

Mineral to Metal: Processing of Titaniferous Ore to Synthetic Rutile (TiO_2) and Ti metal



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Objective

To produce ultra pure high grade synthetic rutile (TiO_2) from ilmenite ore and Ti metal from anatase or rutile



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Outline

1. Introduction
2. Why titaniferous minerals?
3. Processing Methods for synthetic rutile (TiO_2)
 - (i) Alkali Roasting
 - (ii) Reduction followed by leaching
5. Results and discussion
6. Commercialisation
7. Conclusion
8. Bradford Metallurgy on Ti metal powder production
9. Future Plans



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Introduction

- Titanium always exist as bonded to other elements in nature.
- It is the ninth-most abundant element in the Earth.
- It is widely distributed and occurs primarily in the minerals such as anatase, brookite, ilmenite, perovskite, rutile and titanite (sphene).
- Among these minerals, only rutile and ilmenite have economic importance



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Ilmenite deposit in Chavara, Kerala, India



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Applications of TiO₂

- White powder pigment - brightness and very high refractive index - Sunscreens use TiO₂ - high refractive index - protect the skin from UV light.
- TiO₂ photocatalysts - electrolytic splitting of water into hydrogen and oxygen, - produce electricity in nanoparticle form -light-emitting diodes, etc.
- Paints- paper – catalysts, etc.

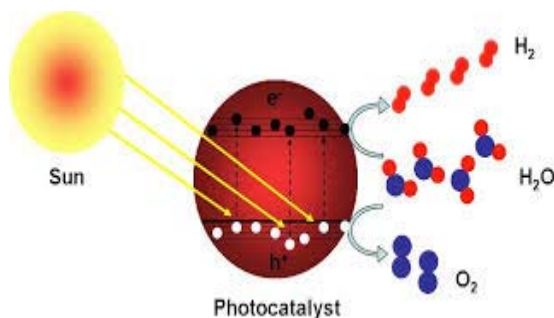
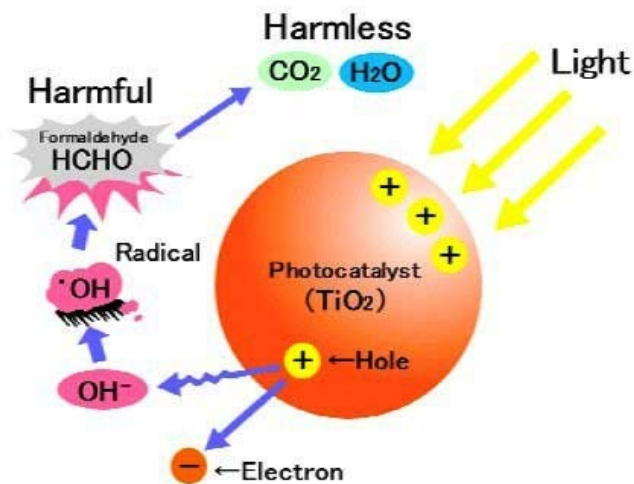
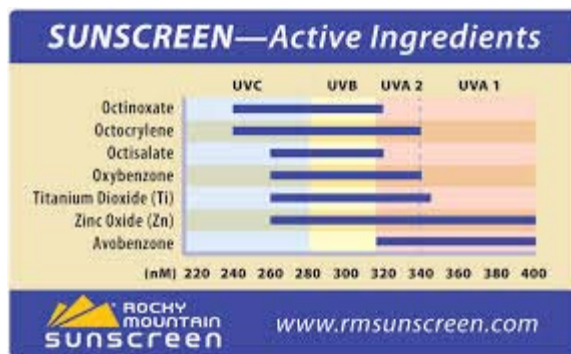


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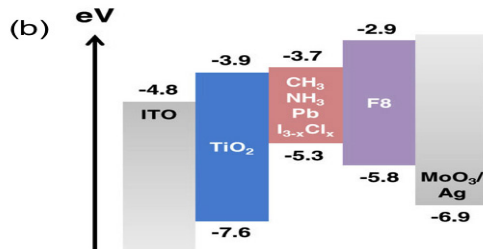
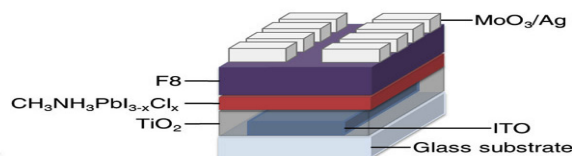
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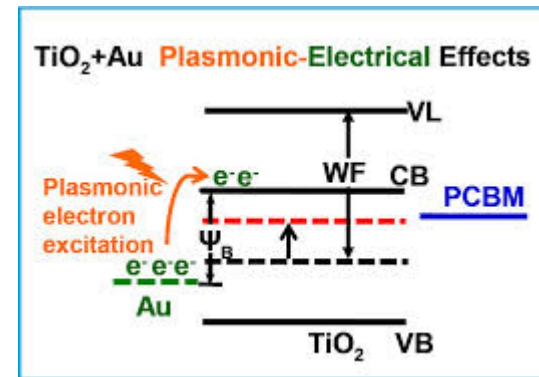
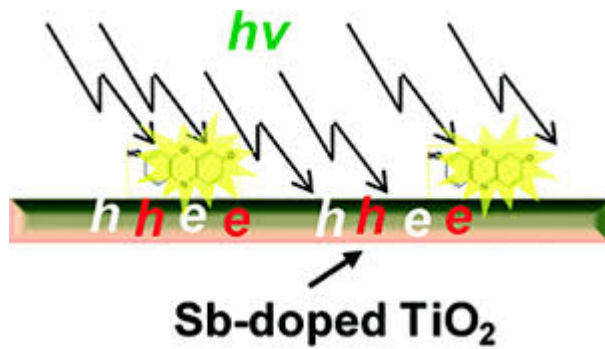
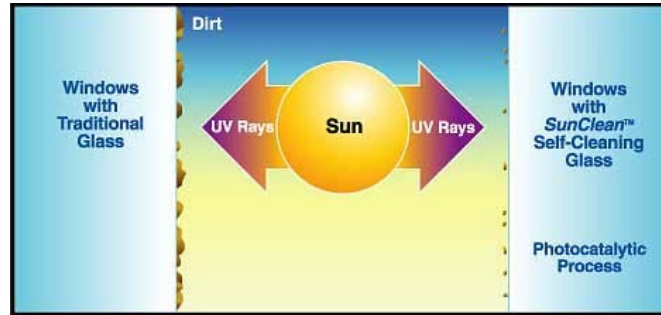
(a)



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Why Titanium Metal

- Titanium is corrosion resistant, very strong and has a high melting point. It has a relatively low density (about 60% that of iron).
- Titanium is used, for example: in the aerospace industry - for aircraft engines and air frames;
- Implants - replacement hip joints, for pipes, etc, in the nuclear, oil and chemical industries where corrosion is likely to occur.



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Aerospace Applications: high-temperature performance, creep resistance, strength, and metallurgical structure.

Jet Engines: wide chord titanium fan blades increase efficiency while reducing noise.

Airframes: innovative alloys replace steel and nickel alloys in landing gear

Industrial Applications: Titanium forms a surface oxide layer, which is an outstanding corrosion inhibitor.

Human Implants: Titanium is completely inert to human body fluids, making it ideal for medical replacement structures such as hip and knee implants.



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Extraction Methods



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CONVENTIONAL ROUTES

ORES : ilmenite, Rutile, Anatase, and Perovskites

Pyrometallurgical Benefication: reduction of iron oxides :
$$\text{Fe}_x\text{O}_y + y\text{C} = x\text{Fe} + y\text{CO}$$

ACID-LEACHING

Chloride Process

Sulphate process

TiO₂ pigment grade



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Alkali Roasting

Principle: Ilmenite when roasted with soda ash at high temperature, the iron values in the ore will form sodium ferrite which is soluble in water and the titanium values will form sodium titanate which is insoluble. Therefore preferential separation is possible



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Alkali roasting of ilmenite and anatase ores (Bomar ilmenite)

Temperature - 1073 – 1273 K

Time - 120 min.

