

Preparing graphitic schist as a pressure sensor precursor by carbon separation using electromagnetic techniques

K. KOKKORIS, K. PANAGOPOULOS, P. E. TSAKIRIDIS, E. HRISTOFOROU*

School of Mining and Metallurgy Engineering, National Technical University of Athens, Zografou Campus, Athens 15780, Greece

In this paper the possible application of carbon-free graphitic schist as precursor for electronic pressure sensors is presented. The sensor principle is based on the change of the dielectric properties of the carbon-free ore, provided that the rest of the stoichiometry remains unchanged. Microwave and radio frequency techniques have been developed to obtain such carbon separation. Dielectric constant response suggests a monotonic dependence on ambient pressure.

(Received March 16, 2006; accepted May 18, 2006)

Keywords: Graphitic schist, Electromagnetic separation, Dielectric materials

1. Introduction

Aggregate materials may play an important role in engineering applications [1]. Apart from their use in mining and civil engineering applications, like additives to cement and building development, they can also find applications in chemical engineering like painting additives [2].

Graphitic Schist is one of those raw materials used in the aforementioned engineering fields. It generally consists of very fine grained carbonaceous material, quartz, micas, Fe-chloritoid, rutile and graphite in varying proportions with minor amounts of sulphide minerals [3]. Many XRD studies have been conducted on the transformation of organic matter to graphite during metamorphism; all the intermediary terms from amorphous carbon to well-ordered graphite have been seen [4].

Such an ore has been extracted from a mine appeared in the area of Stefani, at the prefecture of Boeotia, Greece. The engineering applications of this ore, up to now have mainly been in cement industry as an additive [5]. However, considering that the painting production sector has an increasing tendency in the Greek and international market, the application of this ore in painting additives is very promising. The most important painting products are the enameled and oil paintings, corresponding to the 80% of the total painting producing activity, followed by shiners, as well as pigments for plastics. The graphite additives are regarded as a distinguished raw material in painting development, followed by talk, kaoline, baryte, marble powder and silicates.

Targeting alternative possibilities of using this ore in other engineering applications, the purpose was to exclusively separate carbon from the ore, in such a way that the stoichiometry of the rest of the ore does not change. The motivation of such separation was the study of the dielectric properties of the carbon-free material, in order to evaluate its possible use in electronic sensing applications, especially in pressure sensing applications.

Graphite minerals are the most efficient mineral conductors. Pore waters contained in underground

formations also conduct electricity very well, and it is the very presence of these waters which makes electrical prospecting methods possible. In most rock materials, the amount of porosity and the chemistry of pore waters have a greater influence on conductivity than do metallic mineral grains. Where the pore waters contain salts (such as sodium chloride) in solution, the methods work especially well. Clay minerals containing only a slight amount of moisture are also easily ionized [3].

Targeting an alternative method for carbon separation, without destroying the rest of the ore contents, high frequency inductive heating was examined. The selective fast heating of the graphite and consequently its evaporation could be performed in a microwave oven, due to the induced eddy currents caused by the high frequency electromagnetic field. The optimum frequency of the electromagnetic radiation can be determined with respect to the size of the graphite powder. The skin depth of eddy current is given by:

$$\delta \cong \sqrt{\frac{1}{\omega\sigma\mu}} \quad (1)$$

where ω is the cyclic frequency of the induced electromagnetic radiation, σ is the electric conductivity of the targeted material and μ is the magnetic permeability. Apparently, the skin depth for the dielectric part of the ore is meaningless due to the very small conductivity, thus allowing high penetration depth and therefore relatively slower heat up process due to eddy currents.

