same composition fired at peak firing temperature of 600 °C. The estimated grain size at this stage is about 92 μm.

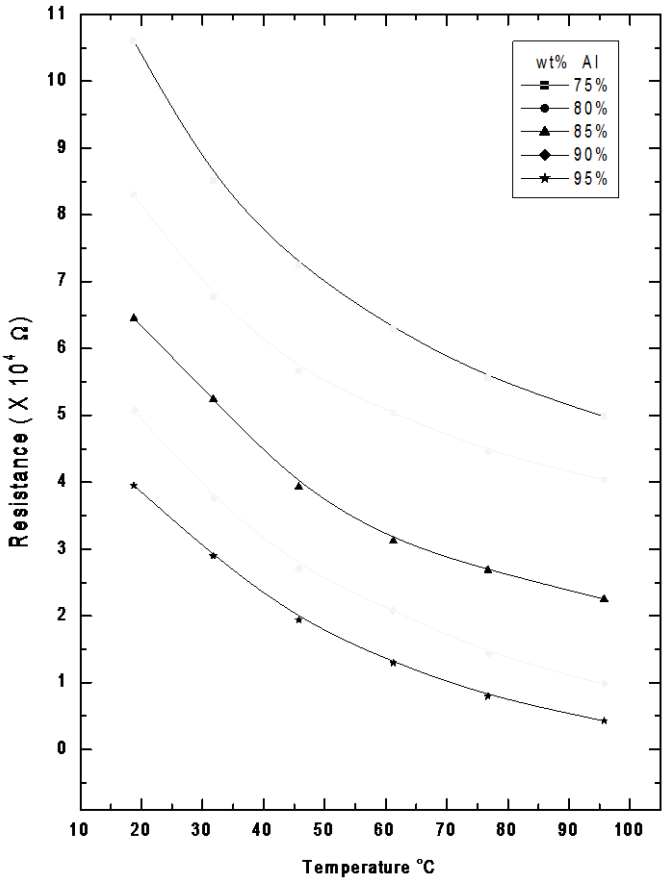

Figure 6. Variation of Resistance with temperature for Cermets initially fired at T_F = 200 °C.

However, for T_F 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. 2(c). The conduction mechanism at this stage is basically percolation of the electrons through the metallic backbone as indicated by the low resistance values obtained.

The panels in Fig. 8 show the X-ray diffraction spectra of 80wt% cermets, classified as untreated (Fig. 9(a)), fired at TF = 300 °C (Fig. 9(b)) and TF = 800 °C (Fig. 9(c)) respectively. The relatively high intensity peaks observed at d-spacing (d_{hkl}) of 7.11 Å (001) and 3.59 Å (002) shown in Fig. 9(a) for the unfired cermet, indicates the presence of kaolinte (Kim 1998). These peaks are first and second order reflection from the basal plane of the kaolinite clay platelets. The high intensity peak at d-spacing of 4.66 Å (110) indicates the presence of Al_2O_3. A comparison of Figs. 9(b) and 9(c) shows that the intensity of the Al_2O_3 peak becomes stronger as the firing temperature increases. This increase in intensity results from further oxidation of the aluminum grains. The intensity peaks observed at 2.39 Å (111), 1.37 Å (300) and 1.46 Å (220) are characteristic diffraction peaks of aluminum (Suryanarayana, 1998) present in the cermets. The two relatively strong peaks with d-spacing's of 7.11 Å (001) and 3.59 Å (002) observed at the early stage of firing (T_F < 500 °C, Fig. 9(a), Fig. 9(b)) are strongly reduced at T_F = 800 °C. This reduction corresponds to the destruction of kaolinite structure which occurs at 550 °C.

