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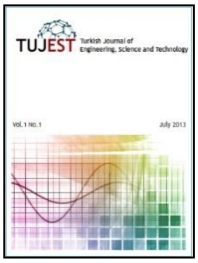

An investigation on Titania formation with Microwave Heat Treatment from Red sediment placer Ilmenite

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Abstract

The badlands topography of Nolia Nuagam Village, Ganjam District, Odisha, possesses red sediments. The typical red sediment fluvial placer deposit contain on average 83.2% total heavy minerals (THM), out of which 78.2% are ilmenite. The other heavy minerals contain sillimanite 4.9%, zircon 0.8%, rutile 0.6%, garnet 0.7%, monazite and other minerals are present in small quantities. The quartz containing 12.1% by weight is the major gangue mineral. The ilmenite concentrate recovered using wet high-intensity magnetic separator followed by high tension separator from the THM concentrate which can be used in titanium pigment and iron-steel industries.

There are many approaches to recover titania from ilmenite mineral. Reduction of ilmenite and recovery of titania slag from conventional furnace or plasma process is one of the approaches. Microwave energy has potential for the efficient heating of minerals. On applying the electromagnetic field in microwave furnace, the mineral sample heat at different rates. Minerals or materials, which couple to microwave energy are called dielectrics and many valuable minerals are found to be dielectric. The placer ilmenite mineral is one which also shows good dielectric heating characteristics. In this present investigation, the effect of microwave reduction of oxidized ilmenite is attempted by using the microwave sintering furnace. The graphitic carbon as a heating agent is used for reduction of ilmenite. The results of preliminary investigations reveal that there is a titania phase formation by using microwave sintering furnace from oxidized ilmenite. These observations are confirmed from XRD studies and SEM -image mapping.

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1. Introduction

Researchers have been attempting on recovery of ilmenite from red sediments of badlands topography for applications in iron-steel industries and for production of titanium dioxide (TiO2). India has the largest mineral sand resources in the world with large reserves of strategic and economically important heavy minerals such as ilmenite, sillimanite, zircon, rutile, garnet and monazite. Red sediments are also among the least exploited resources and have a high potential to meet the world's immediate need for ilmenite (Laxmi, 2011 and Krishna et al., 2012). Ilmenite is highly magnetic, which

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identifies that magnets can be used to separate it from other minerals in mineral sands. Mineral ilmenite is major resource for titanium product, whose major application is for production of Titanium dioxide (TiO2) for pigment application in paints, plastics, papers, inks, etc. Titanium dioxide (TiO2) is commonly found in nature in the form of "ilmenite" ores containing from 30 to 65% TiO2 in association with varying amounts of oxide impurities of the elements iron, manganese, chromium, magnesium, calcium, silicon, aluminium, phosphorus and others. Ilmenite ores are commercially upgraded into titania slag containing typically 70-90 wt. % TiO2 by electro smelting processes conducted at very high temperatures (molten state) in electric arc furnaces (Samal S et al., 2010).

The production of TiO2 pigment from ilmenite in the various industries is presently based on acid leaching process, which is now being banned due to environmental regulations as provided by Govt of India. Further acid leaching process leads to loss of iron metal values as sulphate or chloride which are treated as effluent. Due to this reason, an investigation is performed with microwave energy methods of ilmenite. As country like India, due to the high power cost, the experiments has been carried out for the production of titania rich slag which can reduce power consumption significantly so that the microwave energy process can be commercialized. As well known, microwave energy signal is an electromagnetic signal with frequencies in the range of 0.3–300 GHz and free space wavelengths of 1 m to 1 mm. Since microwaves obey the laws of optics, they can be transmitted, absorbed, refracted and reflected. In microwave heating of minerals, the materials which couple to microwave radiation are termed as dielectrics and contain dipoles. These dipoles align themselves in an applied electric field and will flip around in an alternating electric field. As a consequence, the material will be heated as the stored internal energy is lost to friction. This energy mode conversion has the advantage of being selective to individual mineral phases within a mass (Srikant Satya Sai et al., 2011; Bhima Rao, 2004; Kelly, 1998 and Pickles, 2009).

