



REDUCTION OF TITANIUM DIOXIDE AND OTHER METAL OXIDES BY ELECTRO-DEOXIDATION



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Abstract: Titanium dioxide and other reactive metal compounds are reduced by more reactive metals to form pure metals. These are expensive and time consuming processes which makes these metals very expensive. Many of these metals and alloys have excellent properties, high strength, low density and very good corrosion resistance, but their use is restricted by its high cost. Electro-deoxidation is a very simple technique where an oxide is made cathodic in a fused salt of an alkaline earth chloride. By applying a voltage, below the decomposition potential of the salt, it has been found that the cathodic reaction is the ionization of oxygen from the oxide to leave a pure metal, rather than the reduction of the ion alkaline earth ion element. Laboratory experiments have shown that this approach can be applied to the reduction of a large number of metal oxides. Another important observation is that when a mixture of oxides is used as the cathode, the product is an alloy of uniform composition. This is a considerable advantage for many alloys that are difficult to prepare using conventional technology.

INTRODUCTION

Metals that are prepared by the reduction of a metal compound by a more reactive metal include, the reduction of titanium and zirconium chlorides by magnesium, the reduction of niobium pentoxide by aluminium and the reduction of potassium tantalum fluoride by sodium. Some of these metals are plentiful in the earth's crust. For example, titanium is the ninth most common element in the earth's crust and the fourth most common structural metal after aluminium, magnesium and iron[1]. At the present time, there are two ways of producing titanium and zirconium – the Kroll and Hunter processes. These processes are very similar in that both start with titanium tetrachloride. The Hunter process uses sodium and produces a powdered metal whereas the Kroll process uses magnesium and the product is denser. The difference in morphology is entirely due to the mechanism of reduction as identified by Okabe and Sadoway [2]. In a very careful analysis it was shown that sodium can dissolve to a certain extent in molten sodium chloride and this makes the salt an electronic conductor so that the reactions



and



can take place throughout the melt and a fine powder is produced. Conversely, with the Kroll process, there is negligible solubility of magnesium in magnesium chloride, so that the magnesium chloride remains as an ionic conductor and is electronically insulating. In this case the only way the electrons for the reactions to transfer is in contact with a metallic conductor so that the titanium essentially grows into a massive but porous sponge. The two reactions, in this case, are:



It is considered that the Kroll process produces a better product for the production of ingots so that this process predominates over the Hunter process. However, there are several disadvantages with all



metallothermic processes and these are that the processes can only be operated on a relatively small scale, employ hazardous materials and are very labour intensive. In the Kroll process for the extraction of titanium, the initial step is the loading of magnesium ingots into a steel reactor, which is then welded, shut. The reactor is then heated to 1173 K and the titanium tetrachloride allowed to react for two/three days to produce titanium sponge. The titanium tetrachloride vapour is fed into the reactor very slowly to prevent overheating due to very exothermic nature of the reactants. When the reaction has been completed and all the magnesium consumed to give magnesium chloride, which is tapped off, the vessel is allowed to cool, the weld is broken, and the titanium is removed. As there is always some entrained magnesium chloride. This is removed by vacuum distillation at 1300K. As the product ingot of sponge is inhomogeneous it is either crushed or thoroughly mixed or the outer few cms of the ingot are removed and scrapped. Overall, the world's largest reactors only produce, on average, about one tonne/day and this should be compared to other metal production methods where thousands of tonnes of metal are produced per day. The overall process from the carbon chlorination of the impure oxide to the production of a few tonnes of metal can take nearly three weeks. At some plants the magnesium chloride by-product is electrolysed to produce chlorine for the carbochlorination step and magnesium for the reduction step. In order to produce these reactive metals, two independent metal reduction processes are used.

For most other methods for metal extraction, such as reduction by carbon or electrolysis in a molten salt or an aqueous solution, just require reduction and refining for the less electropositive elements and refining and reduction for the more electropositive elements. It is obvious that the production of elements that can only be prepared by metallothermic reduction are, therefore, far more costly than other reduction methods. As well as the costs associated with reduction, the downstream costs are also significant as many of these metals are highly reactive and require many remelting steps especially if homogeneous alloys are required. In the case of titanium, the post reduction steps increase the cost by a further factor of four making titanium alloys very expensive when compared to steel and aluminium alloys. The overall result is that although titanium is very common in the earth's crust, its high cost greatly restricts its application in spite of its excellent properties of low density, high strength and corrosion resistance. There are innumerable possible applications if the price of titanium alloys could be reduced to close to that of the other common metallurgical alloys. The same argument can be applied to many of the other metals produced by metallothermic reduction.