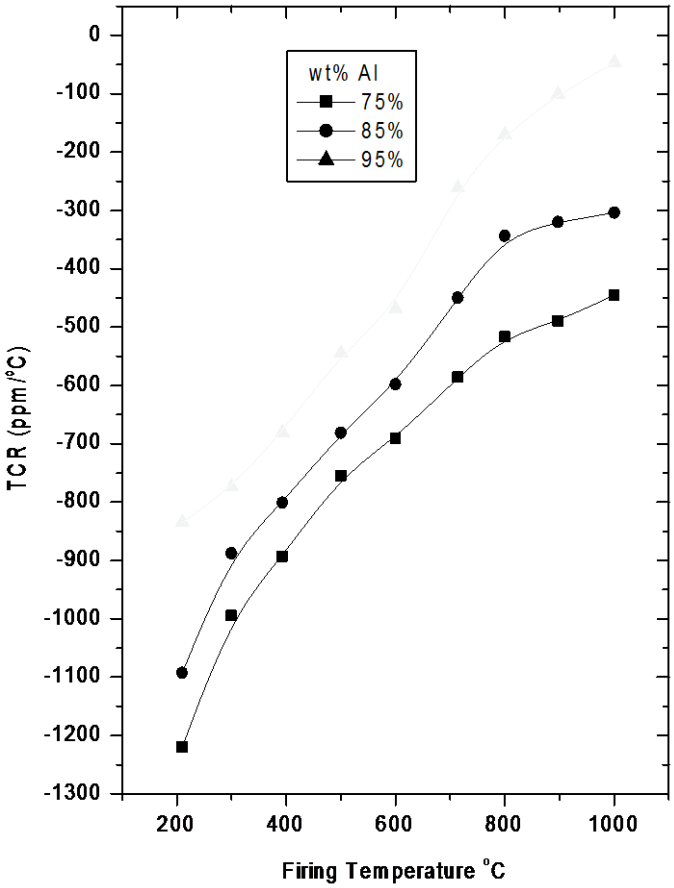

Figure 7. Variation of TCR with firing temperature

4. CONCLUSION.

In this work, we have studied the effect of processing parameters of Al- kaolinite clay based cermets. Our studies have shown that electrical properties vary remarkably with annealing schedule (such as firing temperature, firing time and furnace atmosphere). The resistance was observed to fall rapidly with increasing peak firing temperature, being very rapid at the initial stage of firing and slightly rising again above 700 oC due to oxidation of the aluminum grains by the furnace gases. The TCR values also showed a marked dependence on the initial peak firing temperature with the magnitude decreasing from 1220 ppm/oC to as low as 50 ppm/°C. The range of the TCR obtained shows that by proper fine-tuning and adjustments of the annealing schedule the resistors could find applications in analog sensor and control circuits. A comparative study of the microstructure emphasizes the enhancement of sintering and agglomeration of the conductive particles at increasing peak firing temperatures, independently of the composition of the conducting phase. Based on the requirement of low resistance, low density and stable microsructure a peak firing temperature of 700 °C is identified as the optimum temperature for these cermets.

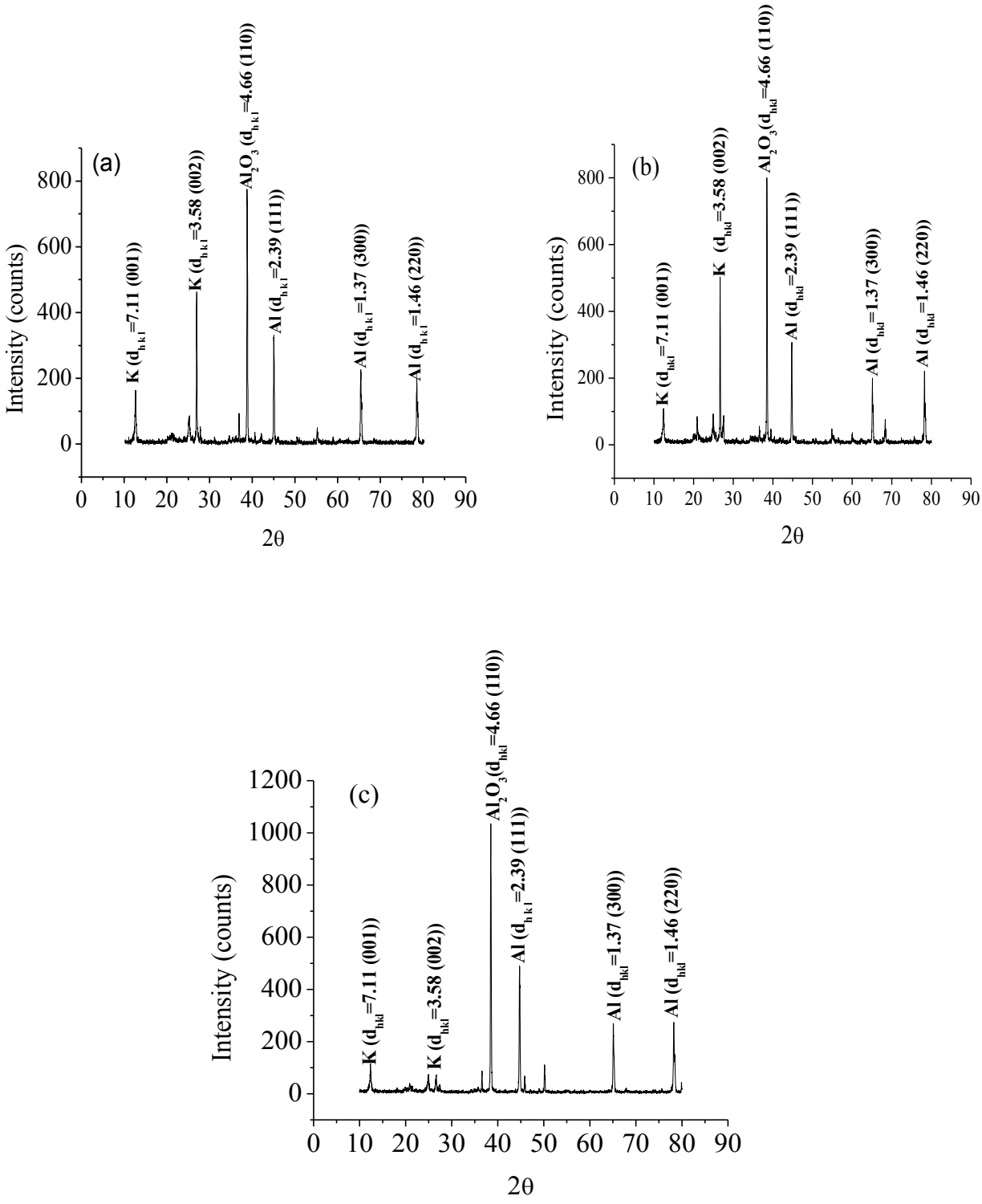

Figure 8. X-ray diffraction spectra of Al-kaolinite clay cermets with 80wt% Al (a) unfired (b) fired at T_F = 300 °C (c) fired at T_F = 700 °C. Kaolinite peaks are denoted "K".

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