Considering the graphite grains as spheres of small diameter and taking into account the graphite relative conductivity which is of the order of 25 kS up to 100 kS and its relative magnetic permeability which is of the order of 1, the eddy current skin depth is:

$$\delta \propto 1,5 \sqrt{\frac{1}{f}} \text{ up to } \delta \propto 3 \sqrt{\frac{1}{f}} \quad (2)$$

in meters. Taking into account the milling process of the ore, the mean value of the carbon radius is not larger than 10 μm . Thus, the optimum region of frequencies to obtain

complete eddy current penetration and fast heating of the carbon, resulting correspondingly in carbon evaporation, is of the order of 5 GHz. Therefore the closer possible industrially approved frequency of microwaves is 2.45 GHz.

In the present paper, the structural characterization and the electrical properties of the material are presented, while microwave and radio frequency techniques to obtain carbon separation are also illustrated. Consequently, results on the dielectric response of the carbon-free ore are presented, illustrating the possible use of the carbon-free ore as a precursor for electronic pressure sensors.

2. Experimental

The ore was received from an area of former mining activity. In fact, twenty (20) different samples have been received in order to obtain representative samples from the ore. These samples have been driven to a jaw crusher with 2 mm output. Thus, the product was homogenized after grinding and samples, 25 g each, were prepared for characterization.

Mineralogical characterization was conducted by means of X-ray diffraction, using the Philips X-ray spectrometer PW 1606/00, with nickel-filtered $\text{CuK}\alpha_1$ radiation ($=1.5405 \text{ \AA}$, 40 kV and 30 mA).

Microstructure characterization was carried out by scanning electron microscopy (SEM) using a Jeol 6100 Scanning Electron Microscope. Experimental conditions involved 20 kV accelerating voltage. Analysis of the material was performed by a Noran TS 5500 Electron Dispersive Spectrometer (EDS) connected to the SEM.

Thermal response and possible phase transformation was done by using differential temperature analysis and scanning calorimetry (Perkin-Elmer 2100 DSC). Type R thermocouple (Pt-13% Rh/Pt) was used for temperature measurements in this instrument. The sample was taken in a ceramic crucible and heated from room temperature to 1000°C at a heating rate of $2^\circ\text{C}/\text{min}$ using air as a medium under static condition. TG/DSC were done simultaneously.

A classic microwave oven in the type-approved 2.45 GHz frequency of operation was used, for carbon evaporation, having the ability of transmitting 300 W, 600 W and 750 W. Using the oven for 10 minutes in 750 W the optimum results were achieved.

Targeting the use of higher power of electromagnetic radiation, the radio frequency oven of the Laboratory of Physical Metallurgy of the National Technical University of Athens, operating in 500 kHz and 10 kW, was used. Samples of 10 g of ore were used in atmospheric pressure. The samples were introduced in quartz tubes, closed in the one end. For all experiments, the full power of the radio frequency generator was used. Samples were heated for 10, 20, 30, 40, 50 and 60 seconds as well as for 2, 3, 4, 5, 6, 7, 8, 9 and 10 minutes. Initially a spectacular evaporation of carbon was optically observed. Thus, carbon was deposited on top of the quartz crucible.

After heating the graphite-free samples were compressed into pellets. An amount of 0.4g was compressed at various pressures. Pellets of 1.30 cm

diameter and about 1.35 mm thick were obtained. The samples were made in the shape of a rectangular bar to ensure that the current flow was parallel and uniformly distributed over its cross section.

Electric properties and their dependence on frequency, temperature and pressure have been obtained as analyzed in previous work [6].

3. Results and discussion

3.1 Material characterization

The chemical analysis of the graphitic schist ore used is shown in Table 1. Silicon, aluminum and iron oxides are the principal components.

Table 1. Chemical analysis of the graphitic schist ore used.

Oxides	Composition (%)
SiO_2	52.61
Al_2O_3	24.56
Fe_2O_3	6.89
CaO	2.89
MgO	2.67
K_2O	4.32
Na_2O	0.31
LOI	5.25
Total	99.50

Pairing the results of X-ray (Fig. 1) with chemical analysis, the oxides that predominate in the ore are seen to be SiO_2 and Al_2O_3 , because of the presence of quartz, clays and feldspars. The other oxides are of: Fe (from clinocllore), K (appears in Illite), Mg (from Illite), Na (mainly from albite) and Ca (from calcite and dolomite).

