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**Abstract**: Fossil fuels will eventually be replaced by renewables. Currently, the most feasible and efficient way of utilising renewable energy is to convert it to electricity. In response to this change, fossil energy-based pyrometallurgical processes will inevitably shift to electricity driven processes. This chapter considers the feasibility of direct conversion of mineral to metal powder using a new electrochemical method, the FFC Cambridge process (Fray, Farthing and Chen). The discussion will be on the background of electrometallurgy and powder metallurgy, the principles of the new process and its application for metal powder production, and the direct route from oxide precursors to alloyed powders.

Key words: alloys, electrolysis, metal oxides, metals, molten salts, powders.

# 2.1 Background of electrometallurgy and powder metallurgy

The predictable exhaustion of fossil resources in the near future<sup>1</sup> challenges the current metallurgical industry which is largely based on carbothermic reduction of minerals to their respective metals.<sup>2</sup> Obviously, without the cheap supply of carbon (e.g. coal and natural gas), production of metals will become expensive or even unaffordable. To maintain the sustainability of metal supply, alternative processes have to be developed that can utilise renewables. In fact, in the carbothermic reduction of metal oxide-based minerals, the carbon functions in two ways: it provides the electrons needed to reduce the minerals to the metals and reacts with oxygen to supply energy (heat) to enable the reduction. Fortunately, these two roles of carbon can be undertaken by electrons which are commonly the direct product of conversion of renewables to electricity. In other words, in the renewable era most, if not all, carbothermic reduction processes will and must be replaced by direct or indirect electrolytic processes.

However, the truth is that metal production via electrolysis has long been established and plays important roles in the extraction and/or refining of some important metals, such as aluminium, nickel and copper. In these industrialised electrolytic processes, a common feature is the cathodic deposition of the metal from an electrolyte containing the metal ion. The differences are found in the anode reaction. In the electrolytic extraction of aluminium, the anodic process is the discharge (or oxidation) of the oxide ion,  $O^{2-}$ . The net process

is the decomposition of the feed alumina, Al<sub>2</sub>O<sub>3</sub>, into aluminium metal and oxygen, which in turn reacts with the carbon (anode) to produce  $CO_2$  at elevated working temperatures (e.g. 900°C). The process does not change the composition of the electrolyte. For nickel extraction, the feed mineral is nickel sulfide, NiS, which is attached to the anode. During electrolysis, the solid sulfide is anodically decomposed into solid sulfur and the nickel ion. Ni<sup>2+</sup>, which enters the electrolyte and is then transported to the cathode to be reduced to nickel metal. Again, the process does not incur changes in the electrolyte. Copper is primarily extracted from copper sulfide, first by converting sulfide to oxide (roast) followed by carbothermic reduction. However, the product still contains too many impurities and needs refining, which is achieved by electrolysis using impure copper as the anode. During electrolysis, the impure copper is anodically oxidised to the copper ion,  $Cu^{2+}$ , leaving most of the impurities, particularly the non-metallic ones, on the anode. The  $Cu^{2+}$  ion then enters the electrolyte, is transported to and is reduced to purer copper at the cathode. In principle, the process should also only separate copper from the non-metallic impurities without altering the electrolyte.

It should be noted that all electrolytic processes occur in a liquid electrolyte which can be an aqueous solution containing an appropriate supporting electrolyte, such as  $H_2SO_4 + CuSO_4$  for copper refining, and  $H_2SO_4 + NiSO_4$  for nickel extraction, or a molten salt at elevated temperatures, for example, the molten mixture of  $Na_3AlF_6$  (cryolite),  $AlF_3$  and  $Al_2O_3$  for aluminium extraction. There are two other types of electrolytes that are more commonly used in laboratories, that is organic electrolyte composed of an organic solvent and an appropriate inorganic or organic salt, and ionic liquids which are basically room temperature molten salts composed of relatively large cations and anions which are often organic.

In comparison with more commonly used pyrometallurgy (particularly via carbothermic reduction), electrometallurgy is advantageous in several aspects. It has a relatively simpler device requirement, has greater process efficiency and a lower environmental impact. The process operation and product quality are also easier to control. One disadvantage is that all electrolytic processes require a higher energy input and hence a greater cost which is offset by the fast increasing cost of using carbon-based fossil resources. The other disadvantage is that all existing electrolytic processes are specific for a particular metal. This situation may change because a more generic technology, that is the FFC Cambridge process (Fray, Farthing and Chen), emerged in recent years and can in principle be applied to the extraction of most pure metals, as well as to direct synthesis of alloys.<sup>3,4</sup> This new process is especially attractive because it can be applied to produce powders of either a pure metal or an alloy, as will be introduced in more detail in the next section.