2. MATERIALS AND METHODS

2.1 Raw Material

The red sediment samples were collected from red sediments of badlands topography of Nolia naugam, Chatrapur, Gangam dist., Odisha. Initially, the representative red sediment sample was scrubbed and de-slimed by using hydrocyclone. The slimes were rejected and the typical deslimed red sediment deposit, on average, consists of 83.2% total heavy minerals (THM), out of which 78.2% are ilmenite. The other heavy minerals contain quartz 12.1%, sillimanite 4.9%, zircon 0.8%, rutile 0.6%, garnet 0.7%, monazite and other minerals are present in small quantities. The ilmenite concentrate recovered using wet high-intensity magnetic separator followed by high tension separator from the THM concentrate which can be used in titanium pigment and iron-steel industries. The ilmenite sample is 98% purity and on an average contains 47.3% TiO2. Graphite 99% purity sample was used as an additive for reduction of ilmenite mineral.

2.2 Microwave reduction of Ilmenite

The raw ilmenite sample obtained from deslimed red sediment sand sample was first heated in a muffle furnace at 1000°C in an air atmosphere for 3 hrs in order to oxidize all the ferrous iron into the ferric state. After oxidation, the sample was mixed with a fine graphitic carbon powder of 400 meshes with stoichiometric amount (i.e. 10 % of graphite) which is needed for reduction process. This graphitic carbon act as a reducing agents and it helps in heating the sample as it lost the dipole formation. An additional amount of 5% graphitic carbon powder was also further added in the oxidized ilmenite sample in order to heat the sample rapidly (Srikant Satya Sai et al., 2011; Bhima Rao, 2004; Kelly, 1998 and Pickles, 2009). The susceptor SiC placed near to sample further facilitate the microwave absorption and heating the sample in microwave furnace. A small amount of SiC powder was also mixed in the oxidized ilmenite sample in order to heat rapidly (Srikant Satya Sai et al., 2011). The oxidized ilmenite sample was heated in the microwave sintering furnace for forty minutes. The microwave sintering furnace used in the present investigations is mwsinter-gntech model, operating frequency: 2.45 GHz, WR 340 Waveguide, infra red pyrometer ranging from 350 – 1800º C, microwave output 6 kW, magnetron power variable from 0.3-6.0 kW, steps 5W. Figure 1 shows the schematic sketch for the heating ilmenite sample placed in microwave furnace.

