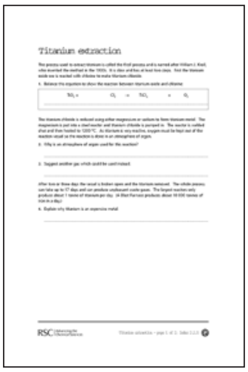
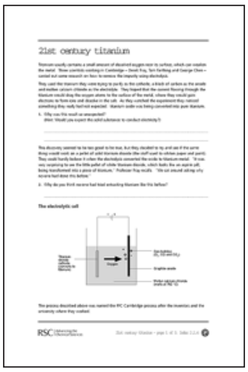
Titanium


Titanium


Titanium extraction


21st century titanium

Index 2.2.4
2 sheets
Index 2.2.5
2 sheets
Index 2.2.6
3 sheets


Titanium – from discovery to Mars


What's the connection?

Index 2.2.7
2 sheets
Index 2.2.8
4 sheets

This activity is aimed at students who have some knowledge of electrolysis and the extraction of metals. The reminder sheet **Extracting metals** – **words** could be used as an introductory activity for those who might need it.

Background information

The story of the discovery of the FFC (Fray-Farthing-Chen) Cambridge electrolysis method for extracting titanium is fascinating.

Titanium is currently extracted by the Kroll process, which was invented by William Kroll in the 1930s. This method involves carbo-chlorinating the titanium minerals rutile and ilmenite to remove oxygen, iron and other impurities and form titanium tetrachloride ($TiCl_4$) vapour. The $TiCl_4$ is reduced by treatment with magnesium metal and the magnesium chloride is removed by vacuum distillation. If sodium metal is used the process is called the Hunter Process. This step has to be carried out under a protective atmosphere of argon or another Noble gas as titanium is extremely reactive. If alloys are to be made, the titanium must be melted with the other metal(s) required. This adds to the already high cost of the process.

Kroll predicted that within 15 years his process would be replaced by an electrolytic one. So far this has not happened. Many methods have been attempted. Both molten titanium chloride and titanium oxide have been investigated as possible electrolytes and many different electrodes have been tried, but none have worked. One reason for this failure is that titanium can have a number of oxidation states and redox recycling occurs between the anode and cathode. Also, any titanium produced is in the form of fine grains which readily oxidise back to titanium oxide on contact with oxygen.

RSC | Advancing the Chemical Sciences

As titanium is extremely reactive, it is often contaminated with a little oxygen. This oxygen significantly weakens the metal and it was during an attempt to remove the oxygen that the electrolytic process was discovered almost by accident.

At the University of Cambridge, Prof Derek Fray, Dr George Chen and Dr Tom Farthing were trying to use electrolysis to remove the oxygen from samples of titanium. It was already known that this could be done in molten calcium chloride. A sample of titanium coated with a titanium oxide layer was used as the cathode, carbon as the anode and molten calcium chloride as the electrolyte. It had been suggested that calcium deposited on the titanium electrode reacts with oxygen in the titanium foil to form CaO, which is soluble in the $CaCl_2$, thus removing the oxygen. An alternative explanation has been put forward by the Cambridge scientists. They suggest that the oxygen reduction occurs at a more positive electrode than the calcium deposition and so direct reduction of titanium oxides to titanium metal can be achieved electrolytically, rather than via the chemical reaction with calcium.

In other words, one explanation involves the following reactions occuring at the titanium/titanium oxide cathode:

$Ca^{2+}(l) + 2\ e^{-} \rightarrow Ca(l)$

then

$TiO_2(s) + 2\ Ca(l) \rightarrow Ti(s) + 2\ CaO(dissolved)$

The alternative explanation involves direct electrolytic reduction of the titanium oxide:

$TiO_2(s) + 4\ e^{-} \rightarrow Ti(s) + 2\ O^{2-}(dissolved)$

Prof Fray realised that if the latter were true, then the electrolytic process might also work for a pellet of titanium oxide. When the experiment was performed, titanium was extracted from the titanium oxide, much to his excitement. The researchers realised that they had found a completely new way to extract titanium and wondered why no-one had tried it before. Other materials scientists had believed that solid titanium dioxide could not be electrolysed because it is an insulator. The Cambridge team's observations suggested that, once some oxygen is removed from titanium dioxide, it will conduct.