Metal or alloy powders can be used for various purposes, but they are mostly applied in powder metallurgy, particularly for the manufacture of metallic products with complicated or near-net shapes.<sup>5,6</sup> There are a number of conventional manufacturing methods for producing metallic products, such as melting and casting, and machining. The former requires the metal to be melted at elevated temperatures and hence is energy intensive. The latter produces a large quantity of waste (e.g. turnings and spent lubricant). In contrast, powder metallurgy produces specially shaped products directly from the powder of either pure metal or alloy through sintering, often pressurised, at temperatures much lower than that used to melt the metal. It is therefore simple in processing equipment and operation, effective in product quality control, and low in energy input, and produces less waste. In addition, powder metallurgy is also preferred to traditional melting and casting technologies to produce and process metal alloys containing metals of very different reactivities, densities and melting points. These advantages of powder metallurgy can only be realised on the basis of the low cost availability of the various metal and alloy powders.

Metal powders are industrially produced by two main techniques. For metals with low melting points such as aluminium, the so-called atomisation process is usually chosen.<sup>7</sup> The principle of atomisation is to force a liquid metal together with a stream of gas through a small orifice that turns the liquid into small droplets which, upon cooling, solidify into fine particles. The direct product from atomisation usually features spheres, as shown in Fig. 2.1(a).<sup>8</sup> The particle sizes of metal powders produced by atomisation vary, ranging from tens of micrometres to sub-micrometres, although products can be made more uniform by process control and/or post-process sieving.

Atomisation is possibly the most applied method for producing metal powders. However, for metals with high melting points, other techniques are needed. For example, chromium powders find many applications, including high-performance non-ferrous alloys,<sup>9</sup> sputter target material for plasma or



*2.1* (a) Aluminium<sup>8</sup> and (b) chromium<sup>17</sup> powders produced by atomisation and milling, respectively.

spray coating,<sup>10</sup> and cermets, which are metal-ceramic composites with high electric conductivity, thermal stability and corrosion (oxidation) resistance.<sup>5,6</sup> Chromium has a melting temperature of 1857°C. Thus, chromium powder is very difficult, if not impossible, to produce by the atomisation method. At present, commercial production of chromium powder involves two main steps: (1) metallothermic (e.g. Al or Ca) or electrolytic (extraction) reduction, and (2) mechanical milling,  $^{2, 11}$  which both contribute significantly to the high market price of the material (US\$6-10 per kg). The chromium products of these extraction methods are brittle, particularly the electrolytic product which is contaminated by hydrogen<sup>2,11</sup> and can be crushed and milled into powder. However, the milling process not only has a long operation time. but also involves the risk of contamination of the powder product by constituents in air and by the mill tools.<sup>12</sup> In addition, the milled powder has a wide range of particle sizes and shapes and very fine materials are usually screened out and rejected. Figure 2.1(b) shows a typical example of the commercial chromium powder prepared by milling. It can be seen that the powder particles have a great number of irregular shapes and very many different sizes, ranging from sub-micrometres to a few tens of micrometres.

There are, of course, other methods for production of metal powders,<sup>5,6</sup> but they are all a follow-on step to the extraction of the metal from the mineral. It will obviously be advantageous if the metal powder can be produced directly from the mineral, which is a more direct process and also saves energy. In the following sections, the recent development of the FFC Cambridge process is reviewed for making metal powders directly from the mineral precursors, for example oxides and sulfides, using molten salts as the electrolytes.

# 2.2 Principle and main technological prospects for the FFC Cambridge process

The FFC Cambridge process was proposed in late 1990s, named after the inventors, Derek J. Fray, Tom W. Farthing and George Z. Chen who were then working at the University of Cambridge.<sup>13,14</sup> To date, most reported studies have revealed that the energy consumption of the FFC Cambridge process is generally lower than that of other existing technologies, although variations can be significant between different metal oxides.<sup>4,15–20</sup> For example, according to published literature, the electrolysis energy consumption in making titanium by the FFC Cambridge process is below 20 kWh kg<sup>-1</sup> Ti in laboratory,<sup>16</sup> whilst the overall energy consumption is over 50 kWh kg<sup>-1</sup> Ti in the Kroll process which is currently the dominant industrial method for extraction of titanium and zirconium. Similar findings are reported for other metals and alloys in the form of either a porous body or powder,<sup>4,15–20</sup> making this new process a potential commercial alternative to existing carbon-based technologies.