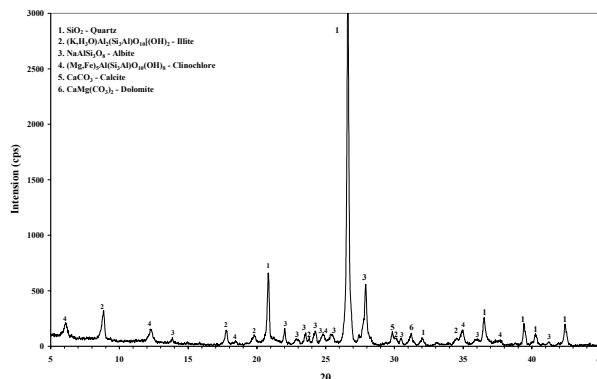
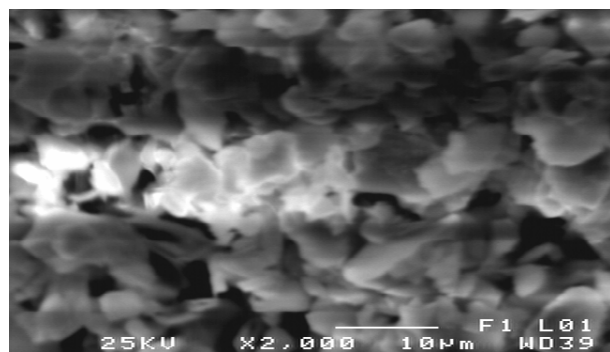
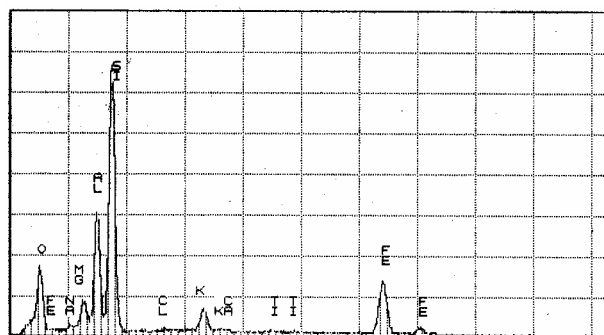


Fig. 1. Mineralogical phases of the graphitic schist ore used.



(a)



(b)

Fig. 2. SEM micrograph of the graphitic schist ore used: (a) A typical micrograph of a fined grained sample of the as-received ore, (b) A typical EDAX compositional of the as-received ore.

Scanning electron microscopy studies followed by EDAX examination was also tried. A typical micrograph of a fined grained sample is illustrated in Fig. 2a. A typical EDAX compositional response is illustrated in Fig. 2b. From XRD and SEM studies it has been observed that Si-rich and Al-rich grains exist in the ore.

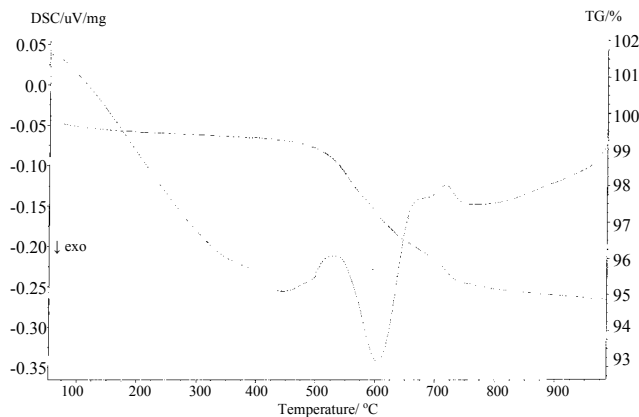


Fig. 3. T. G. and D. T. A. analysis of the graphitic schist ore used.