As soon as the Kroll process became established in the 1950s, William Kroll predicted that his process for titanium would be replaced by an electrolytic process within fifteen years[3]. This has never been achieved even though there have been several attempts to produce titanium by an electrolytic process. Most of the processes have concentrated on the electrochemical reduction of a titanium chloride[4-6], although recently, Ginatta has proposed the concept of reduction from fluoride salts[7 to produce liquid titanium rather than a solid product]. There are several problems associated with titanium tetrachloride, as its boiling point is 439 K, whereas most salt mixtures are not molten until heated to around 800 K. The tetrachloride has either to be reduced electrochemically or by reacting it with titanium to obtain the dichloride which is less volatile and, therefore, has a higher solubility in the melt. In electrolytes containing titanium dichloride, there are two possible anodic reactions:



or



Thermodynamically, reaction (6) is the favoured reaction and the Ti^{4+} can then diffuse back to the cathode where the following reaction can take place:





or can be lost as the tetrachloride. The net result is that considerable quantities of electrical energy are consumed but no titanium is produced. The oxidation of Ti^{2+} can be prevented by a diaphragm surrounding the anode which allows the diffusion of the faster diffusing chloride ion but restricts the diffusion of the slower moving titanium ion. However, probably the greatest problem is at the cathode where, due to the high temperature, the electrochemical reactions occur at a faster rate than the mass transfer of the ions and this leads to a very dendritic deposit that offers a very high surface for

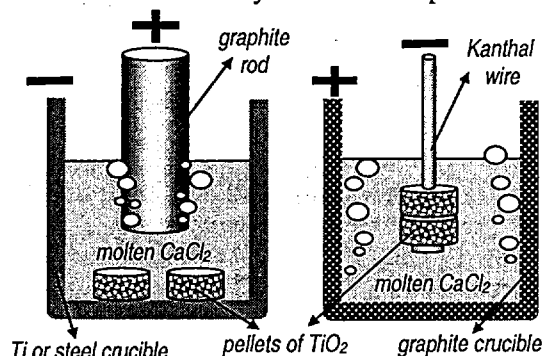


Fig. 1 Schematic representations of two electrolytic cells for electro-deoxidation of titanium dioxide in molten calcium chloride.

oxidation. Also it is not mechanically strong so that when the cathode is removed from the melt, some dendrites may become detached from the cathode. This applies whenever metals are deposited below their melting points from molten salts. What is needed is an innovative electrochemical method, which overcomes these problems.

ELECTRO-DEOXIDATION OF TITANIUM

In the early 1960s, Ward and Hoar published some very interesting results on the removal of impurities from molten copper by making it the cathode in a bath of molten barium chloride [8]. Surprisingly, it was found that elements that formed anions, such as oxygen, sulfur, selenium and tellurium, ionized and were removed from the copper. The overall cell reaction was assumed to be:



In 1993, Okabe and co-workers used a similar approach to remove oxygen, down to very low levels, from several reactive and rare earth metals [9-12]. Again, in order to explain the results, it was assumed that the voltage generated a calcium activity at the cathode and the calcium reacted with the dissolved oxygen to form calcium oxide that dissolved, at a low activity, in the calcium chloride melt. It should be noted that, unlike the vast majority of chlorides, the alkaline earth chlorides demonstrate substantial solubility for their respective oxides [13].

For most metals there is very limited solubility of oxygen in the solid state but for the Group IV elements, there is substantial solubility of oxygen in the metal [14]. This means that whenever the group IV elements are fabricated at elevated temperatures in an oxidising environment, a surface coating of oxygen rich titanium, harder and more brittle than pure titanium metal, is formed as well as a surface oxide coating. Conventionally, the alpha-case, as it is called, has to be removed by either grinding the layer away or leaching in an aggressive leachant. Both methods result in change in the dimensions of the artefact and creation of disposal problems for the grindings or leachant. A far better technique would be to remove the oxygen electrochemically, which would not result in a change in the dimensions of the artefact. This was achieved by Chen et al in a pure calcium chloride melt using oxidised titanium samples by applying a voltage, below the decomposition potential of calcium chloride, between the cathodic titanium and a carbon anode [15]. The process was simply monitored by removing samples after known periods of time and performing a microhardness profile close to the surface of the sample. Oxygen affects the hardness of titanium so that it was easy to detect the level of oxygen in the titanium [16]. Cyclic voltammetry was used to define the cathodic reactions that were



taking place. These measurements demonstrated that, on increasing the cathodic potential, the first