Briefly, the FFC Cambridge process can be explained using the solid state electroreduction of  $SiO_2$  to Si as an example.<sup>18,19</sup> It starts by making the oxide into a cathode which is then placed in the molten salt, typically CaCl<sub>2</sub> at 900°C. After inserting the anode, for example a graphite rod, electrolysis is carried out between the cathode and the anode at a voltage that is sufficiently higher than the decomposition voltage of the oxide at the cathode. In this process, driven by the negative potential applied on the cathode, the oxide is reduced to silicon which remains on the cathode, whilst the oxygen in SiO<sub>2</sub> is ionised, enters the molten salts, is transported by diffusion and convection to and is discharged at the anode. The electrode and overall cell reactions can be summarised below using a carbon-based anode.

Oxide cathode: 
$$SiO_2 + 4 e = Si + 2 O^{2-}$$
 [2.1]

Carbon anode:  $x O^{2-} + C = CO_x + 2x e (x = 1 \text{ and } 2)$  [2.2]

Cell: 
$$x \operatorname{SiO}_2 + 2 \operatorname{C} = x \operatorname{Si} + 2 \operatorname{CO}_x$$
 [2.3]

In reaction [2.2],  $CO_x$  refers to both CO and  $CO_2$  as observed in past studies of the FFC Cambridge process and other molten salt-based electrochemical processes, such as the aluminium extraction mentioned in the previous section. The ratio of the two gases depends particularly on the temperature and the cell voltage. Obviously, this anode reaction consumes the anode and emits greenhouse gases, although it is supposed to lower the cell voltage. To avoid frequent replacement of the anode and a carbon impact on the environment, effort has long been made to develop a so-called inert anode. This is typically made from materials that are electrochemically and chemically inert in molten salts, but conductive to electrons or the oxide ion,  $O^{2-}$ . A few recent studies have shown promising results using polycrystalline SnO<sub>2</sub> (often doped with Cu and other elements), a composite of CaRuO<sub>3</sub> and CaTiO<sub>3</sub>, and oxide ion conducting membranes for the FFC Cambridge process.<sup>21–25</sup> If this inert anode is used, the cathode reaction will remain the same, but the anode and cell reactions will change as follows:

Inert anode: 
$$2O^{2-} = O_2 + 4 e$$
 [2.4]

Cell: 
$$SiO_2 = Si + O_2$$
 [2.5]

Reactions [2.1] to [2.5] represent the overall electrode and cell reactions in the FFC Cambridge process, but the practice is more complicated, particularly on the cathode as explained in the following sections.

It is worth mentioning that direct electrochemical reduction of a solid compound attached to a cathode has been known for years, for example AgCl to Ag in the commonly used reference electrode, and PbSO<sub>4</sub> to Pb in the well-known lead acid battery. However, before proposal of the FFC Cambridge process, no previous work had succeeded to utilise this electrochemistry

for extraction of metals, particularly reactive metals and semi-metals like titanium and silicon.

Cell designs are a core technological issue in the research and development of the FFC Cambridge process. A number of cell designs have been proposed, as shown in Fig. 2.2, and tested successfully in the laboratory for proof of the concept (I),<sup>3</sup> fundamental research (II to VI),<sup>3,4,17-19,26-30</sup> near-net-shape manufacturing (VII),<sup>30</sup> and scale up (VIII), whilst type IX was specifically proposed for metal powder production.<sup>31</sup> Several other technological issues are discussed below in connection with the configuration of the cell.

The FFC Cambridge process has been mostly researched using metal oxides as the feedstock to construct the cathode,<sup>4</sup> whilst sulfides are emerging as an emission-free option when used together with a graphite anode (see later discussion).<sup>32–34</sup> Because components of air can attack metals at elevated temperatures (e.g. formation of oxides and nitrides), the process needs to be operated with appropriate protection. The electrolytic extraction of aluminium in industry is protected by a solidified surface layer (salt crust) above the molten salt. The 'salt crust approach' is in principle applicable to the FFC Cambridge process, but it is not as convenient as using an inert gas and not necessarily cheaper in laboratory. Argon is often chosen, although nitrogen can be used if it does not react with the metal produced. Vacuum should not be applied for protection to avoid evaporation of the molten salt.