From the study of Fig. 3 (TG and DSC) of the above material the weight loss up to 110 °C can be attributed to the removal of humid water. The TG curve shows that a continuous heating rate originates a slight mass loss below 140 °C, associated with the loss of the loosely bonded adsorbed water on the particle surface, which is accompanied with a weak endothermic effect in the DSC curve. The DSC thermograms demonstrate that the essential weight loss occurs in the range from 220 to 650 °C. The corresponding peak for weight loss in the coal is centering at 400 °C with the accompanying peak at 550 °C. These signify that volatilisation started at a relatively lower temperature and occurred at a slower rate. The area under the DSC curve represents heat evolution during the combustion of the sample, so it could be related to the heating value of the coal. In TG graph a small mass loss between 220 °C and 400 °C is followed by a change in the slope of the TG curve which leads to a faster mass loss from 400 to 580 °C. After this temperature, the mass loss rate decreases and stops at 750 °C. These three stages of mass loss are associated with the dehydroxylation process of clays and originates an endothermic effect (between 400 and 650 °C) centered at 580 °C. In this temperature the endothermic peak also suggests a polymorphous transformation of a-quartz into b-quartz. The small endothermic peak in 780 °C is associated with the decomposition of CaCO_3 and $(\text{Ca,Mg})(\text{CO}_3)_2$ existing in the ore [7].

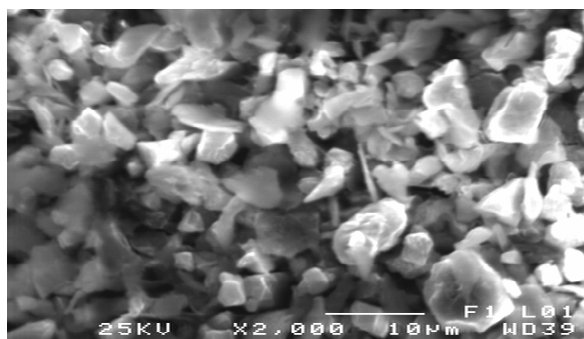


Fig. 4. Microphotograph of the ore before the microwave oven carbon separation.

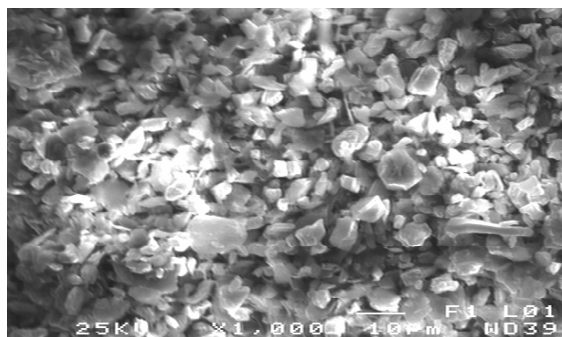


Fig. 5. Microphotograph of the ore after the microwave oven carbon separation.

3.2 Carbon separation

The principle idea for carbon evaporation using microwave oven was that microwave electromagnetic radiation penetrates dielectric materials, while it is reflected after a small skin depth in conductive elements. Therefore, it was expected that the dielectric part of the ore could not be heated and therefore could remain in the ore, while the fast heating of the carbon could result in fast heating and evaporation.

Using the oven for 10 minutes in 750 W the optimum results were achieved. Indeed, as illustrated in Figs. 4 and 5, demonstrating a microphotograph of the ore before and after the microwave oven separation, the graphite powders (black areas) are apparently present in Fig. 4, while they are much reduced in Fig. 5. This has also confirmed by EDAX measurements. Graphite grains were also present even after such microwave heat treatment. This may be attributed to the relatively low power of the microwave oven.