The process discovered by the Cambridge scientists is now called the FFC Cambridge process after the scientists themselves and the university at which they were working. It has been tried on many other metals and is showing promise as a way of extracting a variety of metals that are difficult and expensive to extract by other methods. The process has very little environmetal impact – only a very small amount of CO_2 is produced as a byproduct. It can also be used to produce alloys directly. By using a ground-up mixture of metal oxides as the cathode, the alloy of those metals is produced directly, without the need for the expensive and sometimes difficult process of melting the metals together. This may make it possible to produce alloys which have only been theoretically feasible until now.

The method is now patented and two companies have been formed to exploit the technology. The first of these companies, British Titanium plc, holds a licence solely for the extraction of titanium; Metalysis Ltd has a licence for the extraction of any other metals using the process.

References

Z. G. Chen, D. J. Fray, T. W. Farthing, *Nature*, 2000, **407**, 361–364.

S. Ashley, *Scientific American*, 2003, **289(4)**, 38–39.

S. Hill, *New Scientist*, 2001, **170(2297)**, 44–47.

K. Roberts, *Educ. Chem*, 2004, **41(3)**, Infochem 2–3.

http://www.msm.cam.ac.uk/djf/FFC_Process.htm (accessed November 2005) – webpage of Dr George Chen.

http://www.britishtitanium.co.uk (accessed November 2005) – could be understood by students.

http://www.metalysis.co.uk (accessed November 2005) – covers extraction of metals other than titanium; good section on environmental benefits and would be understood by students.

http://www.msm.cam.ac.uk/index.html (accessed November 2005) – website of the Materials Science and Metallurgy department at the University of Cambridge, where the research described above was carried out; Prof Fray's group is the 'Materials Chemistry' group.

http://www.spectore.com/process.htm (accessed November 2005) – information on the properties and uses of titanium and the traditional Kroll process.

http://aerospacescholars.jsc.nasa.gov/HAS/cirr/em/8/4.cfm (accessed November 2005) – information on the rocks found on the moon and NASA's plans to use them to produce oxygen and other resources.

Alternative activities

- You could ask students to find out about the uses and possibly also the properties of titanium before the lesson. If necessary, they could complete the **Extracting metals – words** activity. Alternatively, begin by showing the **What's the connection?** slide. The connection is that all the items shown are made of titanium.
- **Titanium – from discovery to Mars** – even if students do not work through the questions in this section, it is worth telling them the story.
- Students could write a newspaper article about the discovery of the extraction method. They should think carefully about which newspaper the article is intended for and decide on a suitable headline and style of language. They could use the websites listed above to find further up-to-date information. The science should be accurate and it should be explained in a way that most readers would understand. Alternatively, students could produce an advertising leaflet for a company selling the new, cheaper titanium and explain why it is cheaper now, what its properties are and what it could be used for.

Answers

Titanium

1. Iron is extracted from its ore by heating the ore with carbon.

2. Titanium cannot be extracted in this way because it is more reactive than carbon so would not be displaced by it. In addition, titanium carbide (TiC) might form.

3. Aluminium is extracted by electrolysis.

4. Aluminium is more expensive than iron because electrolysis of its ore uses a lot of electricity, which is more expensive than the carbon used in the blast furnace to extract iron.

5. Titanium could be extracted using magnesium/calcium/sodium/potassium/any more reactive metal.

RSC | Advancing the Chemical Sciences

Titanium extraction

1. $TiO_2 + 2Cl_2 \rightarrow TiCl_4 + O_2$
2. Argon is used because it is a Noble gas and is extremely unreactive. It does not react with titanium so its presence does not affect the quality of the product.
3. Any other Noble gas could be used instead: helium, neon, krypton, xenon.
4. Titanium is expensive because the extraction process is slow, the chlorine and magnesium (or sodium) required are expensive, it costs a lot to heat the reactor and the process is labour intensive. Chlorine is also dangerous and difficult to handle.
5.