Another technological issue is the selection of molten salts. The FFC Cambridge process needs an electrolyte that can dissolve and transport the anions released at the cathode, e.g.  $O^{2-}$  or  $S^{2-}$ , to the anode. There are only a few pure molten chloride salts that can dissolve and transport the oxide ion, including CaCl<sub>2</sub>, BaCl<sub>2</sub> and LiCl. Of these three, CaCl<sub>2</sub> is the cheapest with the lowest toxicity and hence is widely used. However, one of its main disadvantages is a relatively high melting temperature (762°C) and quite a large electronic conductivity when the applied cell voltage is sufficiently high to force a cathode potential close to that for the reduction of the  $Ca^{2+}$  ion.<sup>29</sup> In a two electrode cell,  $Ca^{2+}$  ion reduction may occur at an applied voltage that decreases from the decomposition voltage of CaCl<sub>2</sub> to that of CaO (3.099 to 2.520 V at 900°C) with an increasing concentration of the  $O^{2-}$  ion in the molten salt. The other common chloride salts, such as NaCl and KCl, have relatively poor solubility for the O<sup>2-</sup> ion, and are thus not suitable to be used alone in the FFC Cambridge process.<sup>35</sup> Of course. two or more of these chloride salts can be mixed to achieve some desired properties, such as a lower working liquid temperature to save energy, and/ or a lower solubility of the  $O^{2-}$  ion to reduce the electronic conductivity of the electrolyte. These changes should be maintained at a certain level so that the reaction kinetics at the electrodes and ion transport through the electrolyte are not compromised too much. More recently, some fluoride



2.2 Cell designs with a cathode of type: (I) pellets-in-crucible,<sup>3</sup> (II) suspended pellet(s),<sup>3</sup> (III) a thin coating (image: cross sections of TiO<sub>2</sub> coated Ti foil before and after electroreduction),<sup>26</sup> (IV) powder-in-cavity (top: SiO<sub>2</sub> powder loaded in the through-hole of a Mo foil; bottom: cracks in the fractured end of Mo wire)<sup>27–29</sup> (V) a disc-with-oxide-sheath,<sup>19</sup> (VI) a contact-pin,<sup>18,30</sup> (VII) porous-oxide-preforms (for near-net-shape manufacturing of engineering components as shown by the images),<sup>30</sup> (VIII) pellets-in-basket,<sup>3,15</sup> (IX) stirred powder-in-ladle.<sup>31</sup>

salts were applied to support the FFC Cambridge process,<sup>36</sup> although the toxicity of these salts may cause environmental concerns if used at large scales.

As will be discussed below, all electrode reactions are driven by the electrode potential or more strictly, the overpotential. Thus, control of the electrode potential is important to ensure high process efficiency and satisfactory product quality. In common electrochemical practices, electrode potential control is achieved using a reference electrode. For molten salts research, the most often used reference electrode is the Ag/AgCl couple contained in a closed thin wall tube of glass, Mullite or quartz.<sup>37–39</sup> However. these container materials are unstable for the long term operation of the FFC Cambridge process in which the molten salt can become rich in  $O^{2-}$  ions which can attack SiO<sub>2</sub>-based materials.<sup>39</sup> The FFC Cambridge process has so far been researched and developed in a two-electrode cell, in most cases, to demonstrate its electrochemical and engineering feasibility. However, it can be anticipated that optimisation of the process for commercial purposes will require further improvement in both process efficiency and product quality, depending on the ability to control the electrode potential. Particularly, in order to produce metal powders with the desired properties, such as particle size and elemental composition, accurate potential control can become a crucial technical issue, calling for effort to develop more reliable and long lasting reference electrodes.

# 2.3 Production of metal powders by the FFC Cambridge process

It is possible to produce metal powders by operating the FFC Cambridge process under appropriate conditions when the feedstock is a metal oxide or sulfide powder and is converted to a porous pellet or other preforms for attachment to the cathode (current collector). Electrolysis temperature and time are the two most important factors. It is generally observed in powder metallurgy that sintering a metal powder becomes significant when the temperature reaches or is above two-thirds of the melting point (in Kelvin) of the metal.<sup>40</sup> The effectiveness of sintering improves with the heating time. To make metal powders by the FFC Cambridge process, sintering should and can be avoided or minimised by applying a temperature below two-thirds of the metal's melting point for a sufficiently short time so that the reduction is completed. The third control parameter is the cell voltage. Because the electroreduction speed increases with the cell voltage, a higher cell voltage means a shorter time for complete reduction and hence less sintering of the metal powder produced at the cathode. Nevertheless, the cell voltage should still be lower than the decomposition voltage of the molten salt(s) to avoid contamination and unwanted by-products.