Na_2CO_3 or NaHCO_3 in the charge was varied
(Stoichiometric amount required for TiO_2 , Fe_2O_3 , Al_2O_3
and SiO_2 in the ore)

Alumina

Leaching

Hot water leaching

Acid leaching

5% HCl solution

343 – 353 K temperature



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Analysis of Ilmenite and Anatase

Sample	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	P ₂ O ₅	Mn ₃ O ₄	MgO	CaO	Cr ₂ O ₃	LOI *
Anatase	57.8	14.61	7.64	1.65	7.65	0.71	0.36	2.13	0.01	6.19
Ilmenite	70.65	21.69	2.51	2.13	0.42	0.72	0.37	<0.10	<0.01	2.01

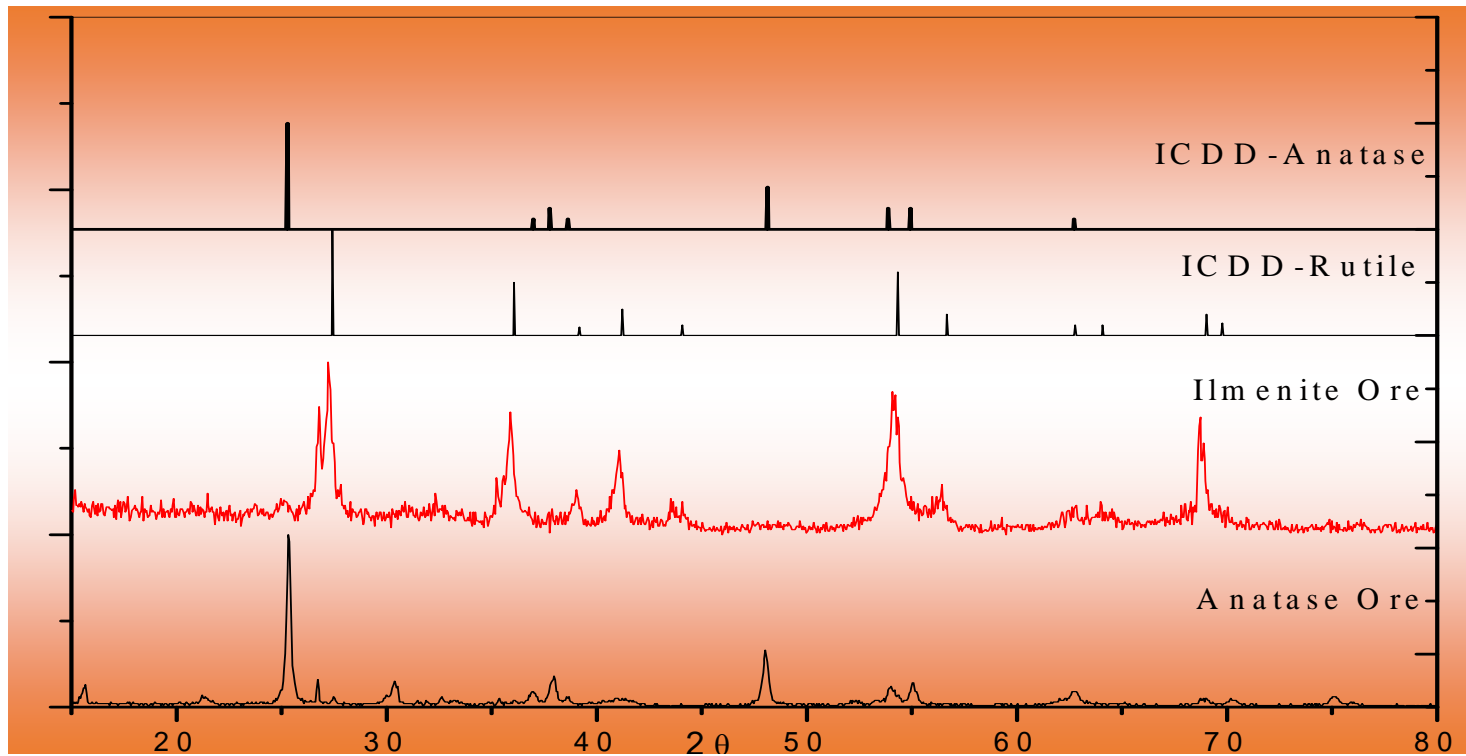


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Characterisation - XRD



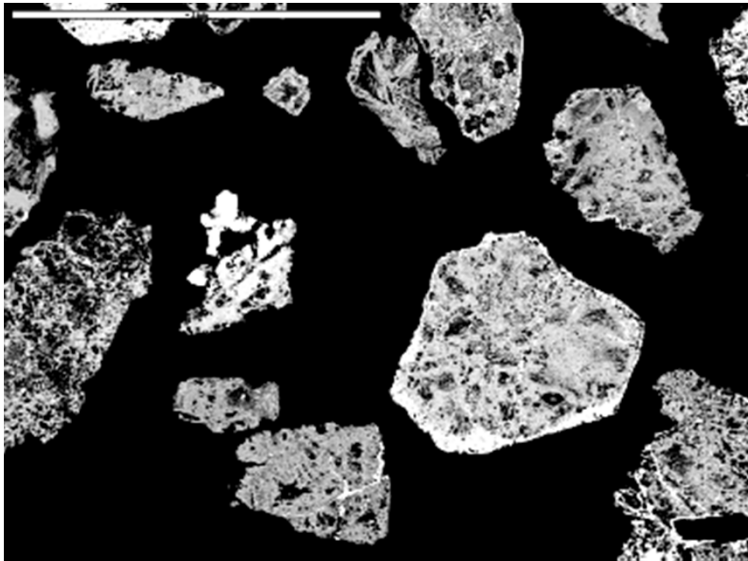
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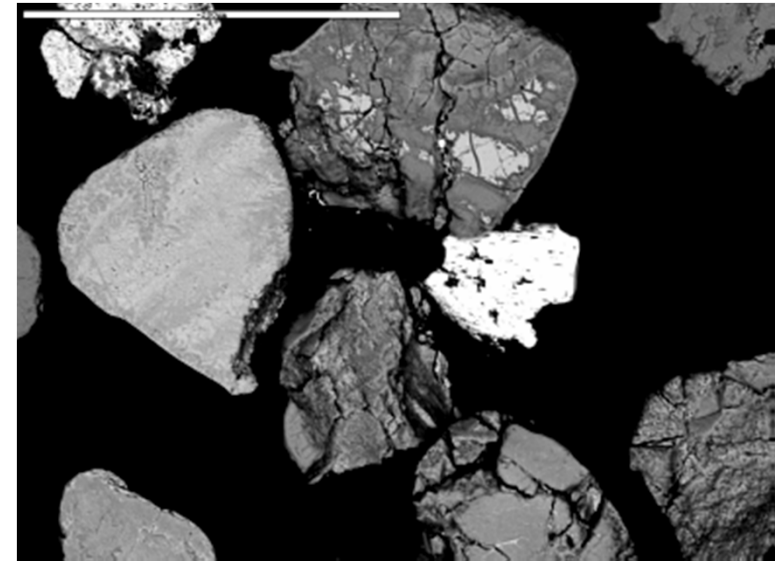
Anatase



The anatase grains (grey colour) are highly porous due to weathering and have light grey colour Fe-rich exsolved phases

MICROSTRUCTURE

Ilmenite



The dark grey colour phase is rutile, the light grey colour phases are pseudorutile/brookite (Ti-Fe-O) phases and bright colour grain is zircon mineral



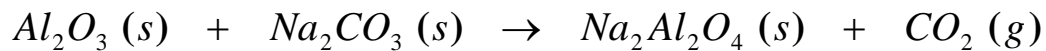
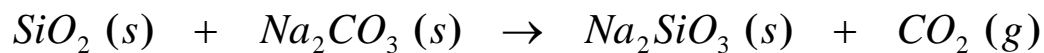
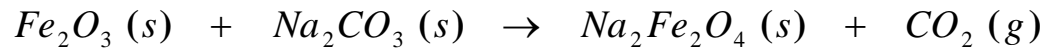
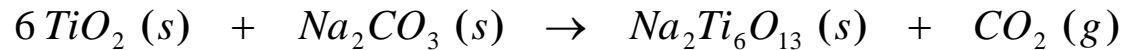
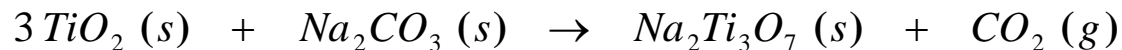
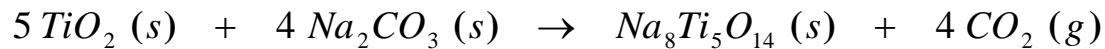
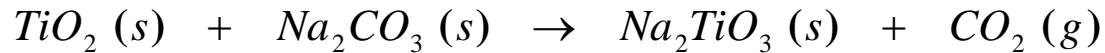
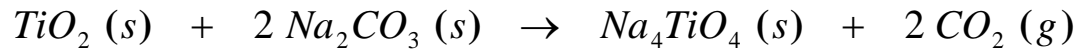
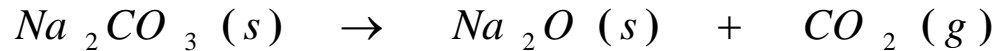
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Chemical reactions during Alkali Roasting