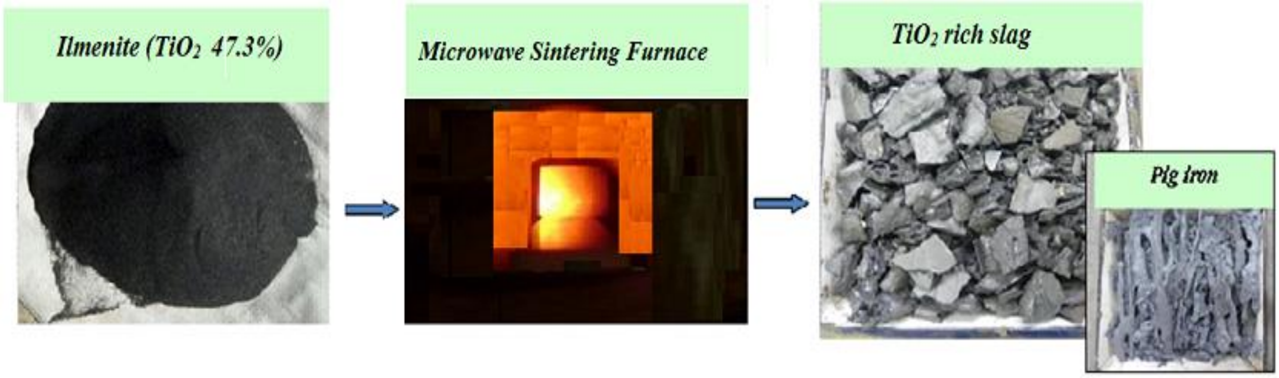

Figure 1. Schematic sketch for heating of ilmenite sample in a microwave furnace

2.3 Analytical methods

PANalytical X-Pert automated X-ray powder diffractometer with Cu-Kα radiation, (λ=1.54056 Ǻ) from 5° to 75° scanning angle at a scanning rate of 0.05° /sec was used for phase analysis of minerals and metals. Details of the X- ray unit used in the present investigations are given in Table 1. Morphological features of heated ilmenite sample were studied using the FESEM (model : Supra 55; Zeiss, Germany) The FESEM has a resolution of 1 nm at 30 KV which is equipped with 20 mm2 Oxford's Energy dispersive X-ray spectroscopy (EDS) detector for imaging of conducting as well as non-conducting samples without gold coating. SEM/EDAX studies were done by using Hitachi VP-SEM S-3400N. It has high SE resolution of 10 nm at 3 KV. The magnification of the instrument is 5X- 300,00X; alternating voltage is 0.3-30 KV. The grains were mounted on a SEM brass stub. The mounted grains were coated with gold in a vacuum evaporator while the sample was being slowly rotated.

Table 1. PHILIPS PANalytical X-Pert XRD parameter

Diffractometer Type	PW3710 Philips PANalytical X-Pert
Radiation Type, source	X-Ray, Cu-Kα, λ=1.54056 Ǻ
Power	40 KV, 20 mA
Detector	Scintillation counter
Instrumental profile breadth	0.05(1) 0 2θ, 5-75
Specimen motion	Stationary
Intensity measurement	Peak height

3. RESULTS AND DISCUSSION

3.1 Characterization of ilmenite

The complete chemical analysis of the recovered ilmenite sample from red sediments badlands topography is shown in Table 2 which indicates that the ilmenite sample contain around 47.3 % TiO2.

Table 2. Complete chemical analysis of the ilmenite concentrate

Compound Name	Conc.(%)	Compound Name	Conc.(%)
TiO_2	47.332	MnO	0.500
Fe_2O_3	38.473	Na_2O	0.053
SiO_2	9.803	MgO	0.321
Al_2O_3	1.038	Cl	0.060
ZrO_2	0.527	SO_3	0.026
ThO_2	0.166	K_2O	0.092
Y_2O_3	0.022	CaO	0.056
Nb_2O_5	0.080	Cr_2O_3	0.060
La_2O_3	0.133	Nd_2O_3	0.251
CeO_2	0.315	P_2O_5	0.692

3.2 Studies on formation of titania slag from ilmenite using microwave heat treatment

Effect of microwave heating on oxidized ilmenite with graphitic carbon on formation of metallic iron phase and titania phase in form of slag are distinctly observed. The microwave heat treatment using microwave furnace heated in presence of SiC with 5% extra graphitic carbon apart from the 10 % stochiometric carbon and a small amount of SiC powder results in the separation of titania and iron in the form of rich slag and metallic iron respectively (Kelly, 1998 and Srikant Satya Sai et al., 2011 and Haque, 1999). Addition of more carbon than the above combinations would affect the slag quality. Iron was found to be a major impurity in the slag (10–20%). The pig iron obtained contains more than 85-95% Fe content with very low level of sulphur and phosphorus content makes it ideal for automobile industry.

It is also observed after metallisation is over, metallised ilmenite undergoes magnetic separation in which ash and unreacted carbon gets separated. Final product of metallised ilmenite contains a maximum of 5% of additional graphitic carbon which does not affect quality of slag, rather it will benefit for the second stage of reduction. The metallised ilmenite mixed consists of ilmenite mixed with unreacted 5 % of additional graphitic carbon which subjects it to a very high temperature treatment. Hence additional 5% unreacted graphitic carbon plays the triple role of reductant, source of heat as well as the addition of carbon to slag (Samal et al., 2010). About 65 – 80% TiO2 slag could be recovered from the above experiment.

The investigation shows that the heated sample reached the temperature of 1200°C -1350°C (Kelly, 1998 and Haque, 1999) during microwave heat treatment of 40 min with an input of microwave power of 1.5 kW, which is perfect for the reduced ilmenite sample to form titanium product. This microwave reduction in presence of additional unreacted graphitic carbon completely forms the carbothermal reduction process which not only help in separating the TiO2 from the oxides, but also reduced the oxides to their metallic form. It is also observed that the TiO2 content had increased and metallic iron was also found in the reduced sample. The general schematic for the performed microwave heat treatment for ilmenite is shown in Figure 2.