When using a metal oxide powder as the feedstock, the basic change in the FFC Cambridge process is the removal of large oxide ions, leaving the small metal atoms on the cathode. Consequently, both the mass and the volume of the material left on the cathode would in most cases be reduced (unless the molar volume of the metal is larger than that of the metal oxide). In all successful cases using the FFC Cambridge process to extract metals from their oxide precursors, the molar volume of the metal is always smaller than that of the oxide. Otherwise, as in the case of MgO and Mg, the electroreduction would be unable to continue.<sup>16</sup> Therefore, if sintering is avoided, the particle size of the produced metal powder will be smaller than that of the metal oxide powder. For example, the molar volume of tantalum is  $V_{T_2} = 10.868$ cm<sup>3</sup> mol<sup>-1</sup>, whilst that of its oxide, Ta<sub>2</sub>O<sub>5</sub> is  $V_{Ta_2O_5} = 53.889$  cm<sup>3</sup> mol<sup>-1</sup>. This change in molar volume corresponds to a dimension reduction of  $(2V_{T_a}/V_{T_a,\Omega_5})^{1/3} = 0.739$ . In other words, a Ta<sub>2</sub>O<sub>5</sub> powder with a particle size of 300 nm can be reduced to a Ta powder 200 nm in size. This feature of the FFC Cambridge process is useful because smaller Ta particles give greater specific surface areas and larger capacitance.<sup>41</sup>

According to the literature, it is interesting to note that the body shapes of the oxide or sulfide precursors (e.g. porous cylindrical pellets) are retained in metallised products in FFC Cambridge process, presenting an opportunity for near-net-shape manufacturing, see Fig. 2.2 part VI.<sup>42</sup> However, at particulate levels, there is no direct relationship between the feedstock and the product. As shown in Fig. 2.3, the electrolytically produced metal powders can be lightly interconnected nodules (Fig. 2.3(b) and (d)) (Ti, Ta, Nb, Zr, Ni, Mo, W),<sup>3,32,34,41-43</sup> more regularly shaped crystallites, such as cuboids (Fig. 2.3(f)) (Cr, Fe)<sup>17,44</sup> and even micro- and nano-wires (Fig. 2.3h) (Si, Cu).<sup>45</sup> The causes of such differences in particle morphology are not fully understood, although it is possible to start from the discussion below to develop understanding further.

The cathode reactions in the FFC Cambridge process can be basically explained by the models of charge transfer at the compound/metal/molten salt three phase interline (3PI) (boundary), particularly if the compound, such as oxide and sulfide, has poor conductivity. Whilst details of the 3PI models can be found in the literature, <sup>17,18,30,46</sup> Fig. 3.4 illustrates the concept using a spherical and insulating metal oxide particle as an example. The process starts at the very first 3PI (which could be a point), converting the compound (oxide) there to metal. The newly formed metal with the oxide and molten salt next to it then forms new 3PIs. When these processes continue, the 3PIs move along the surface of the particle until all the surface layer is porous due to the molar volume of the metal being smaller than that of the oxide, molten salt can access the interior of the particle, oxygen ions can move out through the molten salt contained in the pores of the metallised surface and,



2.3 SEM images of the commercial powders of (a)  $Ta_2O_5$ ,<sup>41</sup> (c)  $MoS_2$ ,<sup>44</sup> (e)  $Cr_2O_3$ ,<sup>17</sup> and (g)  $SiO_2$ ,<sup>45</sup> and their electroreduction products (powders), (b) Ta,<sup>41</sup> (d) Mo,<sup>44</sup> (f)  $Cr^{17}$  and (h) Si,<sup>45</sup> prepared under the indicated conditions. Molten  $CaCl_2$  was used in all these cases. Figures 2.3(g) and (h) by permission of The Royal Society of Chemistry.

the reduction continues, accompanied by the 3PIs moving along the depth direction into the interior of the oxide particle.

It is worth pointing out that the boundary connecting three different phases



2.4 Schematic illustration of the propagation of the three phase interlines  $(3Pls)^{30}$  during the electroreduction of two connected spherical particles of a metal oxide (TiO<sub>2</sub> in this figure) whose molar volume is larger than that of the metal.<sup>16</sup> The extra thick lines indicate the 3Pls.

can only be a line or point, although charge transfer reactions involve both electrons and ions in close proximity to the geometric 3PI. The emphasis here, similar to the use of the concept of the 'two phase interface' for conventional electron and ion transfer reactions involving the electrode and

the electrolyte, is on the concept of the 'three phase interline' which helps to focus on the geometric location of the reactions.<sup>46</sup>

Qualitatively, electroreduction will be quicker to complete on smaller metal oxide particles, but the actual time or rate of reduction should also depend on the nature of the metal oxide. For example, at the same applied cathode potential and temperature in molten CaCl<sub>2</sub>, it was observed that NiO or Fe<sub>2</sub>O<sub>3</sub> could be reduced much quicker than TiO<sub>2</sub><sup>20,47</sup>. To explain this phenomenon requires understanding of the reduction mechanism and kinetics which are interdependent.

