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PROCESSING OF ILMENITE ($FeOTiO_2$) FOR VALUE ADDED PRODUCTS

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ABSTRACT

Beach Placer Ilmenite is an important source for production of titanium metal, titania slag and pigment grade titanium dioxide. Besides, these well known applications for which Ilmenite is mined and processed, there are other emerging processes that are being tried for obtaining highvalue products. Synthesis of Ilmenite based materials for varistor applications and direct electrochemical reduction of Ilmenite to produce ferrotitanium are two such attempts being discussed in this work.

In this paper, recent efforts undertaken to study the electrical and magnetic characteristics are discussed. Ilmenite, $FeTiO_3$, is one of the mixed-valence transition metalbearing minerals, inwhich Fe can be in two different oxidation states, Fe^{2+} and Fe^{3+}.. Similarly, Ti can be in Ti^{3+} and Ti^{4+}.Ilmenite is inherently suitable for making Varistors, which are devices, used for limiting the transient voltage surges in a circuit. Varistors produced from Ilmenite can withstand harsh environments seen in nuclear reactors and outerspace. Electrochemical reduction of Ilmenite can be used to prepare ferrotitanium directly without any reductant. The process essentially involves removal of oxygen from the mineral through electrolytic action using calcium chloride as electrolyte and graphite as anode. At a temperature of 950°C, it is shown to be possible that all the oxygen can be removed from the Ilmenite sample, which passes through the electrolyte, to form CO/CO_2 at the anode. The process has immense potential for cost effective production of titanium metal as well. Results of the above developmental works are presented in this paper.

Keywords: beach placer ileminite, varistor applications

INTRODUCTION

Ilmenite, $FeOTiO_2$, is a naturally-occurring mineral commonly found in the beach placer deposits. Natural Ilmenite is also a common mineral found in metamorphic and igneous rocks onearth and also on the surface of the moon. The structural, electronic, and magnetic properties of$FeOTiO_2$ are of great interest in the materials and earth sciences. Ilmenite is known to be a wideband- gap semiconductor, which can be exploited to realize multifunctional semiconductordevices. Ilmenite ($FeOTiO_2$) mineral constitutes about 90% of the known world titanium minerals. Rich Ilmenite deposits are mainly found in Australia, South Africa, Canada, China, India and Norway. World reserves of Ilmenite are estimated at 650 billion tons [Ohno*et al*, 1996] (in terms ofTiO_2 content) and India possesses nearly 15% of the world reserves. Predominantly, the IndianIlmenite deposits are of placer type and occur all along the southern peninsular coasts startingfrom Orissa in the east to Gujarat in the western India. Most of the titanium mineral concentrates are globally used in the manufacture of pigment grade titanium dioxide (TiO_2). Titanium dioxide as a pigment has excellent attributes such as high opacity, brightness, corrosion/erosion resistance, biocompatible, tenacity etc. Various other value added products that can be derived from Ilmenite are titanium tetrachloride, synthetic rutile (90-95%TiO_2), TiO_2 pigment, titanium sponge, ferro-titanium, titanium/ titanium alloy ingot metal etc. Nevertheless, as can be seen in Figure.1, the highest value addition is achieved in the extraction of metal. Synthesis of Beach placer Ilmenite based materials for varistor applications and direct electrochemical reduction of Ilmenite to produce ferrotitanium, are two such attempts being discussed in this work, which can be of value addition to Ilmenite

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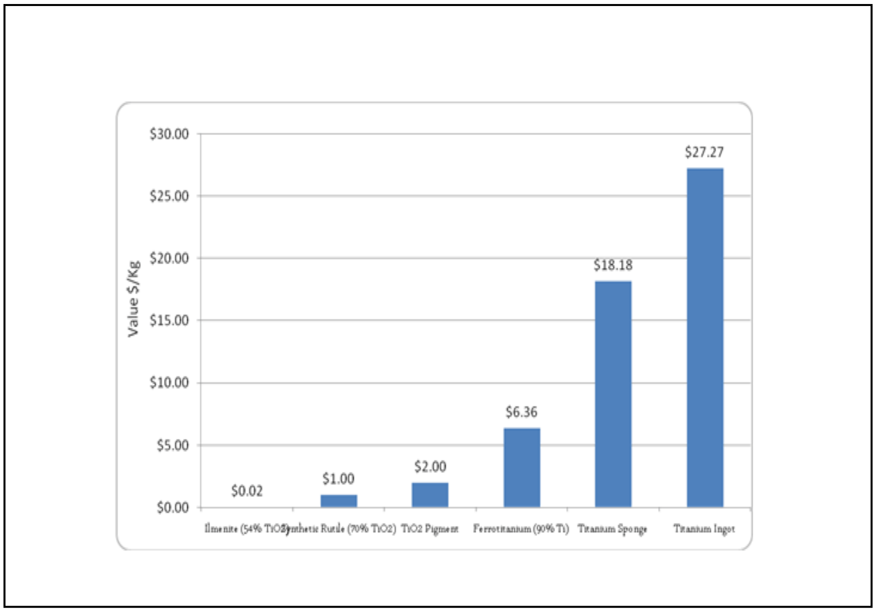