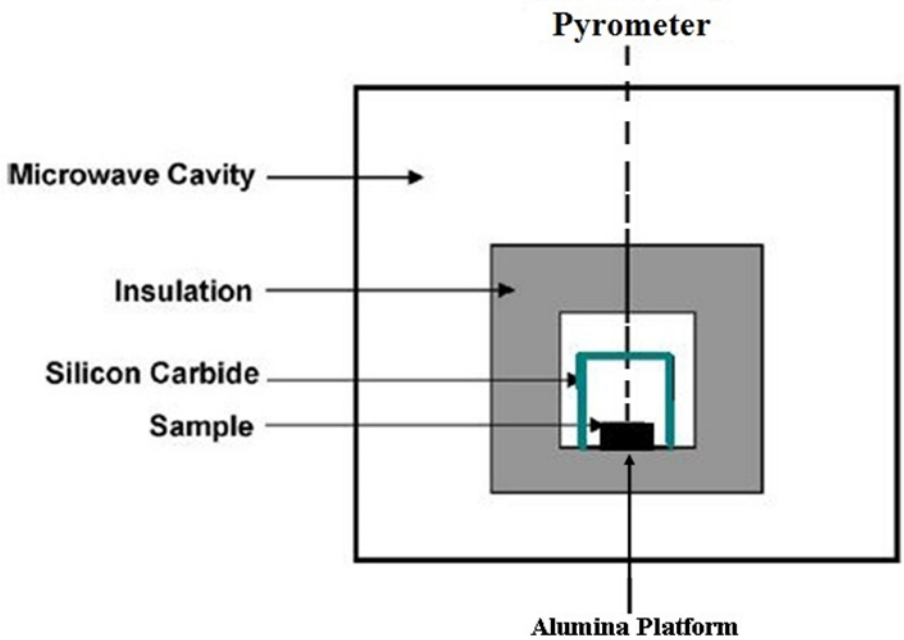

Figure 2. General schematic for microwave heat treatment process.

3.3 Structural and morphological characterization of titania slag

The XRD patterns after microwave reduction of ilmenite in microwave sintering furnace is shown in Figure 3 which clearly shows titania slag formation (82.6 %) and a small amount of metallic iron (2.1 %). The titania slag forms within forty minutes after microwave reduction of ilmenite in microwave sintering furnace.The chemical analysis of titania slag obtained after microwave treatment of ilmenite sample is shown in Table 3.

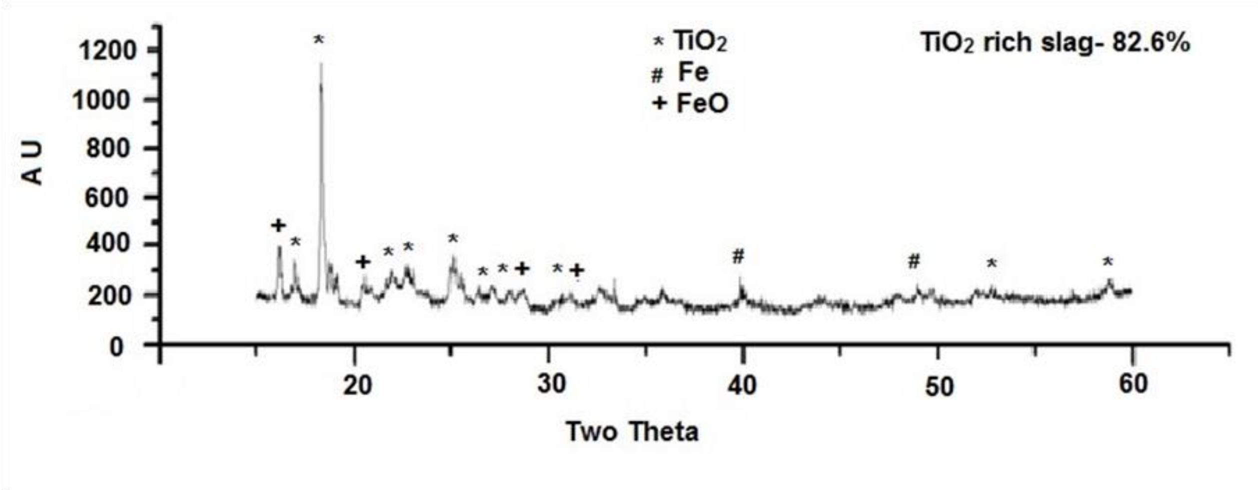

Figure 3. XRD results after microwave treatment of ilmenite.