Electrochemical reactions are largely driven by the applied electrode potential. The comparison of the rates between different electrode reduction reactions needs to be made on the basis of how much the applied potential, E, is more negative than the standard reduction potential of each oxide,  $E^{\circ}$ . The difference is defined as the overpotential,  $\eta = |E^{\circ} - E|$ . The value of  $E^{\circ}$  can be derived from the Gibbs free energy of formation,  $\Delta G^{\circ}$  for each compound at a given temperature, for example, at 900°C, it is 1.960 V (vs. Ca/Ca<sup>2+</sup>) for NiO/Ni, 1.089 V for TiO<sub>2</sub>/TiO, and 0.421 V for TiO/Ti. Note that the thermodynamically calculated potential for TiO<sub>2</sub> to Ti is easier than from TiO to Ti. However, because the reduction from TiO<sub>2</sub> to TiO occurs at a more positive potential, formation of TiO is inevitable during the reduction of TiO<sub>2</sub>, in agreement with experimental findings.<sup>16,26</sup> Thus, to obtain Ti metal from TiO<sub>2</sub>, the potential applied needs to be at or less positive than 0.421 V for TiO/Ti.

Besides the applied potential (or overpotential), it is commonly observed that the electroreduction of a metal oxide often includes intermediate steps where, in the case of electroreduction of TiO<sub>2</sub> in molten CaCl<sub>2</sub>, various calcium titanate (or perovskite) phases are formed.<sup>26,28,31</sup> These intermediate phases may be formed either electrochemically or chemically and exert a detrimental effect on process efficiency.<sup>28</sup> This is because the inclusion of Ca expands the local volume in the cathode and blocks nearby pores that are needed to transport the O<sup>2–</sup> ions. A couple of recent reports show that the influence of the perovskites may be minimised by properly engineering the oxide precursors, such as perovskitisation of the oxide precursors,<sup>28</sup> or making the precursor highly porous using NH<sub>4</sub>HCO<sub>3</sub> as a fugitive porogenic agent.<sup>16</sup>

However, in making reactive metal powders, the FFC Cambridge process suffers from the same problem as the other metal powder production techniques. Because of the relatively large specific surface area of a powder, upon exposing it to air or water, natural oxidation of the reactive metal occurs readily on the surface of the metal particles. The added challenge to the FFC Cambridge process is to separate the metal powder from the solidified molten salt. Washing with water is effective because of the large solubility of alkali and alkaline earth chlorides. However, for reactive metals such as Ti and Zr, oxidation of the surface occurs spontaneously in water. The formed oxide layer may be only a few nanometres thick, but the overall oxygen content can increase significantly with decreasing particle size. For example, for Ti spherical particles 2  $\mu$ m in diameter with a 3 nm thick surface oxide layer, the oxygen content can be about 3900 ppm, which agrees very well with a recent study of the Ti product from the FFC Cambridge process.<sup>16</sup>

To minimise the influence of water, attempts were made in the past to use a non-aqueous solvent to wash rare earth metal powders produced by the FFC Cambridge process. (In fact, it is impossible to use water for rare earth metals because they react with each other.) The tests were fairly successful in the laboratory, but require further development at larger scales to assess the effectiveness, costs and environmental impact. Nevertheless, it is worth mentioning that inorganic chloride salts are usually poorly soluble in an organic solvent, whilst in many cases the residual water in the solvent might have produced interesting effects. In fact, even under strictly dry conditions (e.g. in a working glovebox), dissolving alkali and alkaline earth chlorides into an organic solvent may be assisted by using a chelating ligand, such as crown ethers whose ring sizes offer good selectivity towards different cations. These organic systems are an area that is worthy of further investigation, particularly in association with production of reactive metal powders by the FFC Cambridge process.

On the other hand, in principle, separation of the solidified molten salt from the metal powder may be achieved through distillation under vacuum, which is a standard step in the Kroll process. In addition to increased energy consumption, the application of vacuum distillation to the FFC Cambridge process also requires technical modification considering the boiling temperature of the molten salt used. At present, CaCl<sub>2</sub> is commonly studied in laboratories for the FFC Cambridge process, whilst in the Kroll process, MgCl<sub>2</sub> by-product must be removed. The boiling temperature is 1412°C for MgCl<sub>2</sub>, but it is higher than 1600°C for CaCl<sub>2</sub>. To compromise, it is technically possible to apply a higher vacuum to distil CaCl<sub>2</sub> by balancing energy consumption in terms of heating and vacuum.