Atom	Number	Atomic mass	Number x atomic mass
Mg	2	24	48
Cl	4	35.5	142
Ti	1	48	48
Total			238

Table 1 Calculating the atom economy of titanium extraction

Total mass of reactants = 238 g

Mass of desired product = 48 g

Atom economy = $\frac{\text{mass of desired product}}{\text{total mass of reactants}}$ x 100% = $\frac{48}{238}$ = 20%

The atom economy of the Kroll process is 20%.

6. The real atom economy will be even lower than the calculated value as the calculation does not take into account the atoms lost in the first stage of the process.

21st century titanium

1. The result was unexpected because titanium oxide is not a metal and would not be expected to conduct in the solid state. (It is a covalent compound – although as it is a compound of a metal and a non-metal, students may think that it would be ionic.)
2. No-one had tried extracting titanium like this before as they did not expect a covalent/non-metallic solid to be able to conduct electricity and act as an electrode.
3. $O + 2\,e^- \rightarrow O^{2-}$
4. $2\,O^{2-} \rightarrow O_2 + 4\,e^-$
5. If a carbon anode is used, some of the oxygen produced reacts with the electrode to produce CO and CO_2.
6. This could be prevented by using an inert (unreactive) substance as the anode.
7. Mass of desired product: 48

   Total mass of reactants: 80

   Atom economy = $\frac{48 \times 100}{80}$ = 60%

8. If the oxygen was collected and sold the atom economy would be 100%.

9. The atom economy of the FFC Cambridge process is far better than that of the Kroll process.

10. The FFC Cambridge process is likely to be cheaper because it requires less expensive starting materials, is faster and produces less waste.

11. This is an example of Green Chemistry in the following ways:

- Prevention is better than cure – it is better to design a process that produces no waste than to clear it up. The FFC process produces far less waste than the Kroll process.
- Green processes should minimise waste products and put the maximum possible amount of the raw materials into the final product – the FFC Cambridge process has a much higher atom economy than the Kroll process.
- Lower toxicity of the products – some of the byproducts of the Kroll process are extremely unpleasant whereas the FFC Cambridge process produces oxygen and a little carbon dioxide as byproducts.

Note: students will require a reference sheet of the **Twelve Principles of Green Chemistry** (Index 6.4.4) to answer this question.

Extension questions

12. Zinc chloride is not used because zinc is lower in the reactivity series than titanium. The zinc ions would be reduced and the titanium left unchanged. (Note: the reason is actually that zinc is lower in the reactivity series than oxygen, although the above is also true and is an appropriate student answer.)

13. This process is similar to the extraction of aluminium in a number of ways: both use electrolysis; oxygen is produced at the anode; if carbon is used at the anode then carbon dioxide is a byproduct; the processes are carried out at similar temperatures. They are different in that: aluminium oxide (dissolved in cryolite) is the electrolyte in aluminium extraction, whereas titanium oxide is the cathode in the titanium process and calcium chloride is used as the electrolyte.

Titanium – from discovery to Mars

1. The defence agency might use titanium for producing lighter aircraft, tanks and other vehicles. A titanium ship would be lighter, sit higher in the water and might move faster than a steel one. Students may be able to think of a range of other benefits.

2. Titanium might be useful for:

a. Aircraft – titanium is already used in some aircraft as it is very light and strong. A whole plane made of titanium (including the engine) would use less fuel than existing aircraft because it would be lighter. However, not all parts of the engine could be made of titanium as the combustion of the fuel raises the temperature of the gases above the upper limit for the use of titanium.

b. The motor industry – as well as being light and strong, titanium is very corrosion resistant. If the engine had titanium parts it would be much lighter and use less fuel. The steel used in car bodies is so cheap that it will be a long time before it is replaced by titanium.

c. Engineering/building – titanium looks good and has already been used on the surface of the Guggenheim Museum building in Bilbao, Spain. This could become a more common practice if the price falls. In addition, titanium is very strong and corrosion resistant so engineers could use it in the design of bigger and longer-lasting bridges and skyscrapers (although it is not as stiff as steel).