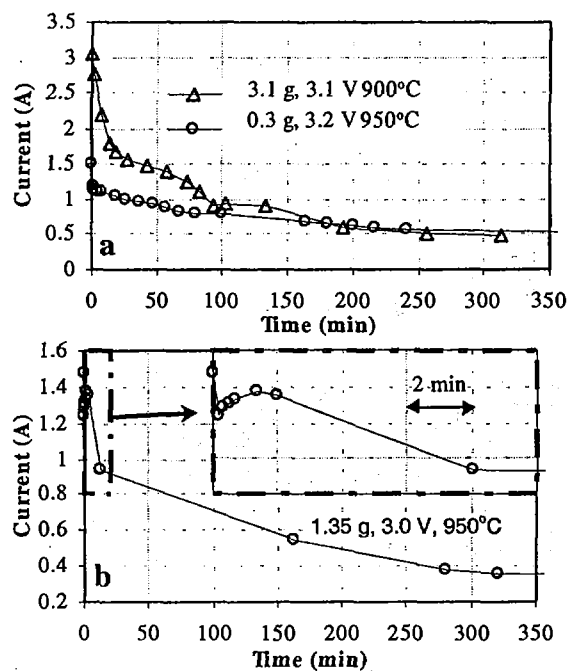


Fig. 2 Comparison of current variations with time during electrolysis of TiO₂ pellets in molten CaCl₂ in (a) the left and (b) the right cells of Fig 1.

reaction to occur was the ionisation of oxygen followed by the deposition of calcium. It appeared that it was not necessary to invoke the presence of calcium in order for the reaction to occur. The cathodic reaction is simply:



And is termed electro-deoxidation.

TITANIUM DIOXIDE REDUCTION

As oxygen was removed from titanium, it was hypothesised that it might be possible to reduce oxides using the same technique although the mechanism might be different, as removal oxygen from the lattice of an insulating oxide is unlikely to be the same as the removal of oxygen dissolved in an electronically conducting metal. Titanium dioxide pellets, about 1 cm in diameter and 5 mm thick, were made from quarter micron titanium dioxide powder by either pressing or slip casting and then firing to give sufficient strength to survive in the molten salt. The pellets were either placed into a titanium crucible or suspended on a wire in the melt, as shown in Fig. 1. A voltage lower than the decomposition potential of calcium chloride, was applied and it was found that, almost immediately, the current quickly rose to several amperes, which was dependent upon the number of pellets in the crucible (Fig. 2). The current then fell over a period of a few hours to a plateau value that was independent of the number of pellets. On removal from the crucible, the pellets had changed from white, the colour of titanium dioxide, to a dull grey.

Examination under the scanning electron microscope showed that the product was titanium metal, containing a small amount of oxygen [17, 18] as is shown in Fig. 3. It should be noted that the particle size had grown from a quarter micron powder to 2–10 micron granular titanium product. These results have been repeated at QinetiQ, Farnborough, UK on a kg scale with similar results. At QinetiQ, the oxygen content of the titanium was reduced to about 60 ppm in 24 hours. The product was also very uniform in composition, unlike the sponge produced by the Kroll process [18].



Subsequently, it was found that many compounds between calcium oxide and the various oxides of titanium are present before TiO forms. It is thought that the peak in the current is due to formation of these compounds and the current-time plateau is where the reduction of TiO to titanium metal takes place [20]. (An example of such behaviour is shown in the insert of Fig.2b, however, it was also observed that surface metallisation of the oxide pellet also contributed to the initial current peak) Once all the titanium dioxide has been reduced to titanium monoxide, the process then slows considerably as the rate of oxygen removal is dependent upon the diffusion of titanium from the interior of the granules to the titanium/molten salt interface. At this stage, it is proposed that the oxygen ionises at the interface, dissolves in the calcium chloride, and then diffuses through the capillaries to bulk salt, where convective mass transfer takes the oxygen ions to the anode where discharge takes place. The anodes, used in the laboratory experiments, were made from a relatively inert form of carbon, and only a small fraction of the evolved oxygen reacted with the carbon; most was evolved as oxygen.