The other potential approach is to replace molten  $CaCl_2$  by another molten salt with a lower boiling temperature. In the current literature, molten LiCl is one of the few systems studied. LiCl has a boiling temperature below 1400°C and is thus easier to distil. Molten LiCl with added Li<sub>2</sub>O was successfully used to accommodate the electroreduction of uranium oxides to uranium metal.<sup>48</sup> However, different results were reported for the electroreduction of TiO<sub>2</sub> in molten LiCl,<sup>49,50</sup> calling for further investigations to explore the potential benefit to the separation of solidified salt from the reactive metal product by vacuum distillation. Considering the electrochemical aspects, the standard potential of the TiO/Ti couple is 56.2 mV vs. Li/Li<sup>+</sup> at 900°C. Such a small difference between TiO/Ti and Li/Li<sup>+</sup> makes it a practical challenge to reduce  $TiO_2$  to Ti in molten LiCl. However, to make high quality powders of those less reactive metals, molten LiCl remains a candidate worthy of investigation.

In more recent years, the FFC Cambridge process has been applied to prepare metal powders from their sulfide precursors, with results promising an emission free, low energy and fast metal powder production method whilst still using a carbon anode. Metal sulfides that were successfully tested include CuS, MoS<sub>2</sub> and WS<sub>2</sub>.<sup>32-34</sup> There are similarities and differences between electroreduction of metal oxide and metal sulfide. The sulfide cathode process is very similar to reaction [2.1], just replacing the oxide ion,  $O^{2-}$ , by the sulfide ion,  $S^{2-}$ . The products of electroreduction of metal sulfides are also nodular in shape as exemplified in Fig. 2.3(d). However, on a carbon anode, the discharge of the  $O^{2-}$  ion makes CO and CO<sub>2</sub>, whilst discharge of  $S^{2-}$  ion produces only sulfur vapour,  $S_2$ , which condenses to solid readily after moving from the electrolyser to a collector at ambient temperature. In other words, the carbon anode behaves as an inert anode in the discharge of  $S^{2-}$ , making the anode reaction similar to reaction [2.4] by replacing O with S. Figure 2.5(a) shows photographs of a carbon anode before and after use in a 60 h sulfide electrolysis experiment, confirming the absence of any noticeable erosive or corrosive attack on the carbon, even at microscopic levels.34



2.5 Photographs of a graphite rod anode before (a) and after (b) electrolysis of WS<sub>2</sub> in molten equimolar NaCl–KCl at 2.7 V and 700°C for 60 h.<sup>34</sup> The two boxed regions in (a) and (b) are enlarged in (c) and (d) respectively to show that machining marks remain almost unchanged, proving the inertness of the graphite towards the anodic discharge of sulfide ion.

#### 2.4 Direct route from oxide precursors to alloyed powders

In conventional alloy making processes, there are at least two main steps: the composing metals of an alloy are extracted separately from their minerals and often refined to a sufficient purity, and the metals are then melted together, probably repeatedly to ensure uniformity, to form the alloy. A special advantage of the FFC Cambridge process is its capability to produce alloys, either a porous body or a powder, directly from the mixed oxide precursor without melting. This approach is energy saving in terms of both thermodynamics and practice. Thermodynamically, each of the composing elements of a stable alloy is in a lower energy state than the pure form of the element. Thus, mixing the component metals by melting, energy is released as heat, which may in theory compensate for the energy input for heating in a continuous process. However, this heat of alloy formation is largely wasted in batch operations. In practice, melting and casting, particularly if repeated, are also energy, time and labour consuming operations. Thus, by avoiding the melting step, the FFC Cambridge process should intrinsically consume less energy than conventional melting-casting techniques for production of alloys.

It is worth pointing out that one of the reasons for repeated melting and casting operations in the conventional method is to overcome the inhomogeneity in the product containing component metals with a large difference in density and melting temperature. For example, the well known shape memory NiTi alloy, also called Nitinol commercially, finds many applications. However, making this alloy is not straightforward because the two metals have very different melting temperatures, densities and molar volumes, as compared in Table 2.1. Melting is achieved by an electric arc under high vacuum in the water-cooled copper hearth. Particularly, the large difference in density leads to segregation of nickel from titanium in the molten mixture owing to the effect of gravity. Without melting any metal, the NiTi alloy in the porous body or powders, can be readily prepared by the FFC Cambridge process from porous pellets of mixed NiO and TiO<sub>2</sub> powders.<sup>20,51</sup> Figure 2.6 compares the X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images of the products of electrolysis of an equimolar mixture of TiO<sub>2</sub> and NiO powders at different voltages.<sup>20</sup> The differences