Figure 1. Value addition of ilmenite by processing into various products

PART-A

VARISTOR APPLICATIONS:

Experimental

X-ray Diffraction:

Study was carried out on the sample ground to a mesh of 150 using a SIEMENS -D500 X-ray diffractometer with the angle varying from 20 to 90 of 2. The X-ray data which is reproduced here shows that the sample is rich in titanium bearing mineral with small amount of iron in the form of oxides.

Chemical analysis:

Conventional wet chemical analysis was carried out on the ground sample. The results of the analysis are given in the Table-1.

Table 1. Wet chemical analysis of the samples under study

Oxide	Sample D
Al_2O_3	1.12
TiO_2	61.07
Fe_2O_3	23.43
FeO	8.28
SiO_2	0.24

The chemical analysis also further confirms the presence of Ti-bearing minerals in the form of oxides along with oxides of iron in both of its valence states (+2, and +3).

Sample preparation:

Ceramic samples were prepared using standard techniques. Appropriate molar weights of each of ground Ilmenite, Titanium dioxide and carbon were weighed and mixed thoroughly in an agate mortar along with a small amount of acetone to homogenize the mixture. This mixture was taken in an alumina crucible and calcinations were carried out at 1000°C for 2 hours. The furnace was a graphite crucible furnace and a steady flow of argon was maintained during the entire process of heating and cooling. After allowing the sample to cool down to room temperature overnight, it was removed and ground well again in an agate mortar with a small amount of acetone. Then, the material was compacted to green pellets of 1inch diameter and about 2-3 mm thickness. These pellets were then sintered in the same graphite furnace under a flowing argon atmosphere at a temperature of 1100°C for 3 hrs. Small pieces of size 2mmx2mmx4mm were cut from the sintered pellets and used for characterizations. X-ray diffraction was again carried out on the sintered samples.

Resistivity measurements:

For the resistivity measurements, four contacts to the sample were made using a two-part silver epoxy. Vander Pauw's four-point method was used to measure the electrical resistivity. The apparatus used for this measurement consisted of a Keithley constant current source (model 6221) and a Keithleynanovoltmeter (model 2182 A).

Two insulated copper wires were used to pass a constant current, and the voltage drop across the remaining two wires was measured. After an accurate measurement, of the distance between the voltage leads, the resistivity (ρ) of the sample was evaluated using the formula.

$$\rho = RA/L, \tag{1}$$

Where R is the resistance (R = voltage drop/ constant current passed) as measured above, L is the distance between the voltage leads and A is the cross sectional area of the sample under test. Low temperature resistivity study was carried out from room temperature to the lowest possible (around 20K) using a closed cycle refrigerator. The resistivity data was taken for both the cycles i.e., while cooling and heating it back to the room temperature. This confirms the semiconducting behavior of the samples under study.

Vibrating sample magnetometer studies:

Small amounts of the samples were ground to fine powders from the sintered pellets and used for magnetic measurements.

Results and Discussion

X-ray Diffraction:

The X-ray diffraction data of Ilmenite mineral sample and the heat treated solid solution sampleis shown in the figure2 and figure3 respectively. From Figure.2, the X-ray data show the mineral Ilmenite is rich in Ti along with the Fe in its different oxidation states. This confirms that the fact that the starting materials did not have any major impurities as revealed by the X-ray data.

Similarly, the X-ray diffraction study was taken up on the solid solution samples to understand the phase formation figure. 3 shows the X-ray plot of the solid solution samples. It is seen that the solid solution had some possibly unreactedIlmenite, Titanium dioxide in addition to new phases like $FeTi_2O_5$. There was no trace of any un-reacted carbon, on the other hand, formation of Fe_3C has been observed.From the above X-ray data, it is clear that the solid solution of Ilmenite with Titanium dioxide leads to the formation of the new phase $FeTi_2O_5$.