Table 3. Chemical analysis of Titania slag obtained after microwave heat treatment

FeO %	Al_2O_3 %	SiO_2 %	Fe(M) %	MnO %	**TiO_2 %**
12.2	1.3	1.02	2.1	0.80	**82.6**

Formula	**Percent %**
TiO_2	**82.60**
FeO +	**17.40**

The FESEM-EDAX analysis for titania slag formation from red sediment placer ilmenite using microwave heat treated is shown in Figure 4. It is observed that as the metal melts at high temperatures, SiC powder and carbon atoms from the vapour (liquid) helps to form titania products in form of rich slag.

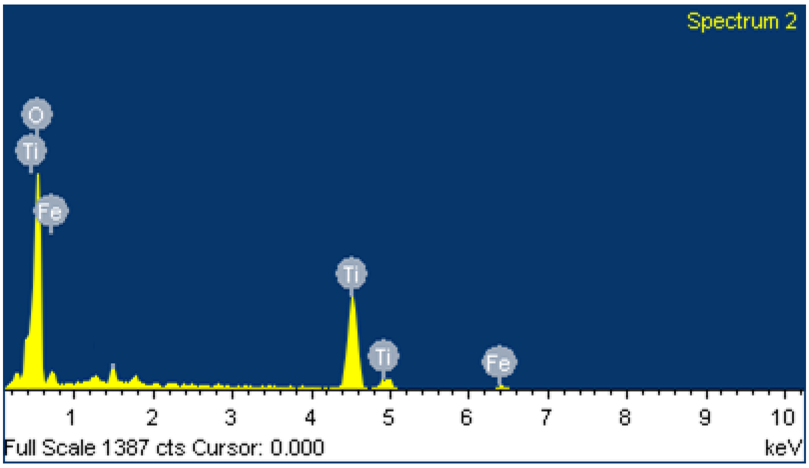

Figure 4. FESEM-EDAX data confirming Titania rich slag formation. **[a].**

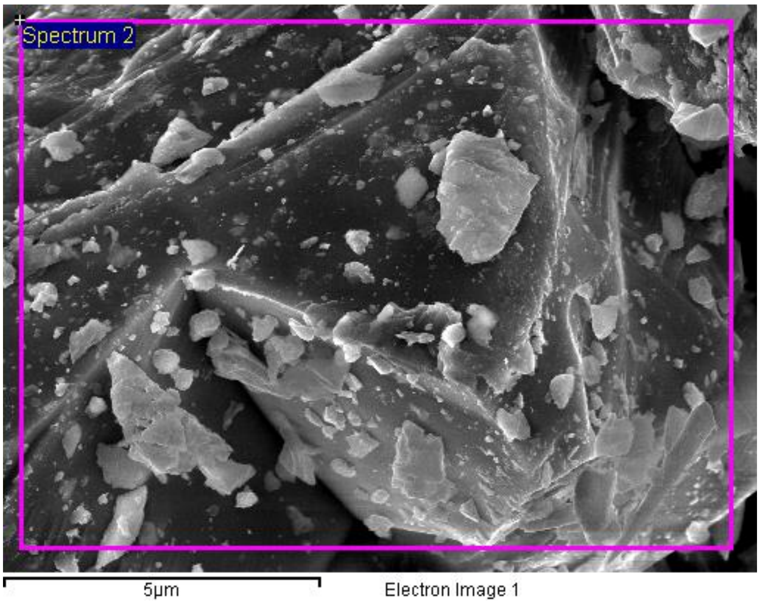

Figure 4. FESEM-EDAX data confirming Titania rich slag formation. **[b].**

It is also observed that after microwave reduction of oxidized ilmenite with 10 % stoichiometric graphitic carbon with additional 5% graphitic carbon in presence of silicon carbide (SiC) susceptor and a small amount of SiC powder, around 82.6 % of titanium dioxide is formed in terms of titania rich slag by using microwave sintering furnace. The corresponding image mapping of Ti, Fe, O and C are shown in Figure 5 which also confirms that the sample contain more of titania than iron oxide with little amount of carbon.