At the end of the experiments, the pellets were simply withdrawn from the melt and allowed to cool. Calcium chloride solidifies at 1045 K so that the salt, which has penetrated throughout the pellet solidifies and essentially prevents the titanium from undergoing oxidation and as the solubility of calcium chloride in water is extremely high (1.59g/ml of H₂O) it is a simple operation to remove the salt. As well its high capacity for oxygen ions and its substantial solubility in water, there are two other important advantages. And these are that it is available as a high purity waste product from the chemical industry and its toxicity is the same as sodium chloride so that there are no hazards associated with its handling or disposal.

REDUCTION OF OTHER METAL OXIDES

As metallothermic reduction is fairly common, it is obvious that this approach can be applied to other systems. Table I shows the ionisation potential of the oxygen from various oxides relative to the deposition of calcium from calcium ions. As calcium forms one of the most stable oxides and, as Okabe and co-workers [9-12] have shown, the activity of calcium oxide in the melt can be maintained at a very low value, this leads to the conclusion that almost any oxide can be reduced by this approach. A significant number of other metal oxides have been reduced in our laboratory and these include, zirconium oxide, hafnium oxide, nickel oxide, chromium oxide, niobium oxide, cerium oxide, tantalum oxide, silicon dioxide and uranium oxide[20]. Many of these reduce in a similar way to titanium initially forming a series of calcium oxide-metal oxide compounds, which are an integral part of the process but are purely transient. However, there are some exceptions. For example, zirconium oxide is an insulator and, as the sole valence state of zirconium is four, it is difficult to introduce defects into the oxide structure. From an examination of a partially reduced pellet, it was found that the reduction started adjacent to the lead wire, and then propagated quickly on the surface of the pellet, leading to the

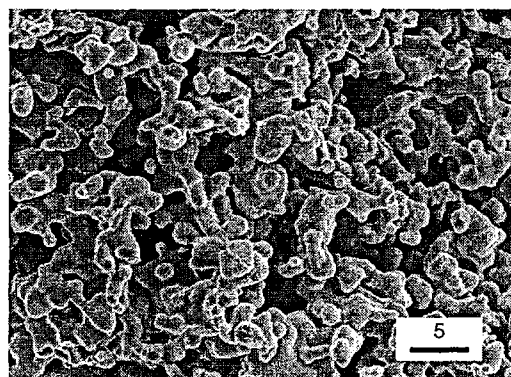


Fig. 3 SEM image of the microstructure of an electro-deoxidised TiO₂ pellet.

formation of a porous zirconium metal surface layer which, by further reduction of the oxide, gradually grew through out the pellet. A similar mechanism was observed during the reduction of silicon dioxide. As the zirconium metal that is formed is porous and the particles are in contact with each other, the



whole pellet becomes conducting and the porosity ensures that there is adequate three phase boundary between the salt, insulating oxide and the electronically conducting metal phase.

Zirconium metal is very similar to titanium in that it has considerable solubility for oxygen in the solid state and, therefore it takes several hours for the oxygen to diffuse in the zirconium granules to the metal/salt interface.

Another striking difference with titanium dioxide reduction is with chromium oxide as there is no solubility of oxygen in chromium metal. In this case, the current time profile is completely different, in that the current rises to a maximum and then falls or remains to a constant until all the oxide has been reduced. When this has occurred, the current falls quickly with time (Fig. 4). As the process does not rely on diffusion in the solid state, the reduction to pure chromium occurs within 2-6 hours depending on the applied voltage and temperature [20].

The other difference that was noted was when the melting point of the metal was relatively close to the temperature at which electro-deoxidation was performed, as in the case of uranium, the reduced metal forms a sintered dense phase with internal porosity. However, it should be stressed that the enclosed pores were completely free of salt [20].