R1

R2

R3

R4

R5

R6

R7

R8

R9

R10



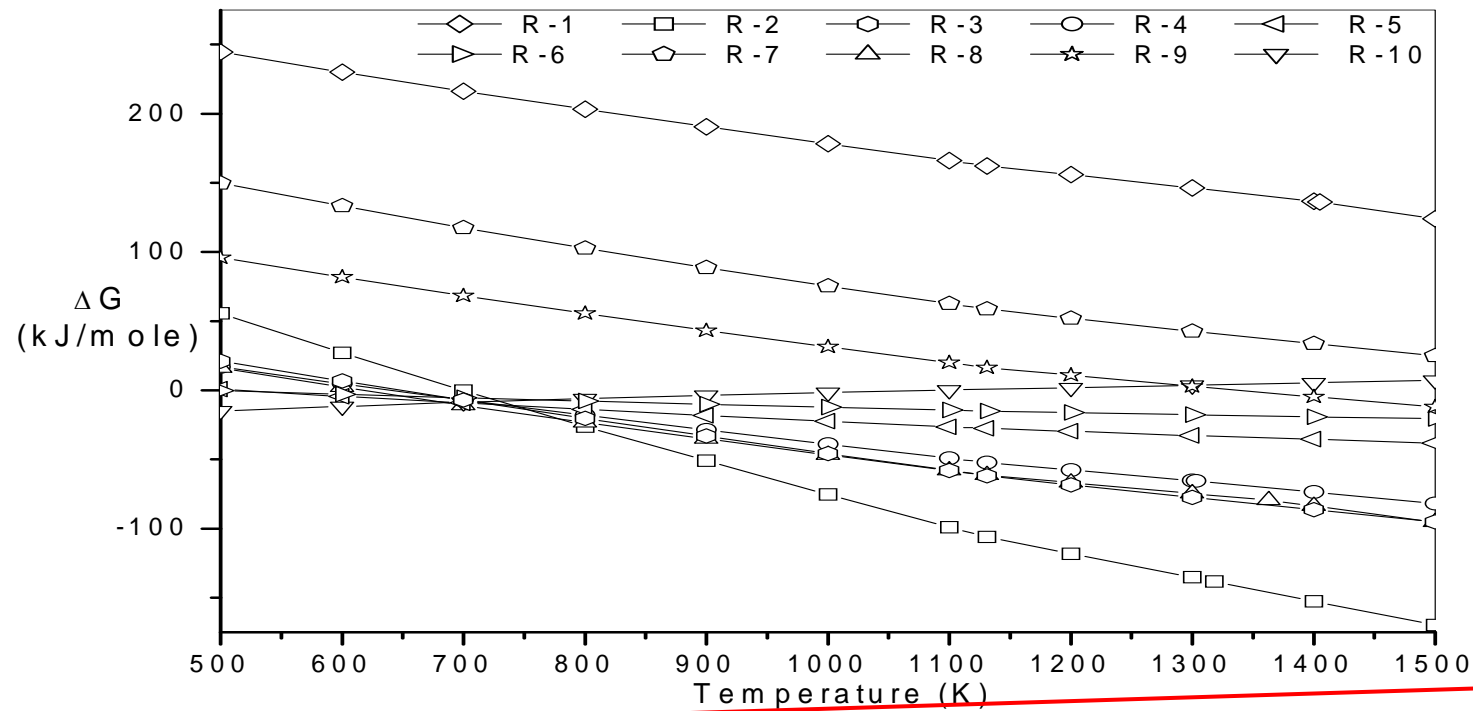
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Alkali Roasting: The plot of Gibbs free energy change versus temperature for the reactions of various oxide constituents in TiO₂ ores.



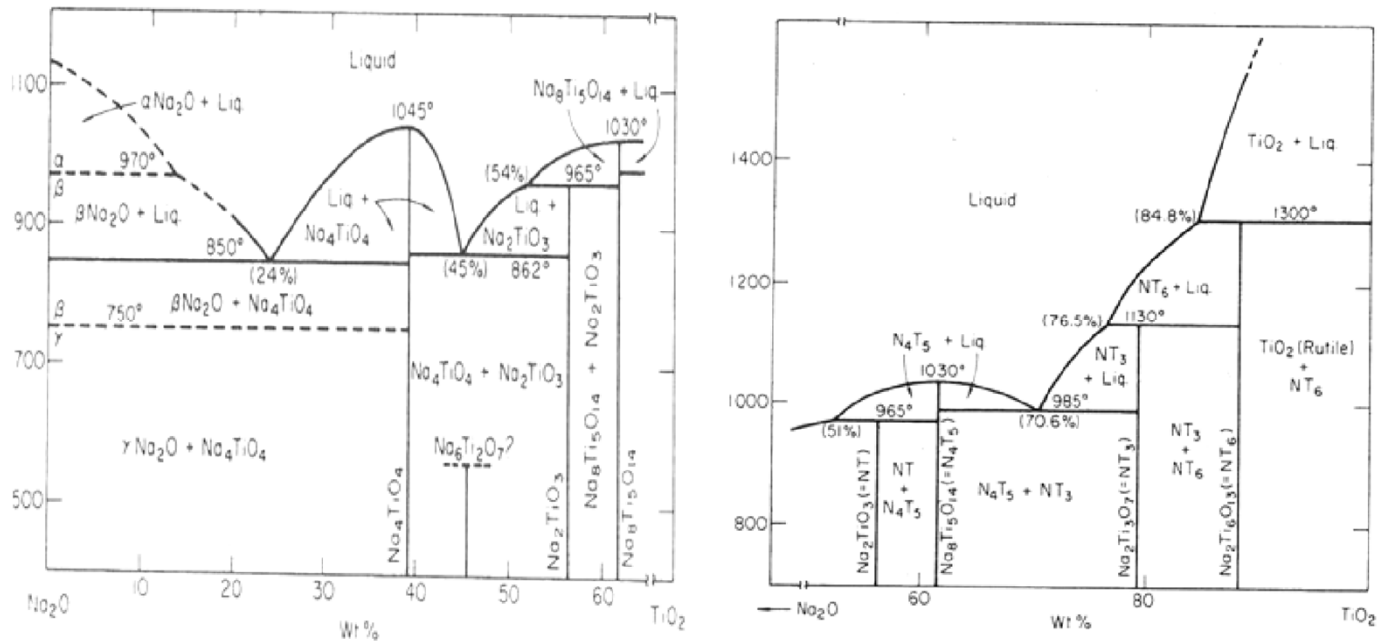
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Na₂O – TiO₂ phase diagram



Ref : Roth, R.S., Negas, T. and Cook, L.P., *Phase Diagrams for Ceramists*, vol. 5, Columbus, Am. Cer. Soc., 1983. Pp. 88.