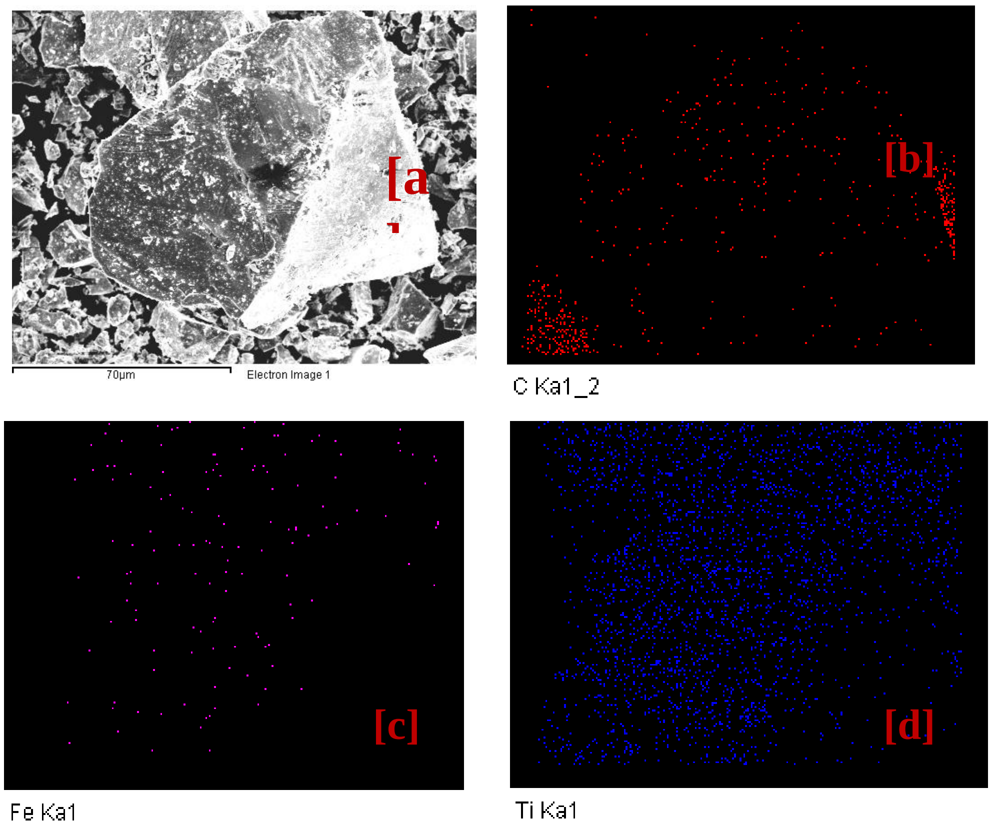

Figure 5. [a] FESEM of titania slag sample; image mappings of [b] carbon C [c] titanium Ti [d] iron (Fe).

4. Conclusion

The following conclusions are drawn from the investigation on titania formation with microwave heat treatment from red sediment placer ilmenite

- The stochiometric ratio of graphitic carbon to the oxidized ilmenite is estimated that graphitic carbon is 10% to the ilmenite concentrate to use in microwave sintering furnace for obtaining more titania slag than metallic iron.
- Addition of extra 5 % of graphitic carbon avoids the presence of any oxides which makes it difficult for the TiO2 to be extracted. So, in order to increase the titanium dioxide (TiO2) product, the reductant of extra 5 % of graphitic carbon and a small amount of SiC powder are very much useful.
- The temperature due to presence of extra 5 % of graphitic carbon and a small amount of SiC powder helps the ilmenite sample in a microwave furnace to attain 1200oC -1350o C within 40 min with 1.5 kW microwave input power to form titania product.
- The XRD data clearly shows that there is a formation of titania slag and less metallic iron after microwave reduction of ilmenite. The amount of titania slag formation contains 82.6 %.
- The FESEM-EDAX and image mapping data are also confirm the formation of titania slag and a small metallic iron phases from reduced ilmenite by using microwave furnace.

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