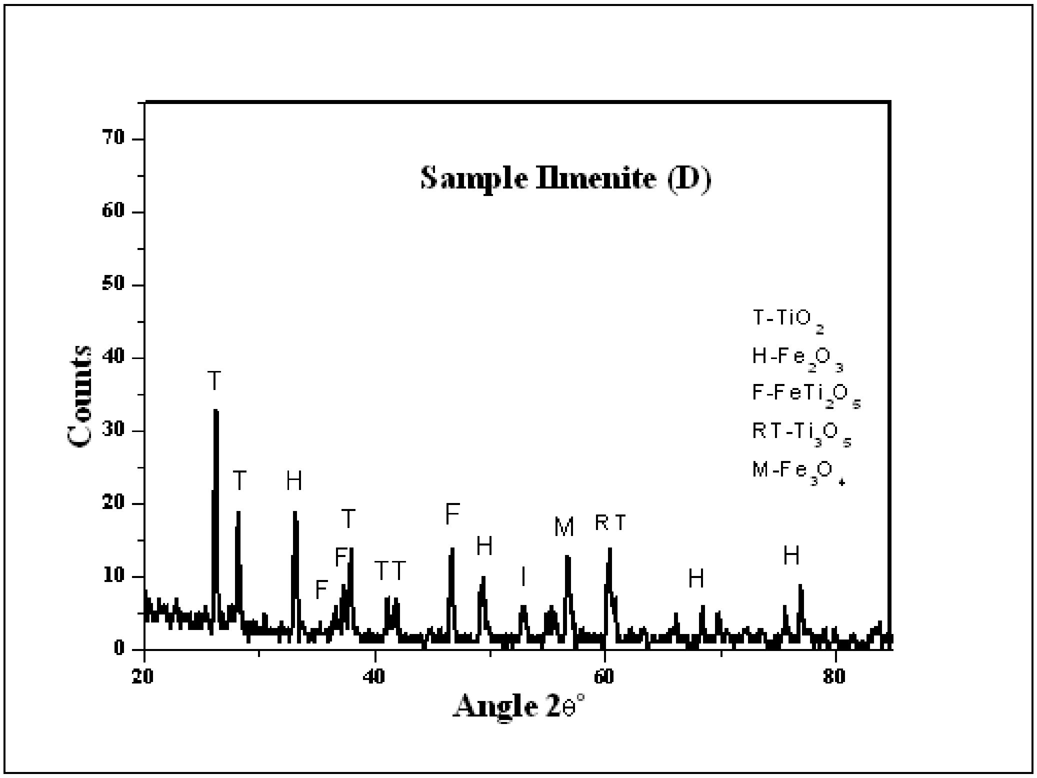

Figure 1. X-ray diffraction plot of mineral Ilmenite

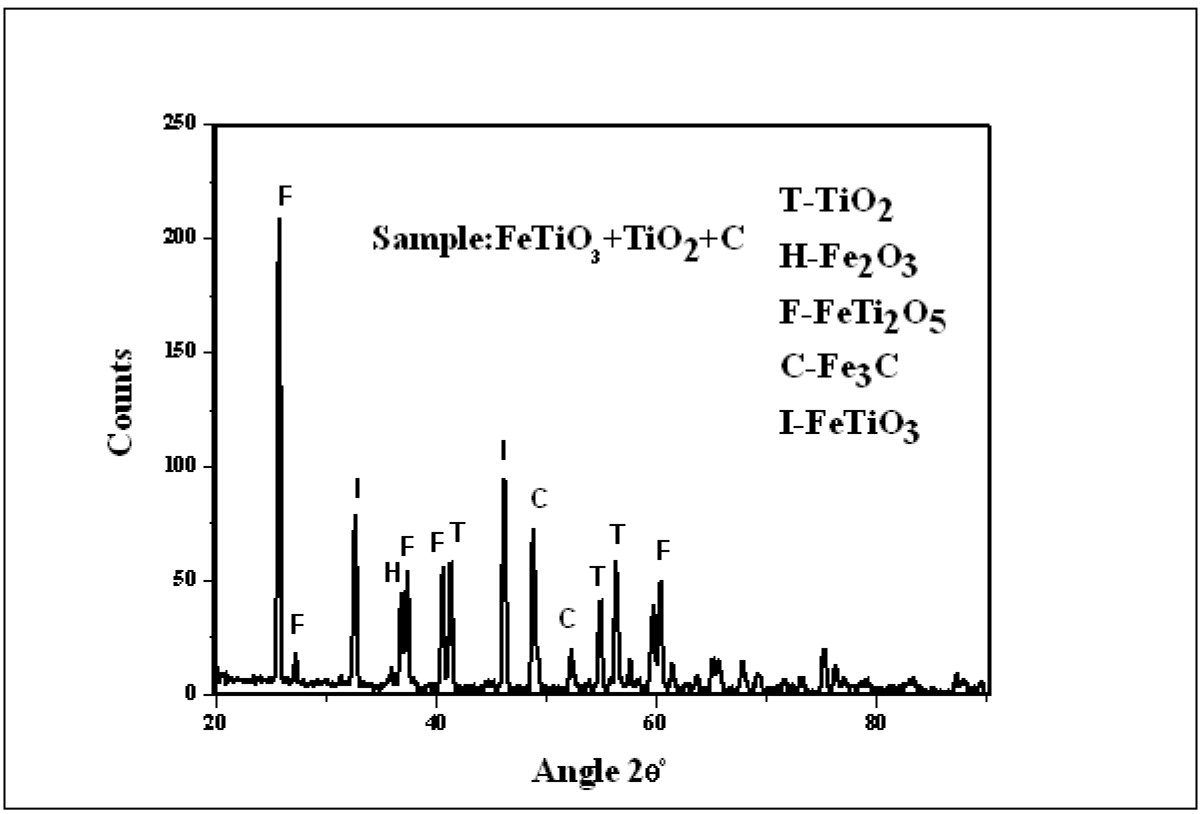

Figure 2.X-ray plot of solid solution of Ilmenite, Titanium oxide and Carbon

Low temperature Resistivity measurements:

Measuring the temperature dependence of resistivity reveals some important differences betweenmetals, insulators, and semiconductors. There is a variety of factors that influence resistivity (and thus its inverse, conductivity. There are two important factors that contribute to the conductivity of a material: the availability of free electrons and the ability of these electrons to move freely through a material. For a conducting metal, with free valence electrons, the factor limiting conductivity is the lattice vibrations which scatter moving electrons; as temperature decreases, these vibrations (and thus the resistivity) also decrease. In an insulator, the electrons are unable to break free from the filled valence band, so there is little conduction. For a semiconductor, the energy gap is small enough that there are some free electrons at higher temperatures. Since the factor limiting conductivity for a semiconductor is the availability of free electrons, resistance decreases with increasing temperature, which is the reverse of the behavior observed in a metal.

In the figure.4it is seen that the present solid solution of Ilmenite, Titanium dioxide and carbon shows typical behavior of a semiconductor. Thus from the discussion it is clear that the low temperature resistivity data as observed herein suggest the semiconducting behavior of the solid solution samples.