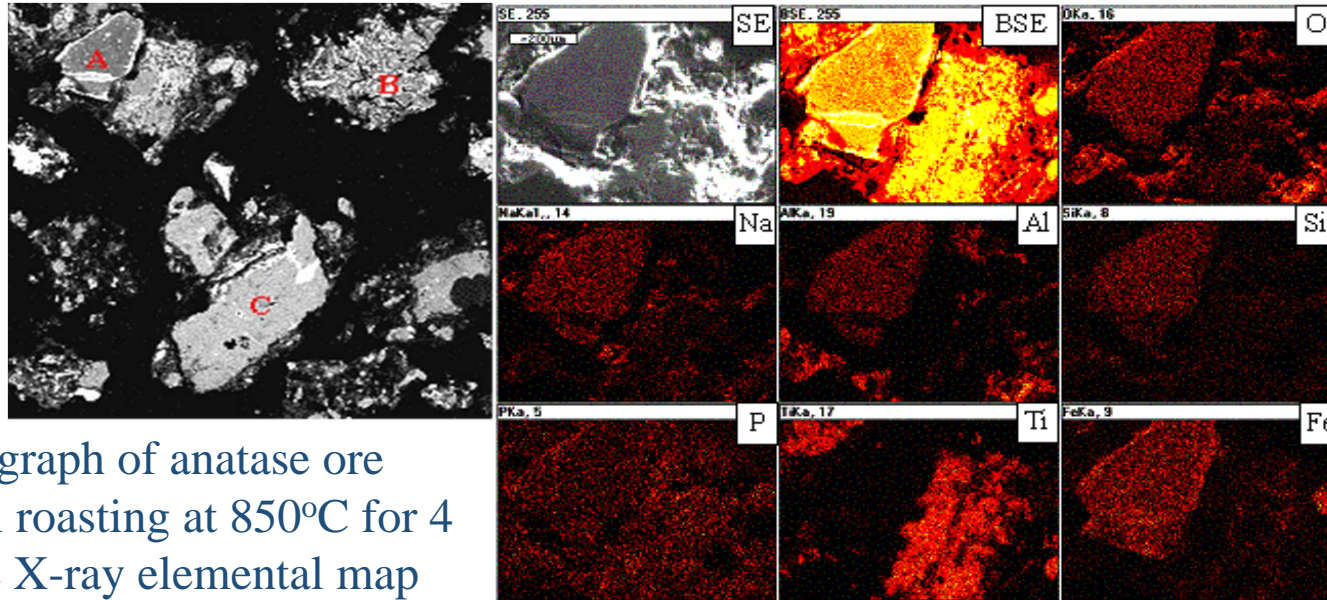
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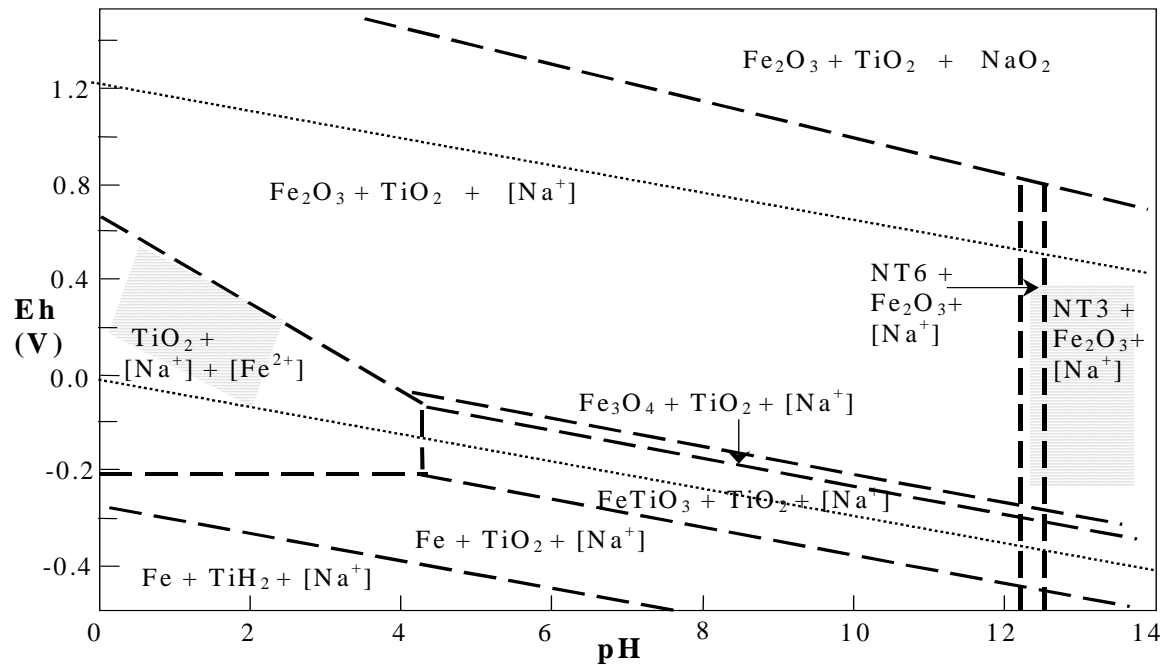


Microstructure of ilmenite ore after alkali roasting



The micrograph of anatase ore after alkali roasting at 850°C for 4 hours. The X-ray elemental map of grain A shows the formation of Na-Al-Fe-Si-O complex phase.

The Eh-pH diagram of Na – Ti – Fe – O system calculated by using FACT-Sage programme. The hatched areas show the water and acid leaching conditions.



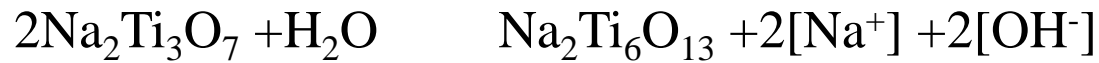
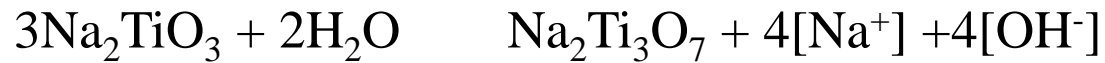
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Water leaching :



Acid leaching :

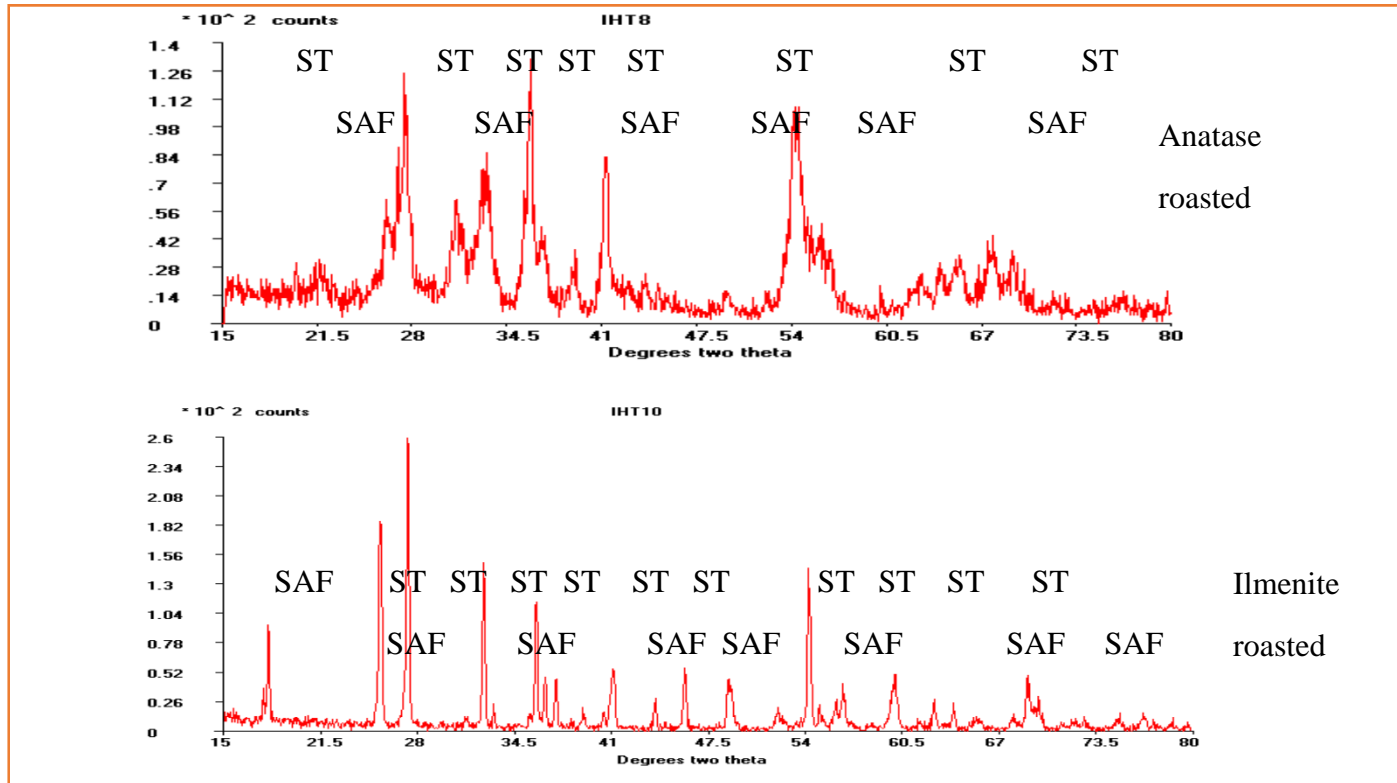


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ST – sodium titanate, SAF – Sodium aluminium ferrite