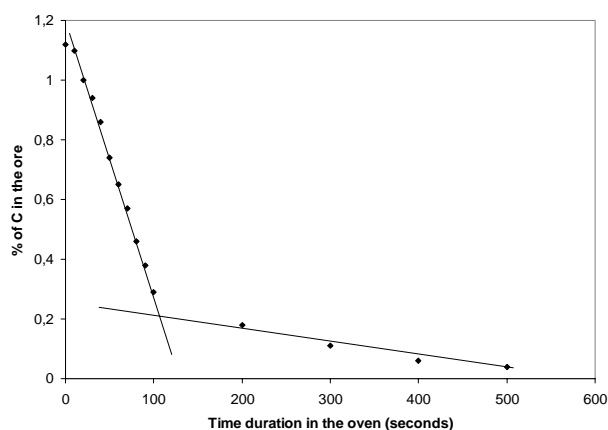


Fig. 6. The dependence of carbon % on the heating time of the radio frequency amplifier. Measurement error 0.05%.

In Fig. 6 the dependence of carbon % on the heating time is illustrated. Two linear regions of the C % are observed in this response. It is worth noting that these results are surprisingly better than the microwave oven results. This is attributed to two reasons: the relatively large expected penetration depth of the electromagnetic radiation of 500 kHz results in a relatively uniform distribution of the current density in the depth of the material with respect to the same activity of the microwave oven frequency of 2.45 GHz. The second (and after our opinion most important fact) is that the power of the radio frequency oven is so great that, together with the uniform current density along the depth of the graphite grains, provides a large and fast heat up of these grains, resulting in their fast evaporation.

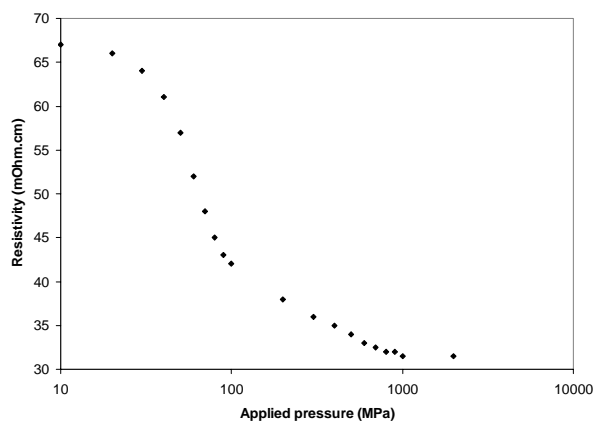


Fig. 7. Pressure dependence of resistivity of the as-received ore.

3.3 The carbon-free graphitic schist as pressure sensor precursor

Testing the dielectric dependence of the as-received ore on pressure, a non-monotonic and non-repeatable response was observed. This was attributed to the presence of graphite, in the ore. In the contrary, the pressure dependence of resistivity of the as-received ore, illustrated a rather monotonic and decreasing response, as illustrated in Fig. 7, suggesting that carbon allows conducting ways in the under test sample. Testing the dielectric dependence of the ore burnt in 650 °C on pressure, in order to achieve carbon removal, a monotonic, repeatable but not sensitive enough response was obtained as illustrated in Fig. 8. Carbon separation without destroying the rest of the contents of the ore was tried, in order to test the dielectric dependence of remaining phases of the ore on pressure.

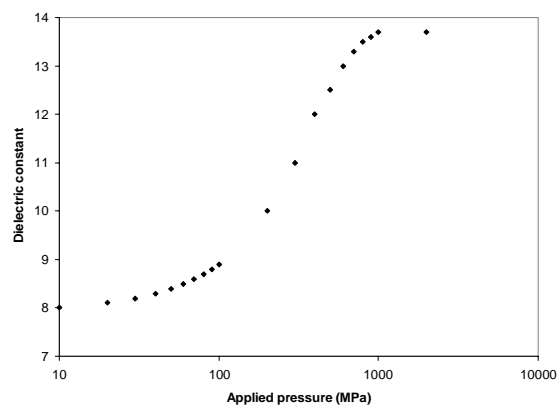


Fig. 8. Dielectric dependence of the ore burnt in 650°C on pressure.

After removing the carbon from the ore without losing the rest of the ore contents, dielectric measurements were performed. Figs. 9 and 10 illustrate the cryogenic temperature and the frequency dependence of the real and imaginary parts of the dielectric constant ϵ of the carbon-free ore, respectively, demonstrating a repeatable response.