ALLOY PREPARATION

From the work on pure oxides, it became evident that only the anionic species were removed from the oxide. From the point of metal refining, this is a disadvantage as no refining of other metals will take place but, on the other hand, this opens up the opportunity for the direct production of alloys, perhaps alloys that cannot be made by any other route. Several alloys have been synthesised simply by mixing the oxides in the correct proportion and reducing by electro-deoxidation and these include Ti-6Al-4V, NbTi, NiTi, Ni₃Al, Nb₃Sn, NbTa and Ti-Fe, [20]. In all cases, the oxides were mixed by ball milling and made into pellets that were lightly sintered so some porosity remained but the pellets were mechanically sound. After reduction, the composition, determined by EDAX analysis, was found to be uniform across the samples except for the Ti-6Al-4V, which, as expected, consisted of the alpha and beta phases. In this case there was a slight loss of aluminium from the alloy due, it was thought, to the formation and vaporization of aluminium trichloride. However, rather surprisingly, the microstructure was the reverse of the normal microstructure for this alloy, [20] in that the beta phase had precipitated around the alpha phase rather than the alpha phase precipitating around the beta phase. The reason for this is that the electro-deoxidation takes place completely in the solid state starting with a mixture of

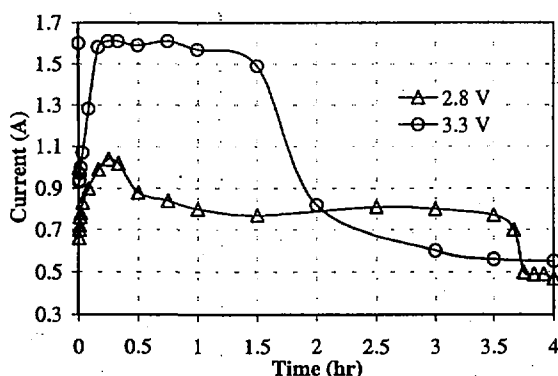


Fig. 4 Comparison of current variations with time during electrolysis of Cr₂O₃ pellets (about 3 g) in molten CaCl₂ at 950°C in the right cell of Fig 1.

oxides and as the oxygen is gradually removed from the system the composition of the alloy moves across the phase diagram from the oxygen rich alpha region to the alpha plus beta region. In the cases of the intermetallic compounds, such as Ni₃Al, X-ray diffraction proved that the correct phases had formed. Furthermore, when the superconducting properties of the NbTi and Nb₃Sn were determined the superconducting/normal transition occurred at the precise temperatures described in the literature.



As well as aluminides, it was also found possible to prepare carbides, borides and silicides by either starting with a mixture of carbon and the oxide or a mixture of oxides in the case of the borides and silicides.

This method of alloy production can be contrasted with the other electrochemical methods for the production of alloys using molten salts. In these other cases where the melts contain a mixture of cations, it is very difficult to get the metals to co-deposit in the correct ratio unless it is arranged that the electrode potentials for the deposition for each of the metals is identical [21]. This is very difficult as it is impossible to form stable complexes in molten salts so as to dramatically change the deposition potentials. With the case of electro-deoxidation, the electrode potentials are far less important, except for defining the order of reduction.

Again, in the production of alloys, it is observed that the calcium oxide metal oxide intermediate compounds formed as an integral part of the reduction process. The oxide compounds will reduce in the order of stability with the least stable oxide being the first to reduce. Due to the very short diffusion distances and the high reactivity of the reduced metals, alloying readily occurs.

POWDERS

The product of the reduction of many of the metal oxides was of the form of grains that are lightly sintered together, which can easily be ground to a powder. One of the surprising features is that the powders are of remarkably uniform size and composition [20]. Varying the particle size of the precursor and the time and temperature of the reduction process can vary the size.