XRD of ilmenite and anatase roasted with soda-ash + alumina at 900°C for 4 hrs

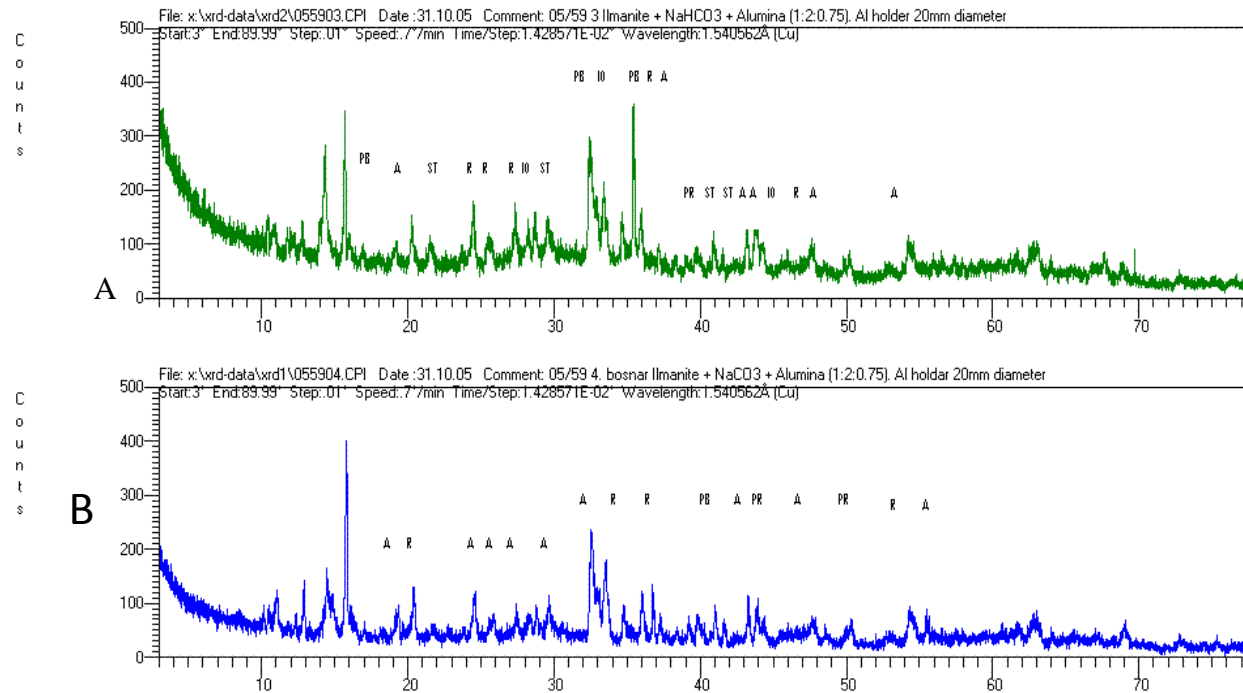


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A – Anatase, ST- sodium titanate, R – Rutile, PR-Pseudorutile, PB-Pseudobrookite

A XRD of processed ilmenite after aeration leaching. B XRD of synthetic rutile after acid wash. Phases such as anatase, pseudobrookite and rutile are present after acid wash.



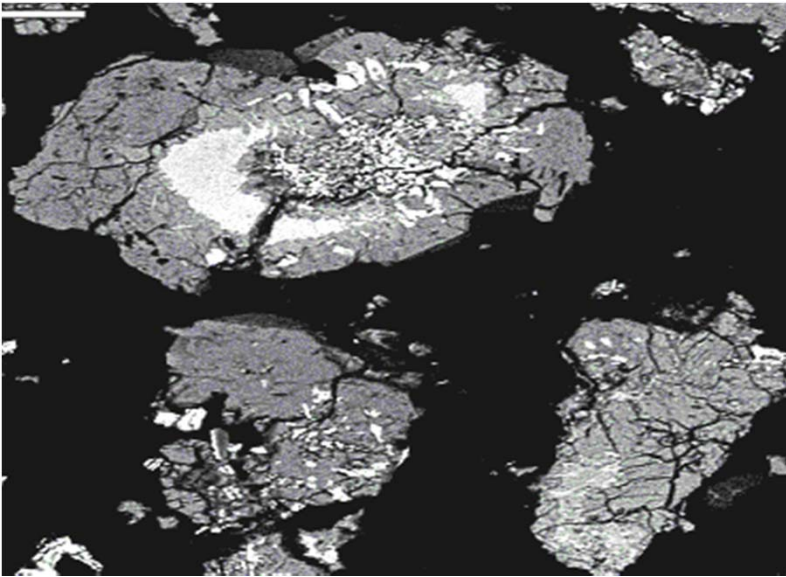
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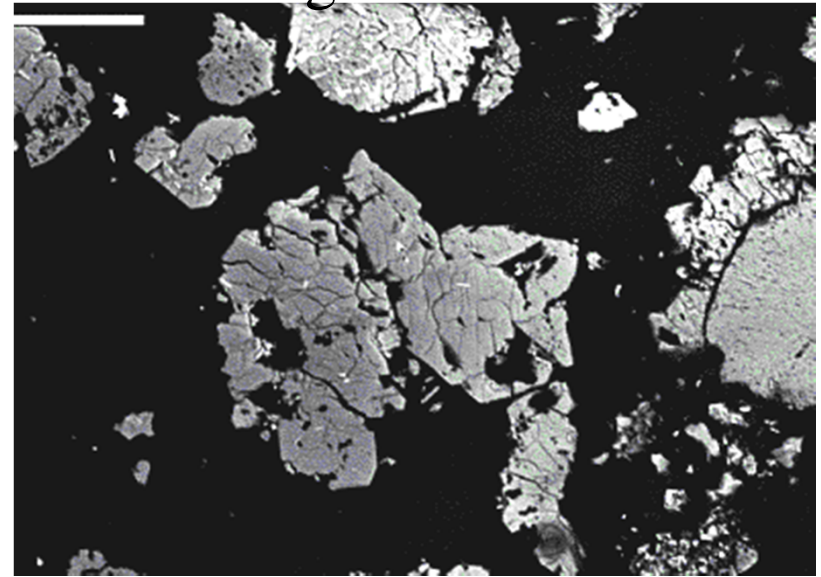
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Water and Acid leaching



(a) After water leaching



(b) After acid leaching

The microstructure of **ilmenite ore** after alkali roasting at 950°C for 4 hours followed by water and acid leaching. Dark grey phase on the surface of the grey colour sodium titanate grain in (a) is complex Na-Fe-Si-O salt phase which is not dissolved in the aqueous medium, whereas the bright phase in the core is unreacted pseudorutile phase. The grey colour grains in (b) are of rutile with small bright colour particles of unreacted ore particles.

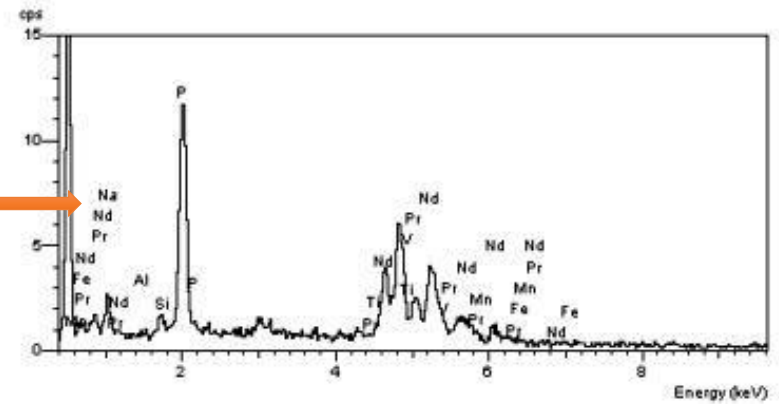
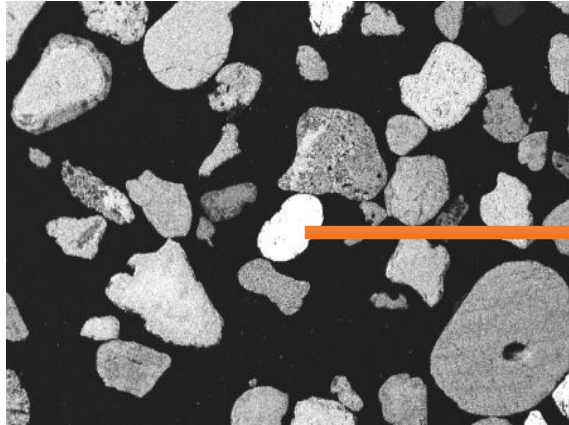