3. Fuel consumption would be cut as the metal is lighter than the commonly used material (steel).

4. One answer could be to allow humans on a mission to the moon to breathe. Oxygen is possibly even more crucial as an oxidiser to burn fuel. The largest component (up to 85% by weight) of any rocket is the oxidiser and locally produced oxygen for rocket propulsion could give the greatest cost and mass saving of any non-terrestrial resource. It is therefore important for the achievement of a sustained programme to explore Mars.

Answer to **To think about:** A large proportion of the surface of Mars is made of ilmenite – a mineral that largely consists of titanium oxide. NASA wants to extract the oxygen from this ore as there is no free oxygen on the moon. For further details, see the website **http://aerospacescholars.jsc.nasa.gov/HAS/cirr/em/8/4.cfm** (accessed November 2005.)

Titanium

Titanium is a metal with incredible properties: it is lighter than steel; strong and tough enough to survive in space or at the bottom of the ocean; oxidation and corrosion resistant. And it looks good. What is more, it is very common – the ninth most common element in the Earth's crust (found in the form of titanium oxide).

You might wonder why we do not use it more, but titanium has one real drawback: its cost. It is currently more than five times the price of stainless steel.

Metal	Cost per tonne
Titanium	£8000
Iron	£250
Stainless steel	£1500
Aluminium	£1500
Titanium alloys	£25000

Reactivity series of metals

Element	Symbol
Potassium	K
Sodium	Na
Calcium	Ca
Magnesium	Mg
Titanium	Ti
Aluminium	Al
Carbon	**C**
Zinc	Zn
Iron	Fe
Lead	Pb
Hydrogen	**H**
Copper	Cu
Silver	Ag
Gold	Au

Note: Carbon and hydrogen are not metals.

1. How is iron extracted from its ore?

....

....

2. Why is this method not suitable for extracting titanium?

....

3. What method is used to extract aluminium from its ore?

....

4. Why is aluminium more expensive than iron?

....

Scientists have been trying to extract titanium by electrolysis since the 1950s without success. Instead, it is extracted using a more reactive metal to displace it from its ore.

5. Suggest a metal that could be used to displace titanium from its ore.

....

Titanium extraction

The process used to extract titanium is called the Kroll process and is named after William J. Kroll, who invented the method in the 1930s. It is slow and has at least two steps. First the titanium oxide ore is reacted with chlorine to make titanium chloride.

1. Balance this equation to show the reaction between titanium oxide and chlorine:

$$TiO_2 \quad + \quad Cl_2 \rightarrow TiCl_4 \quad + \quad O_2$$

The titanium chloride is reduced using either magnesium or sodium to form titanium metal. The magnesium is put into a steel reactor and titanium chloride is pumped in. The reactor is welded shut and then heated to 1200 °C. As titanium is very reactive, oxygen must be kept out of the reaction vessel so the reaction is done in an atmosphere of argon.

2. Why is an atmosphere of argon used for this reaction?

....

3. Suggest another gas which could be used instead.

....

After two or three days the vessel is broken open and the titanium removed. The whole process can take up to 17 days and can produce unpleasant waste gases. The largest reactors only produce about 1 tonne of titanium per day. (A Blast Furnace produces about 10 000 tonnes of iron in a day.)

4. Explain why titanium is an expensive metal.

....

....

....