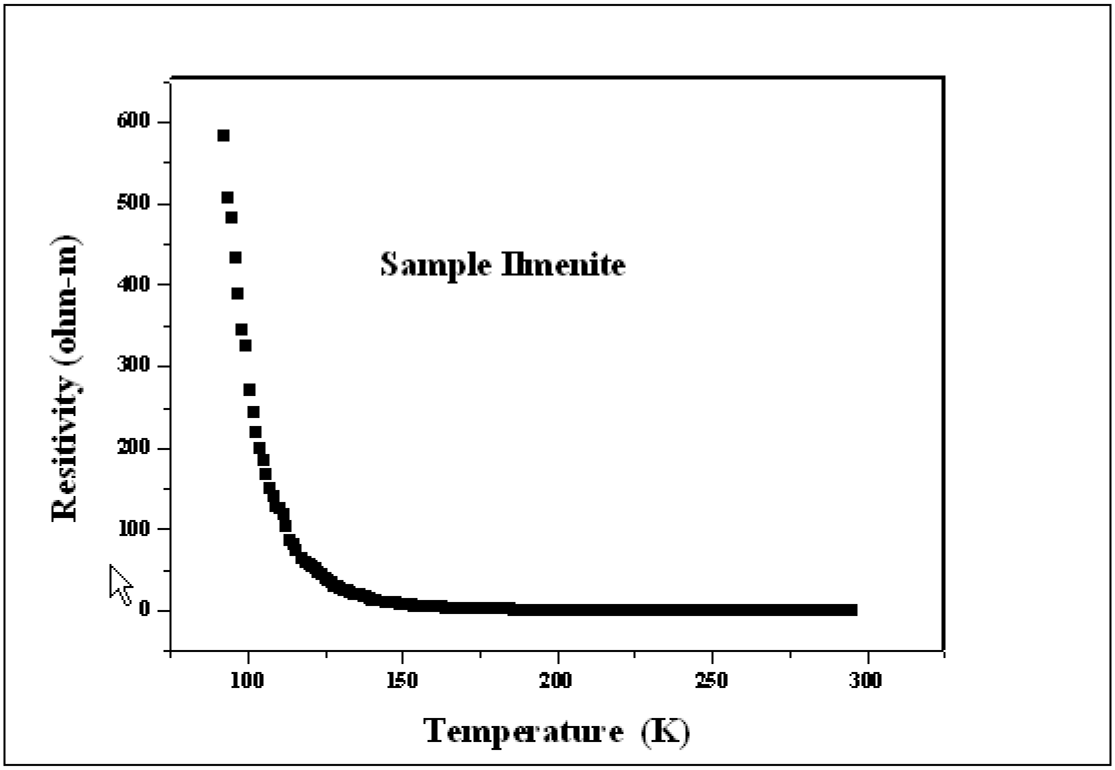

Figure 3. Low temperature Resistivity of solid solution of Ilmenite, Titanium oxide and Carbon

Magnetic properties of reduced Iilmenite:

The Hysteresis loop of Ilmenite sample as well as the solid solution are shown in figure 5.

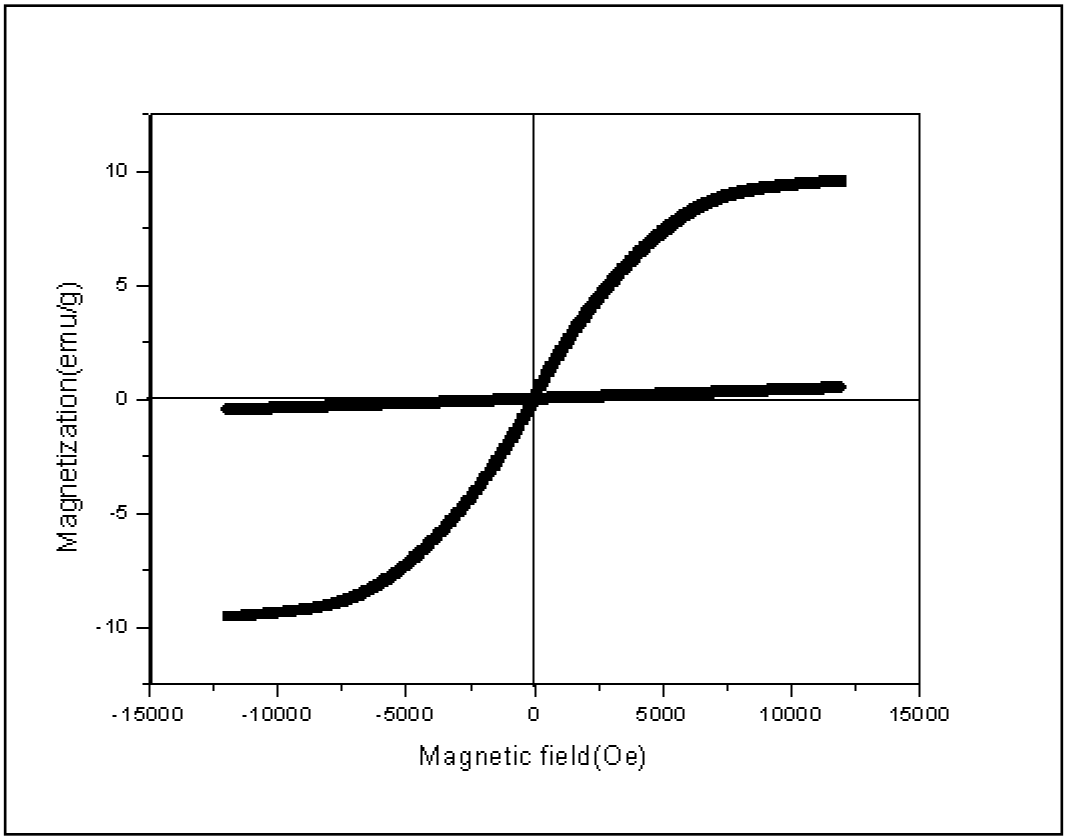

Figure 4. Hysteresis loop of Ilmenite sample

The room temperature hysteresis curves of Ilmenite sintered with carbon and raw ilmenite indicate the good magnetic homogeneity of Ilmenite sample after addition of Titanium dioxide and carbon; carbon as a reducing agent in this sample. The magnetic properties of the samples are in shown in the Table-2. The data indicate that the sample treated with Titanium dioxide and carbon shows better magnetic characteristics in terms of the coecivity, magnetization and retentivity.