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Rare earth particle separated un-attacked by the chemical processing steps



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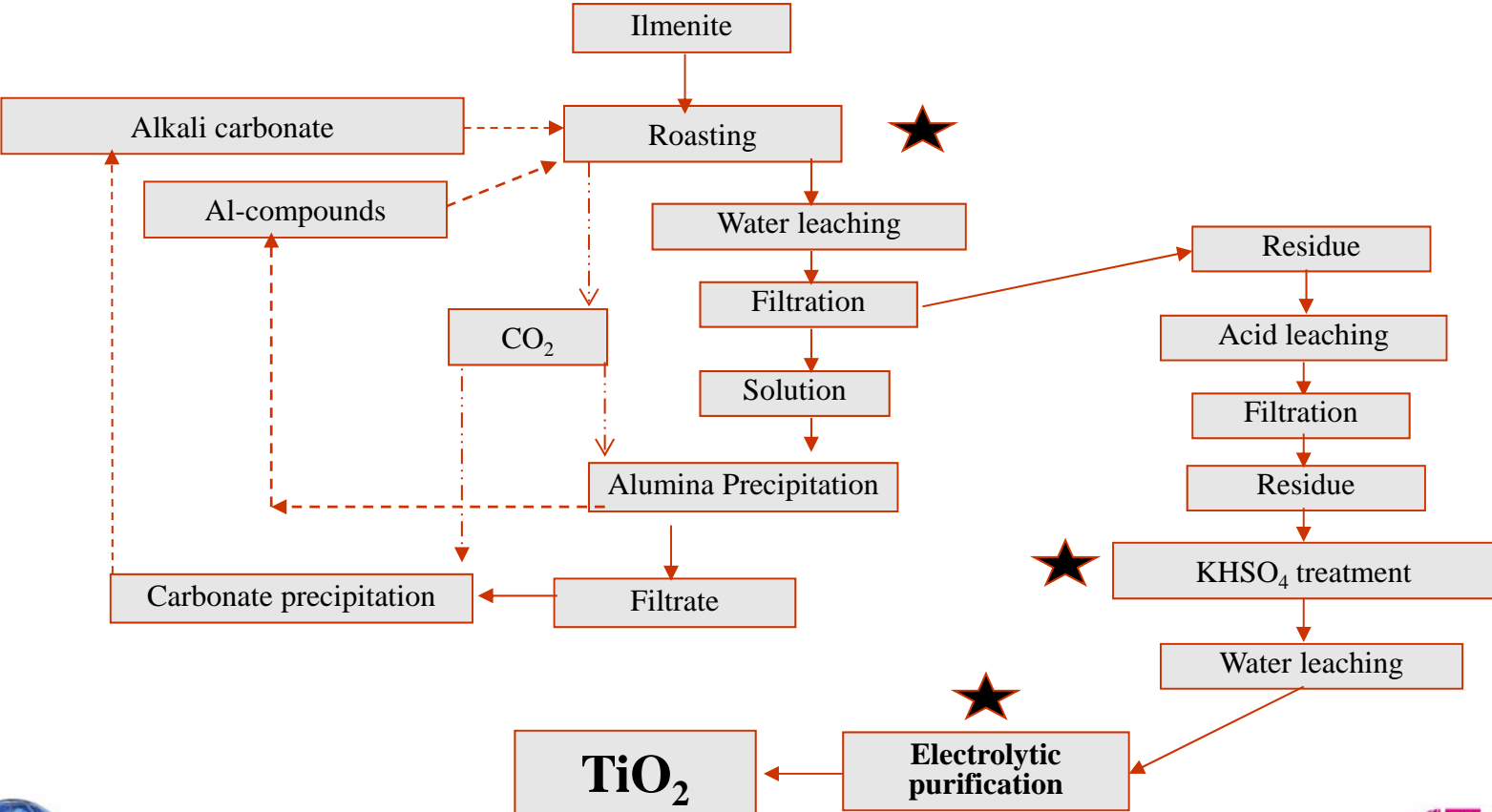
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PROCESS FLOW DIAGRAM



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Processing of Kerala Ilmenite (CSIR-NIIST, Trivandrum, Kerala, India) PhD work

Constituent	Content (%)
TiO ₂	60.60
Fe ₂ O ₃	26.10
FeO	9.60
MnO	0.50
Cr ₂ O ₃	0.40
V ₂ O ₅	0.12
MgO	0.15
P ₂ O ₅	0.50
ZrO ₂	0.15
SiO ₂	0.40
Rare Earths	0.80

Analysis of Kerala ilmenite



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Principle

Ilmenite – carbothermic reduction – metallic iron formed – rusted in the presence of NH_4Cl – iron hydroxide formed – iron hydroxide slurry is separated from TiO_2 by repeated washing. Analyse the samples for TiO_2 and total iron.

Reduction at high temperature

Rusting

Rutilation

Acid wash

Problem: Rusting step takes about 16 – 20 hrs for completion making the process uneconomical for the industries



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Constituent	Content (%)
TiO ₂	62.64
Total Iron	28.32
Metallic Iron	24.03
P	0.12
C	1.00
S	0.15
MgO	2.80
Cr ₂ O ₃	0.80
Al ₂ O ₃	1.50
MnO	0.45
SiO ₂	1.00
Others (V, Zr, etc.)	0.26

Composition of a reduced ilmenite



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Solid – liquid ratio 1:4
RPM – 800 per minute
Air: 4 – 5 lit/min

Experimental set up used for Rusting



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Time Vs % Iron Removal

Time (hr)	% Iron Removal			
	NH ₄ Cl	NH ₄ Cl + fructose	NH ₄ Cl + glucose	NH ₄ Cl + glyoxal
0	0	0	0	0
1	12.2	38.3	39.2	40.01
2	23	64.2	65.3	66.5
3	33	82.3	83.2	84.3
4	44.3	91.3	92.4	93.2
5	45.2	92.5	93.8	94.5