COMPARISON WITH EXISTING TECHNOLOGY AND DEVELOPING TECHNOLOGIES

Electro-deoxidation can be compared with the conventional methods of reducing metal oxides. Compared to the Kroll process, the feed is an oxide that can be obtained via the chloride or sulfate routes giving the process greater flexibility. In the case of the sulfate process, it is possible to use some of the intermediate products making the feed material cheaper. It is also possible to use ores such as rutile and ilmenite but in this case the product is an alloy of titanium and iron and some other elements but as the starting material is very cheap compared to pigment grade titanium dioxide, there may be incentives to examine the properties and applications of such alloys. The starting material is a solid rather than a gas, as in the case of titanium tetrachloride, and no obnoxious gases are involved and if an inert anode is selected the only products are oxygen and metal. The form of the metal is similar to Kroll sponge but of higher and more uniform purity and the oxygen content of the metal can be accurately controlled, depending on the time of electro-deoxidation. Nitrogen may also ionise during electro-deoxidation, depending on the electrolyte, and, therefore, nitride inclusions should not form. One can imagine the cells to be modular and therefore, there should be a greater throughput with less labour and far less pollution. The product is also of a size that spontaneous combustion should not take place unlike the fines from the Kroll and Hunter processes. The downstream processing of Kroll sponge is also very expensive in that some alloys are difficult to make, either due to reactivity of one of the components or the density difference of the individual elements, which means many remelting steps to ensure homogeneity. This is expensive when electron beam melting has to be used. With electro-deoxidation, the alloys are of very uniform composition and can be used directly.

Most titanium powders are made from high purity titanium and it is difficult to avoid contamination with oxygen. Powders, both of pure metals and alloys, can simply be made by the electro-deoxidation technique. As these powders will be considerably cheaper than conventional powders this may increase the application of powder metallurgical techniques and the manufacture of near net shape components. It should also be possible to remove the oxide layers and alpha case from swarf and scrap, allowing a greater degree of recycling.

Compared to the other electrolytic techniques that have been tried in the past two decades for production of titanium and other Group IV elements, electro-deoxidation is much simpler. The starting material is an inert oxide rather than a volatile chloride and the products of the electrolysis process are oxygen, if an inert anode is used, and a granular product, which is relatively resistant to oxidation. This can be compared with the highly dendritic nature of the cathodic product when conventional



electrolysis takes place in molten salts. Lastly, there is no concern regarding the number of valence states of the cation, as it is the oxygen that ionises and not the cation. In fact, a multiplicity of valence states is an advantage as it means that the oxide is unlikely to be stoichiometric and, therefore, electronically conducting. It is also possible to produce alloys directly by simply starting with a mixture of oxides.

Recently a similar method has been developed by Ono and Susuki [22]. In the Ono and Susuki (OS) process, calcium chloride, containing calcium chloride, is electrolysed to produce calcium and this reacts with the titanium dioxide to titanium metal with the calcium oxide dissolving in the salt. The perceived problems with this approach is that it is difficult to control the rate of reaction so that this can lead to the solubility limit of calcium oxide being exceeded contributing to the entrapment of oxide which is difficult to remove. The second disadvantage of this approach is that the deposited calcium can dissolve into the melt raising the electronic conductivity of the melt making the electrolysis process relatively inefficient.

Okabe has also introduced a new approach where calcium vapour is allowed to reduce a preform of titanium dioxide containing calcium chloride [23]. The advantage of this approach is that the calcium oxide dissolves in the calcium chloride making it easier to leach. However, at the present time, calcium is a relatively expensive metal so unless it can be produced cheaply, it is difficult to see how this process can be economic.

PRESENT STATE OF DEVELOPMENT OF THE PROCESS

Most of the results presented in this paper were obtained in the laboratories of the Department of Materials Science and Metallurgy, University of Cambridge. The University has patented the technology for titanium and have licensed it to QinetiQ who have sub-licensed it to British Titanium plc. QinetiQ have their own pilot plant and intend to go into powder production in 2004. British Titanium plc has a pilot plant facility in Cambridge. Recently, DARPA awarded a substantial contract to TIMET Corporation to build a pilot facility in the US. The technology for non-titanium metals Cambridge. All the pilot facilities in the UK are producing several hundred gramme samples per batch.

CONCLUSIONS

Electro-deoxidation, where an oxide is made a cathode in molten bath of alkaline earth chloride, in particular, calcium chloride, is shown to be a simple method for the reduction of many metal oxides to their metals and appears to offer advantages, both in ease of operation and economics, over metallothermic reduction using sodium or magnesium. As the reductant is essentially the electron, there is no contamination of the metal by the reagent. The product is a granular sponge which can either be processed directly or converted into powder. It should be emphasised that this is a generic technology that can be applied to a large number of metallic oxides.

Alloys and intermetallic compounds can simply be made by the electro-deoxidation of a mixture of oxides. This can have considerable advantages where there are density differences between the alloy components and where one of the components has a very high melting point compared to the other components. Electro-deoxidation may reduce the cost of making alloys and may create opportunities for novel alloys to be synthesised with unique and valuable properties.

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