Thus the present study indicates that mineral Ilmenite in solid solution with Titanium Oxide and carbon shows the semiconducting behavior along with a magnetic nature which can be exploited for devices wherein both are needed. One such application is in the Varistor whichis a voltage limiting device used in electronic circuits. A varistor is an electronic component with a "diode like"non-linear current-voltage characteristic. The name is a portmanteau of variable resistor. Varistors are often used to protect circuits against excessive transient voltages by incorporatingthem into the circuit in such a way that, when triggered, they will shunt the current created by the high voltage away from the sensitive components. A varistor is also known as Voltage Dependent Resistor or VDR. A varistor's function is to conduct significantly increased current when voltage is excessive.

PART-B

PRODUCTION OF FERROTITANIUM BY DIRECT ELECTROCHEMICAL METHOD:

Attempts to produce titanium metal directly from Ilmenite have been reported. Electrochemical reduction of titanium oxide patented by Fray *et al* (1999) of Cambridge University, UK [Fray *et al*, 1999] has been receiving wide attention by researchers as the process offers immense potential for the cost effective production of the metal. The process is also applicable to mixture of oxides to produce alloys directly or to Ilmenite to prepare ferro-titanium. The process has been receiving wider attention by researchers' world over and many fundamental aspects of the process are being explored [Wang *et al*, 2010; Meifeng*et al*, 2005; Schwandt*et al*, 2009; Bertolini*et al*, 2010; Bhagat*et al*, 2010, Maa*et al*, 2006].

The process essentially involves removal of oxygen from the oxide by imparting cathodic treatment at high temperature (950°C) using calcium chloride as electrolyte and graphite as anode. At DMRL-Hyderabad, A.P., India, efforts are being made to develop this process. Attempts have been made with bench scale studies on a few grams scale,and the results are encouraging.

Based on these results [Rao *et al*, 2005, Nagesh*et al*, 2007] the work is being taken up for scale up. Currently experimental work is continuing on 3-5 kg batch scale.

Figure 6shows schematic of the experimental setup used for the study of electrochemical reduction of Ilmenite.

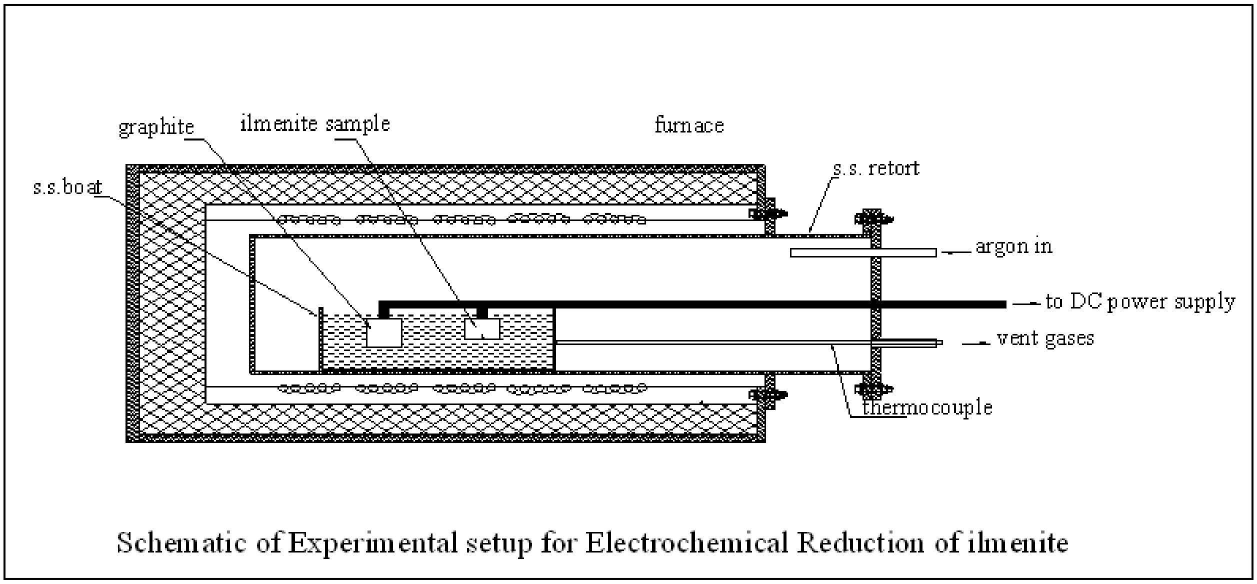

Figure 5. Experimental set-up used for the Electrochemical reduction

It mainly consists of a stainless steel horizontal reactor placed in a 3 kW electrical resistance furnace. A small steel boat is used to hold Ilmenite sample,and a graphite piece immersed in calcium chloride. After heating the electrolyte to high temperature, Ilmenite and graphite are connected to a DC power source and voltage ranging from 3-3.5 V is applied. After specified time of DC voltage application, the sample is cooled to room temperature under argon gas cover. During the experiment, the DC current is constantly monitored (refer Figure.7) as it is indicative of the oxygen removal process.