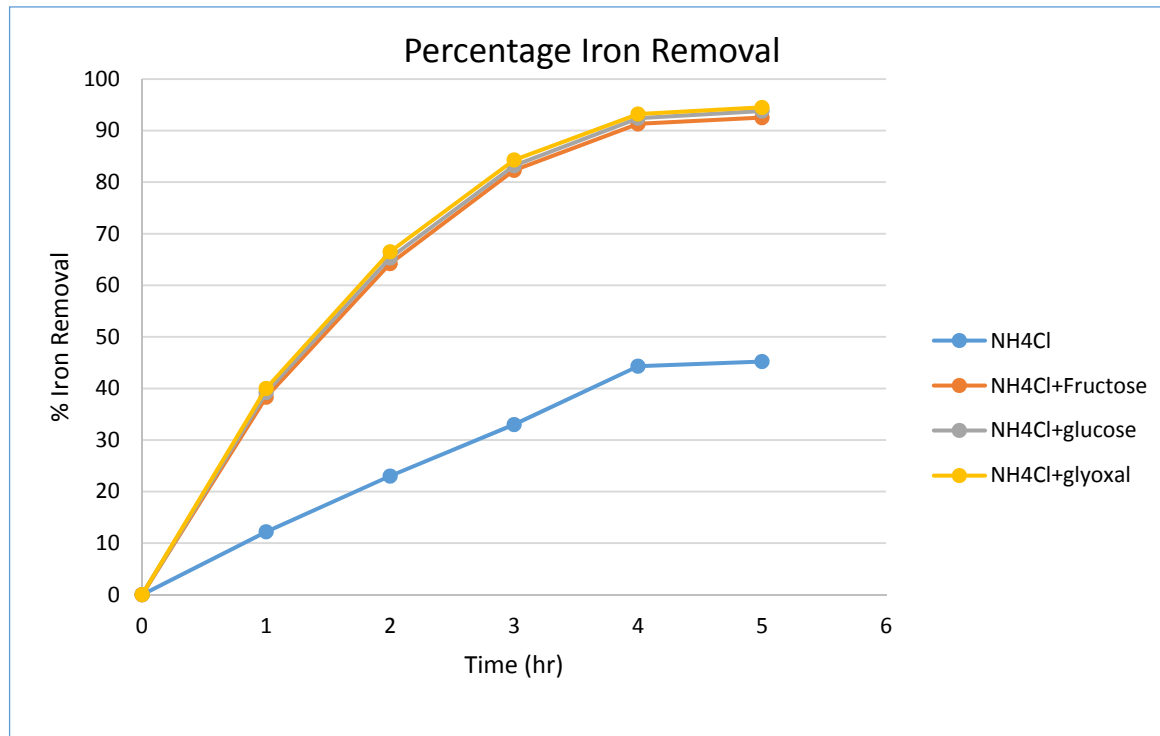


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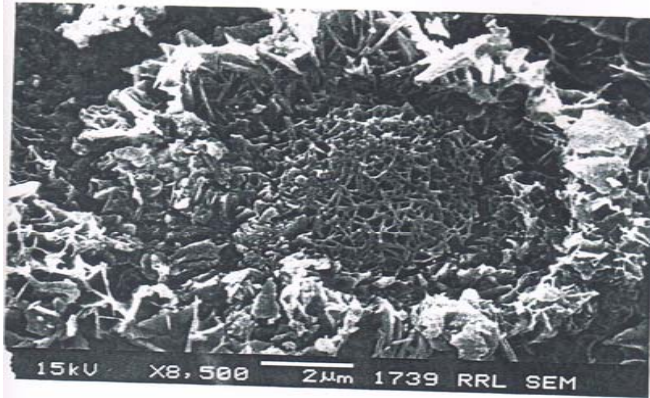


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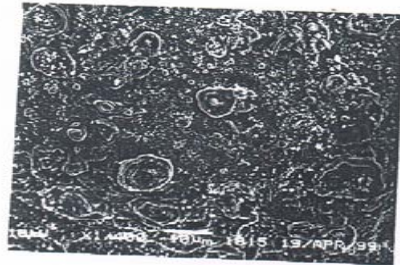
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SEM of a Reduced ilmenite

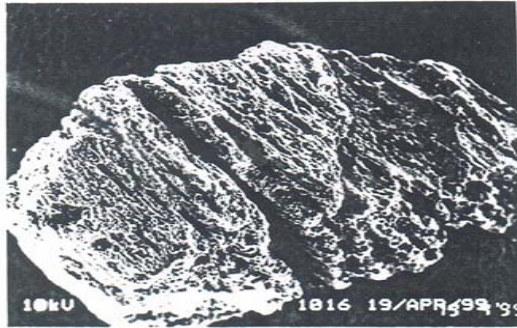


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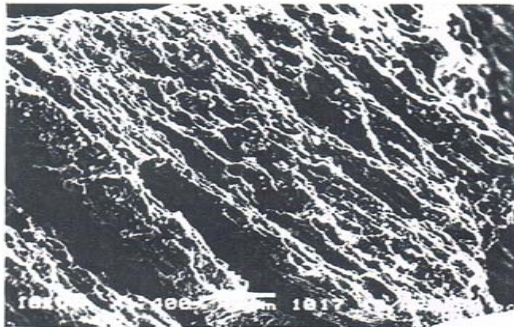
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High grade synthetic rutile
(TiO₂) having >97.5%



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Name of the sample	Surface area (sq.m/g) using 75% metallisation	Surface area (sq.m/g) using 85% metallisation
Reduced ilmenite (RI)	2.3597	2.8757
Synthetic rutile (NH ₄ Cl + glucose)	2.4742	3.2462
Synthetic rutile (NH ₄ Cl + Fructose)	3.1433	3.157
Synthetic rutile (NH ₄ Cl + glyoxal)	2.4824	3.2622

Surface area analysis of reduced ilmenite and synthetic rutile



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Conclusion

- The oxidative alkali roasting process can be used for the production of synthetic rutile from different types of TiO_2 ores.
- The formation of complex alkali salt phase during roasting process helps to separate the Fe_2O_3 and other impurities oxides from the ores, which are removed subsequently in the water and acid leaching processes.
- The increasing the roasting temperature up to 1223 K improved the separation of the impurities. However above 1223 K, the roasted mass fused with the crucible due to the formation of large volumes of liquid phase.



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- The excess addition of alkali in the roasting reaction improved the purity of synthetic rutile to around 92%. But the particle size of the synthetic rutile reduced significantly ($< 100\mu\text{m}$).
- The impurities such as Cr_2O_3 , Al_2O_3 , CaO , and V_2O_5 , which are undesirable for pigment manufacturing process, were also successfully removed by the oxidative alkali roasting techniques.



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Carbothermic reduction followed by rusting helps the removal of iron in an accommodative method

High grade synthetic rutile (TiO_2) of $> 97.5\%$ is obtained

The surface area or the particle size is retained so that the SR can be used for chlorination in FBCR.



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Commercialisation

Highlights:

- NH_4Cl was replaced by another inorganic catalyst
- Set of additional catalysts developed
- Iron oxide obtained during rusting was reduced to sponge iron and sold thus making totally a green process

The technology developed by the CSIR-NIIST, Trivandrum, has been commercialised to the **Cochin Minerals & Rutile Ltd.**

(<http://www.cmrlindia.com/>) after two pilot plant level studies.



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Present and Future work

Following the success of isolation of high pure titanium metal powder from titanium dioxide, we are in the process of optimising the conditions to isolate titanium metal powder from Rutile.



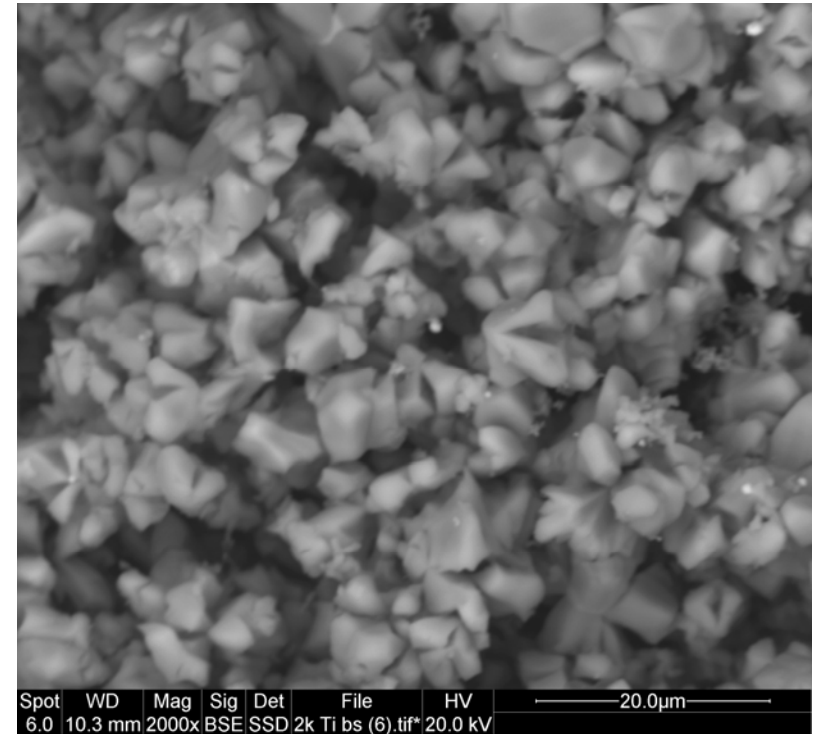
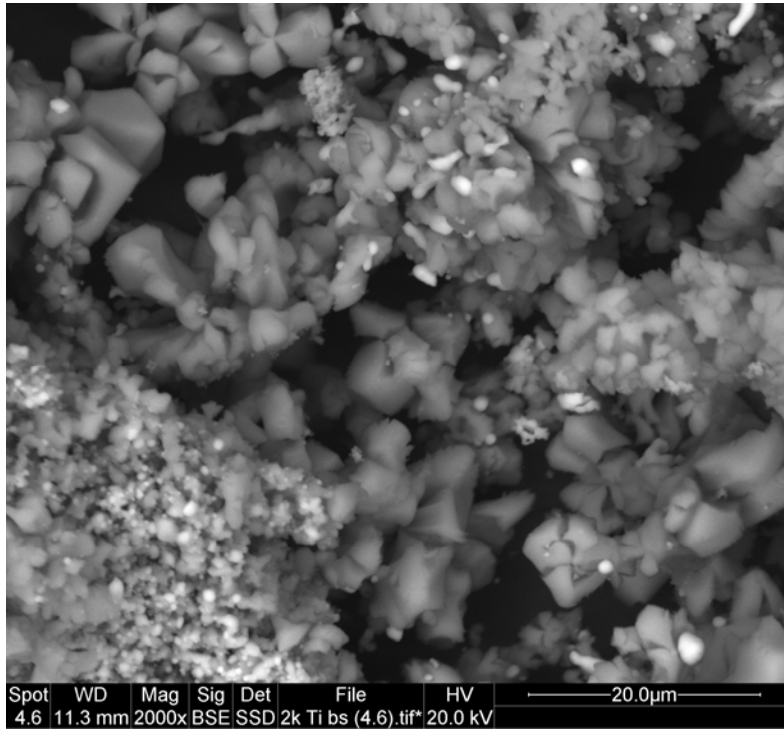
Bradford Metallurgy Plc: We are in the process of setting up of a pilot plant to reduce (1 – 5 kg) of titanium dioxide powder .