The equation for the reduction of titanium chloride with magnesium is:

$2Mg(l) + TiCl_4(l) \rightarrow 2MgCl_2(l) + Ti(s)$

5. Calculate the atom economy of the process used to extract titanium. The guide below may help you.

Work out the total mass of reactants using the table

Atom	Number	Atomic mass	Number x atomic mass
Mg	2	24	48
Total			

Total mass of reactants = ____________ g

Total mass of desired products: ___________ g

Atom economy = $\frac{\text{mass of desired products}}{\text{total mass of reactants}}$ x 100 % = ___________ x 100%

The atom economy of the Kroll process is ________ %

6. The Kroll process is a two-step process.
Will the atom economy of the whole process be higher, lower or the same as the value you have calculated? Explain your answer.

....

....

William Kroll knew that his process was expensive and inefficient. In the 1950s he predicted that within 15 years an electrolytic process would replace his method. However, the Kroll process is still the main method used today and there have been many failed attempts at electrolysis. Scientists have tried using both titanium oxide and titanium chloride dissolved in other salts as the electrolyte. They have also experimented with various metals and carbon as the electrodes but none of the combinations they have tried have worked. Titanium has remained difficult to extract and expensive, although it offers properties that interest the designers of a wide variety of products.

21st century titanium

Titanium usually contains a small amount of dissolved oxygen near its surface, which can weaken the metal. Three scientists working in Cambridge – Derek Fray, Tom Farthing and George Chen – carried out some research on how to remove the impurity using electrolysis.

They used the titanium they were trying to purify as the cathode, a block of carbon as the anode and molten calcium chloride as the electrolyte. They hoped that the current flowing through the titanium would drag the oxygen atoms to the surface of the metal, where they would gain electrons to form ions and dissolve in the salt. As they watched the experiment they noticed something they really had not expected: titanium oxide was being converted into pure titanium.

1. Why was this result so unexpected?
(Hint: Would you expect this solid substance to conduct electricity?)

....

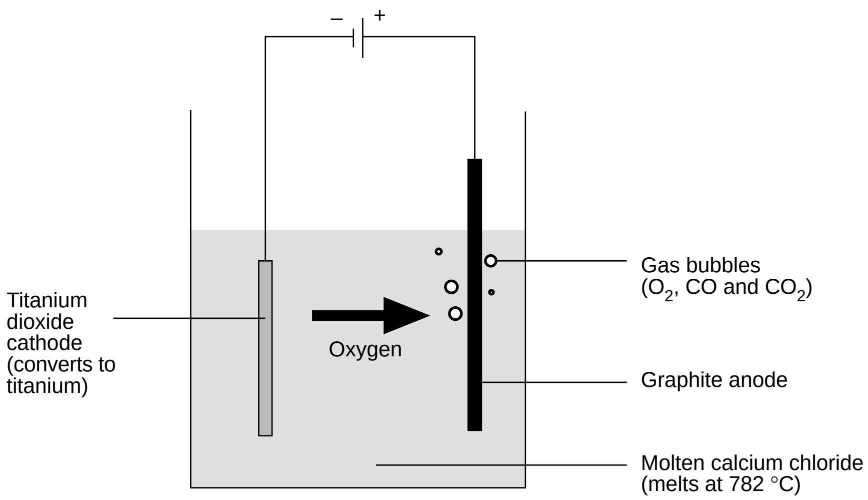
....

This discovery seemed to be too good to be true, but they decided to try and see if the same thing would work on a pellet of solid titanium dioxide (the stuff used to whiten paper and paint). They could hardly believe it when the electrolysis converted the oxide to titanium metal. "It was very surprising to see the little pellet of white titanium dioxide, which looks like an aspirin pill, being transformed into a piece of titanium," Professor Fray recalls. "We sat around asking why no-one had done this before."

2. Why do you think no-one had tried extracting titanium like this before?

....

The electrolytic cell



The process described above was named the FFC Cambridge process after the inventors and the university where they worked.

The formula of titanium dioxide is TiO_2. Although it is a compound of a metal and a non-metal, it is a covalent compound. At the cathode, the oxygen atoms in the compound are reduced to form oxygen ions.

3. Write an equation for the reduction of the oxygen atoms to oxygen ions at the cathode.

The oxygen ions dissolve in the molten calcium chloride, leaving titanium metal behind. The oxygen ions then move through the calcium chloride to the anode where they are turned into oxygen gas.