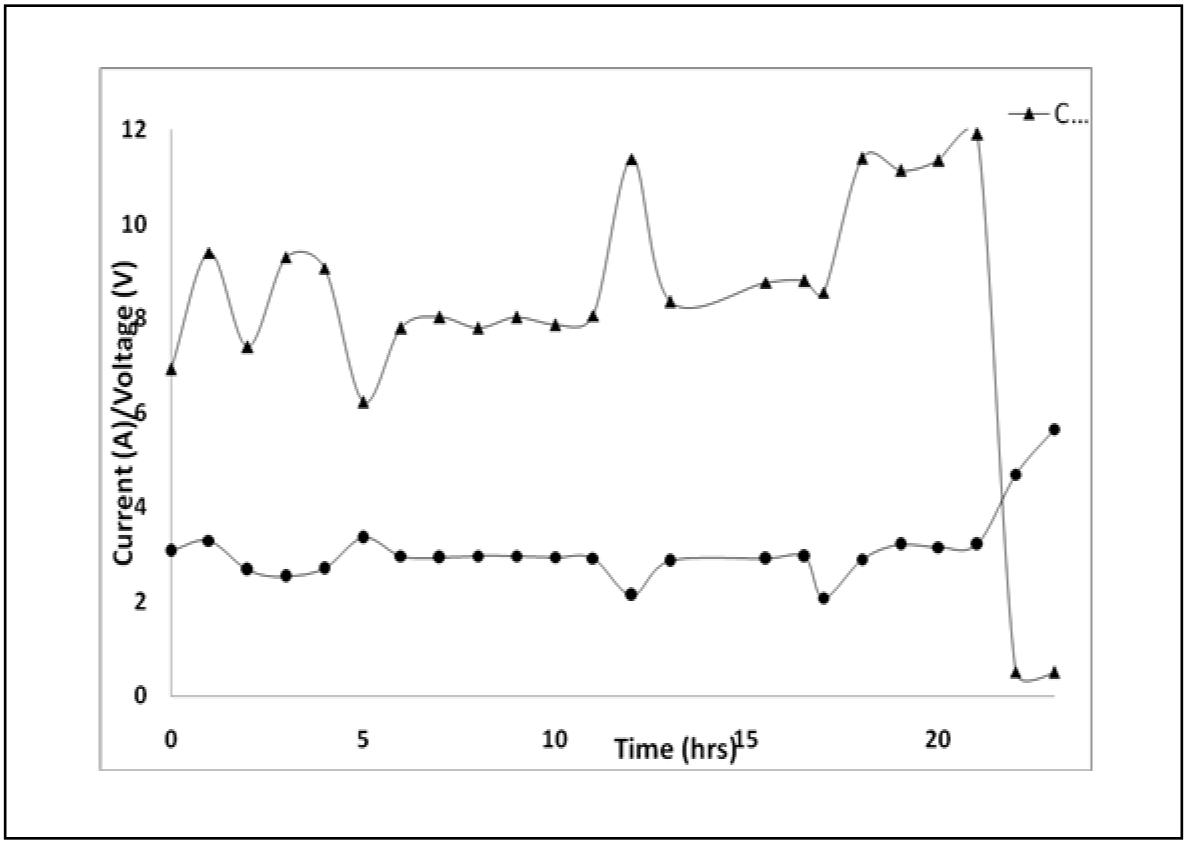

Figure 6. DC Current Variation during experimentation

The treated sample is then washed thoroughly with water, acetic acid and alcohol to remove salt adhered to the sample. Initial studies indicated good metallization in the sample as indicated by preliminary magnetic testing. Figure. 8, shows SEM macrostructure of the treated ilmenite sample showing metallized layers. The initial results are encouraging and experimental work is continuing for further understanding of the process and development.