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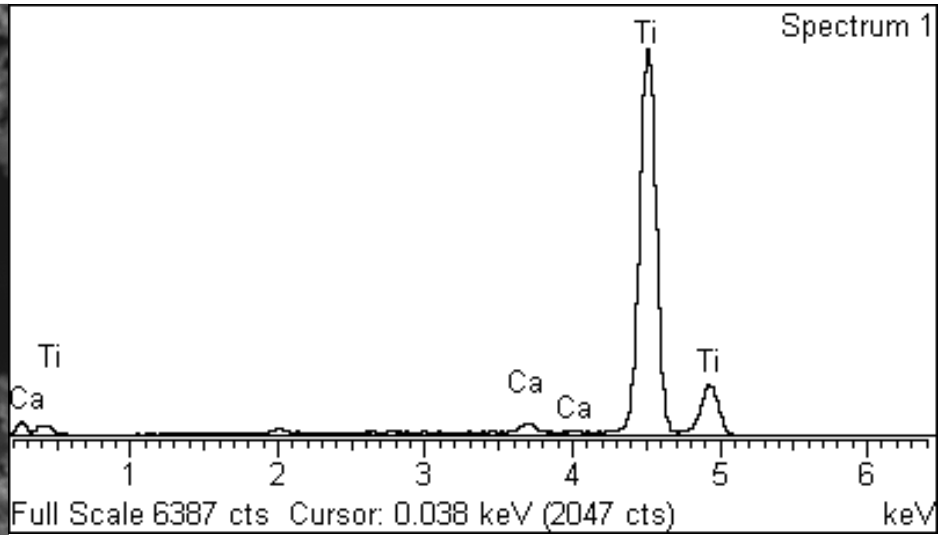
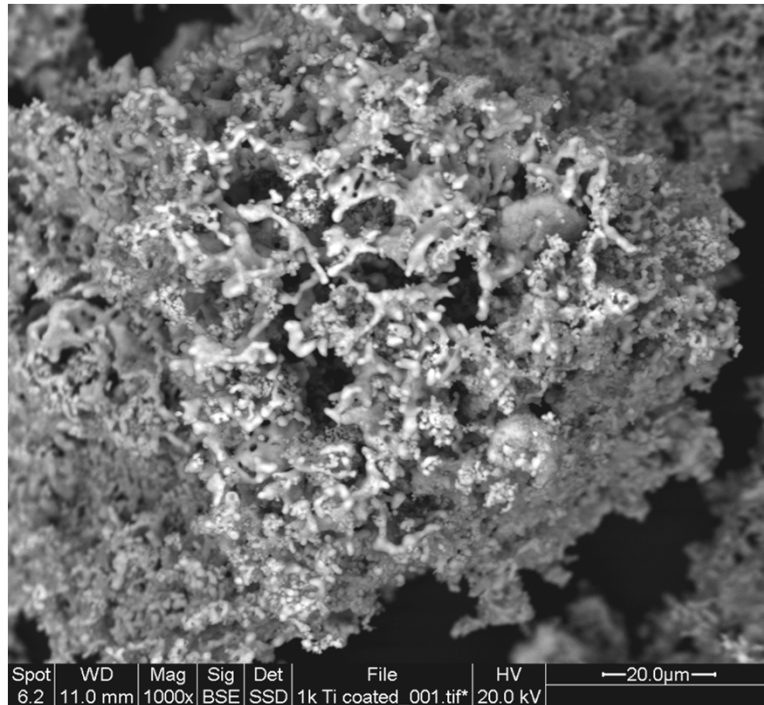


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Ti – 98.46% Ca – 1.54%

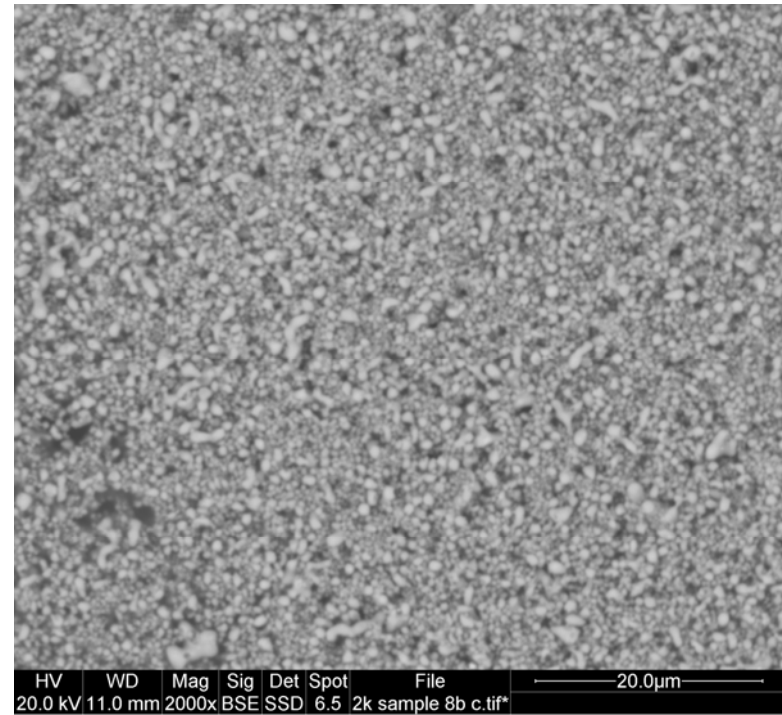
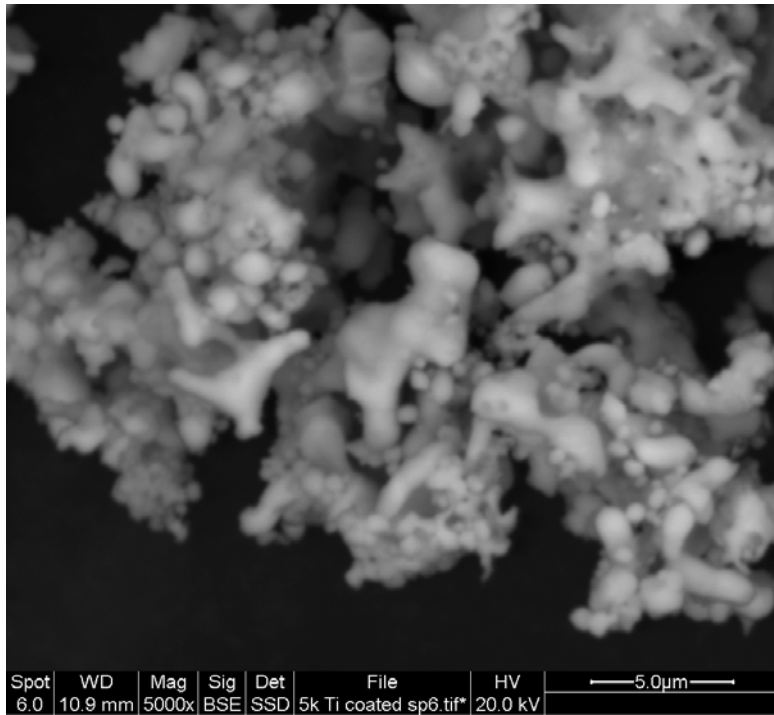


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High pure Titanium Metal powder (> 99%)



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- We thank RKTS, University of Bradford for providing funding for the production of titanium metal powder from titanium dioxide



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Mr Andrew Birch

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Thank You & Any Questions???



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