4. Write an equation for what happens to the oxygen ions at the anode.

5. Why is some CO and CO_2 also produced?

....

6. How could this be prevented?

....

The overall equation for the reaction is:

$TiO_2(s) \rightarrow Ti(s) + O_2(g)$

Remember: $\% \text{ atom economy} = \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100$

7. Calculate the atom economy for the FFC Cambridge process.

....

....

....

8. If the oxygen were to be collected and sold as well as the titanium, what would the atom economy of the process be?

....

9. How does the atom economy of the FFC Cambridge process compare to that of the Kroll process?

....

10. Why is the FFC Cambridge process likely to produce titanium more cheaply than the Kroll process?

....

....

11. In what ways is this an example of Green Chemistry? (Compared to the Kroll process.)

....

....

....

....

Extension questions

12. One of the reasons why calcium chloride is used as the electrolyte in the FFC Cambridge process is that it has a low melting point. Zinc chloride also has a low melting point. Leaving aside cost, can you suggest why zinc chloride is not used in this process?

....

....

13. How is this process similar to the extraction of aluminium? How does it differ?

....

....

....

Titanium – from discovery to Mars

The FFC Cambridge process has been tested in successive experiments that have clearly shown it to work. However, across the world the majority of titanium is still produced by the Kroll process. The continuing story of the titanium discovery made by scientists in Cambridge shows that it is not always easy to introduce a new process, even if it has clear benefits.

A year after the team at Cambridge had found their new process for extracting titanium, Professor Fray sent a report to Britain's defence agency, DERA (Defence Evaluation and Research Agency). People at DERA were very excited and offered to develop the technology and scale it up.

1. Why would the defence agency be interested in titanium? What might they use it for?

....

....

....

The DERA and Cambridge scientists worked together on the idea for a while, but more money was needed to build a pilot plant (a small factory where the method for producing larger quantities of the product can be tested and improved). Funding was difficult to find as there was no guarantee that the technology would work on a larger scale, but eventually a pilot plant was built.

The pilot plant now produces kilogram quantities of titanium and there are plans to build a bigger plant and start producing commercial quantities.

If the process scales up to an industrial level as expected, the price of titanium could fall substantially. British Titanium believes that this development could eventually increase the use of titanium from the current level of 60 000 tonnes per year to 1 million tonnes per year. As titanium is the ninth most common element in the Earth's crust there will be no shortage of raw material.

2. Think about the properties of titanium. Why might it be useful for:

a. Aircraft?

....

....

b. The motor industry?

....

....

c. Engineering/building?

....

....

3. What effect would using titanium in planes and cars have on fuel consumption?

....

....

....

There are still many difficulties to overcome to make this process suitable for commercial use and for production on a large scale. Chemical engineers have to work to develop process controls and to find a way of getting reactants in, and products out of the electrochemical cell. Efficient methods for these things will help lower costs.

Whether this process is the one that is eventually used or not, it seems likely that titanium use will rise and its cost will fall over the next few years as its properties are so desirable for a wide range of applications.

That is not the end of the story. In an exciting development, NASA (National Aeronautics and Space Administration) has now become interested in the process. Known for its shuttle programme and successful manned mission to the moon, NASA's latest challenge is to enable man to live on the moon in order to pave the way for a trip to Mars. A large proportion of the moon's surface is ilmenite (a titanium oxide ore). NASA scientists are interested in the FFC Cambridge process not for the production of titanium, but for its byproduct, oxygen.

4. Why would NASA be interested in producing oxygen?

....

....

....

To think about

Why would NASA be interested in the FFC Cambridge process?

This is an excellent illustration that scientific research can result in benefits that can be a million miles away (literally in this case) from what the researcher was anticipating when they began. Professor Fray and his team were just trying to remove the oxide coating from titanium – they might have ended up helping to reduce carbon dioxide emissions and put a man on Mars!

What's the connection?

What's the connection?

What's the connection?

What's the connection?

What's the connection?