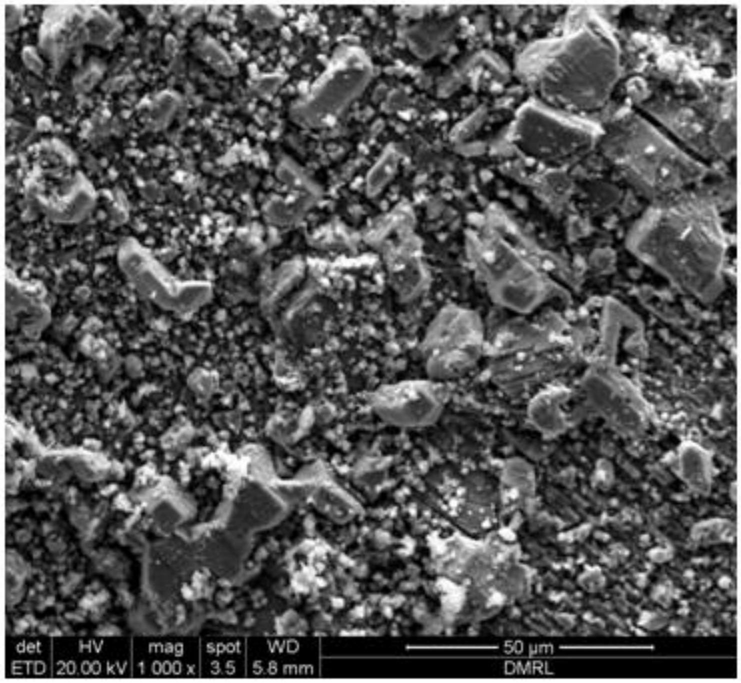

Figure 7. Macrostructure of metallized layers in the ilmenite sample

CONCLUSION

This paper brings out exploratory studies carried out to process ilmenite to value added products such as material for varistor application and ferro-titanium.There is a lot of scope for extending the studies to establish potential use of these processes for the synthesis of ilmenite to new value added products.

REFERENCES

Mineral commodities update, USBM, 2012.

H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. 69, 363 (1996).

H. Ohno, J. Magn. Magn. Mater. 200, 110 (1999).

Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, Science 291, 854 (2001). [MEDLINE].

Y. Ishikawa and S. Akimoto, J. Phys. Soc. Jpn. 12, 1083 (1957). [ISI].

Y. Ishikawa, J. Phys. Soc. Jpn. 17, 1835 (1962).

Y. Ishikawa, J. Phys. Soc. Jpn. 13, 37 (1958). [ISI].

W. H. Butler, A. Bandyopadhyay, and R. Srinivasan, J. Appl. Phys. 93, 7882 (2003). [ISI].

F. Zhou, S. Kotru, and R. K. Pandey, Mater. Lett. 57, 2104 (2003).

Fray, Farthing and Chen, Removal of oxygen from metal oxides and solid solutions by electrolysis in a fused salt, International patent, WO 99/64638, 1999.

Wang Bixia*et al*, Cathode preparation of electrochemical reduction process of TiO_2 to titanium, Rare Metals, Materials and Engineering, Vol 30, 9, Sep 2010, National natural science foundation of China, pp 1513-1518.

Meifeng Liu *et al*, An investigation into electrochemical reduction of TiO_2 pellet, Mineral processing and Extractive metallurgy, June 2005, vol114, pp87-94, Australian Inst. Of Mining and Metallurgy.

C.Schwandt, DTL Alexander and DJ Fray, The electro-deoxidation of porous titanium dioxide precursors in molten calcium chloride under cathodic potential control, ElectrochimicaActa, 54 (2009) 3819-3829.

Mark Bertolini*et al*, The FFC Cambridge process for production of low cost titanium and titanium powders, Key Engineering Materials, vol 436 (2010) pp 75-83.

R.Bhagat*et al*, In situ synchrotron diffraction of the electrochemical reduction pathway of TiO2, ActaMaterialia, 58 (2010) 5057-5062.

MengMa*et al*, Extraction of titanium from different titania precursors by the FFC Cambridge process, J. Of alloys and compounds, 420 (2006), 37-45.

A.V.Rammohan Rao, RVL Narasimha Rao, Ch.RVSNagesh, V.V.Bhanu Prasad and C.S.Ramachandran, Titanium sponge production by a novel electrochemical reduction of TiO_2, DMRL technical report, DMR TR 378 July 2005.

NageshCh.RVS and Ramachandran C.S., Electrochemical process of titanium extraction, Trans. Of Nonferrous metals Soc. Of China, vol 17, 2, April 2007, pp 429-433.