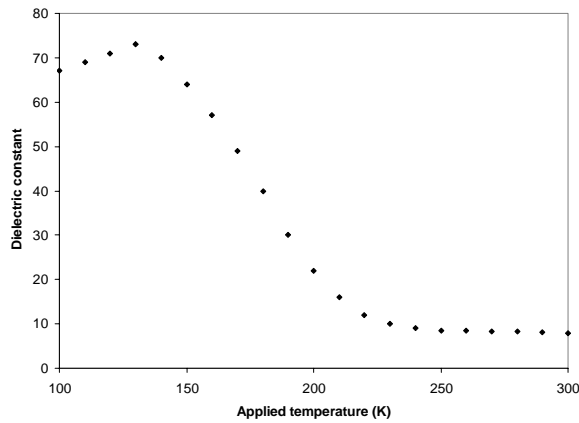


Fig. 9. Dielectric constant ϵ of the carbon-free ore dependence on cryogenic temperature.

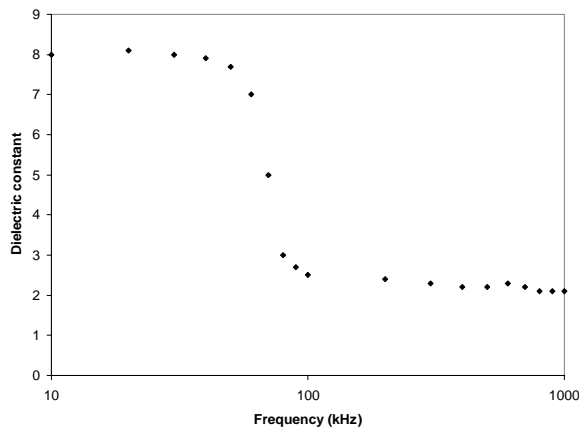


Fig. 10. Dielectric constant ϵ of the carbon-free ore dependence on frequency.

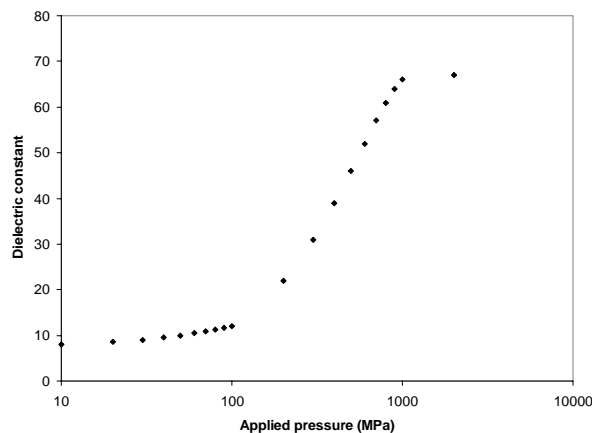


Fig. 11. The dependence of ϵ of the carbon-free ore on the applied pressure.

The dielectric constant ϵ , of the carbon free-ore was tested under pressure, after the radio frequency heating carbon separation. The dependence of ϵ on the applied pressure in MPa, concerning a 5 mm thick and 20 mm diameter carbon-free ore pellet, is illustrated in Fig. 11. A monotonic and unhysteretic behavior was observed for loads up to 1.1 GPa. This may be attributed to the mechanical properties of the carbon free ore, allowing a spring-like material operation for loads up to this level. Thus, the carbon-free ore may be usable as a precursor for pressure sensors based on the dielectric dependence of remaining phases of the ore on the applied pressure.

4. Conclusions

In this paper the possibility of using carbon-free schist graphite as precursor for electronic pressure sensors has been illustrated, thus allowing an alternative application of this ore. The sensor principle has been based on the change of the dielectric properties of the carbon-free ore.

Acknowledgements

Acknowledgements are due to Prof. K. Tsakalakis for fruitful discussions.

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*Corresponding author: eh@metal.ntua.gr