Property	FM	Density (g cm <sup>-3</sup> )	mp (°C)	Molar volume (cm <sup>3</sup> )
Nickel	58.693	8.908	1455	6.59
Titanium	47.867	4.507	1668	10.64

Table 2.1 Basic properties of nickel and titanium<sup>a</sup>

aInformation source: http://www.webelements.com





2.6 (a) XRD patterns and (b,c) SEM images of the products of electroreduction of equimolar mixture of  $TiO_2$  and NiO in molten  $CaCl_2$  at 900°C at the indicated cell voltages for 12 h.<sup>20</sup> Note that at 1.8 V, the product contained small nickel metal particles distributed amongst the much larger perovskite crystallites.

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between these results are indicative of the process starting with the formation of Ni metal particles which then alloys with Ti from the slower reduction of  $TiO_2$ .

The FFC Cambridge process also works very well for making ternary alloy powders. The first example is a Ni<sub>2</sub>MnGa powder which is a ferromagnetic shape memory alloy that plays an important role in highly efficient sound devices.<sup>52</sup> By mixing the three oxide powders in the designated metal ratio, pressing the mixture to a cylindrical pellet and sintering at 540°C for 2 h, electrolysis was very successful at 900°C and 3.0 V in molten CaCl<sub>2</sub> for about a day. The reduced pellet retained its body shape, but can be readily manually ground to a powder. Table 2.2 shows the elemental compositions measured by energy dispersive X-ray spectroscopy (EDX) on two randomly selected locations in the electrolytic powder sample, which matched expectation very well. The XRD pattern of the powder exhibited all the diffraction peaks, in line with those on the standard pattern for Ni<sub>2</sub>MnGa.

Another example of ternary alloy powder is related to so-called giant magnetostrictive materials which usually have the composition  $Tb_rDy_{1-r}Fe_2$  $(0 \le x \le 1)$ .<sup>53</sup> In an initial attempt, the TbFe<sub>2</sub> intermetallic compound was prepared by electroreduction of porous pellets of mixed  $Fe_2O_3$  and  $Tb_4O_7$ powders in which Tb:Fe = 1:2. In molten CaCl<sub>2</sub> at 900°C, the electroreduction proceeded to completion to a phase-pure product (TbFe<sub>2</sub>) within 10 h at 3.1 V. More importantly, the study revealed very high recovery of the expensive Tb, reaching over 97%. The process consumed energy lower than 14 kWh  $kg^{-1}TbFe_2$  with the product containing less than 1300 ppm oxygen. These achievements were claimed to be at least partly a result of pre-compounding the Fe<sub>2</sub>O<sub>3</sub> and Tb<sub>3</sub>O<sub>4</sub> powders at a sintering temperature of 1200°C, which led to the formation of co-oxide phases, such as Tb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> and TbFeO<sub>3</sub>, which were well interfused into a porous structure, as shown in Fig. 2.7(a). An important step adopted in this study was the use of an organic solvent, dimethylsulfoxide (DMSO), to wash the electrolysis product with a magnetic stirrer in a sealed conical flask, which avoided oxidation and washing loss of the magnetic product. A photograph taken during the washing process is displayed in Fig. 2.7(b). Another interesting finding of this study was that the electrolytic product which was composed of 5–10 µm nodules, see Fig. 2.7(c), could be pulverised to smaller particles by application of sonication to assist washing in DMSO, as shown in Fig. 2.7(d). The pre-compounding approach used in the making of TbFe<sub>2</sub> is a simple but highly effective way

Location	Ni (at.%)	Mn (at.%)	Ga (at.%)	χ²
1	49.62	24.67	25.71	1.73
2	49.18	27.56	23.26	1.53

Table 2.2 EDX analyses of electrolytic Ni<sub>2</sub>MnGa alloy powders<sup>52</sup>



2.7 SEM images of the interiors of the  $Tb_4O_7$ -Fe<sub>2</sub>O<sub>3</sub> (Tb:Fe = 1:2) pellet: (a) sintered in air at 1200°C for 2 h, and (b) its as-electrolysed product at 2.6 V and 900°C for 12 h.<sup>27</sup> (c) shows alignment along the magnetic lines of the particles of the collected TbFe<sub>2</sub> powder on the magnetic stirrer during washing in DMSO in a sealed conical flask. The SEM image of the TbFe<sub>2</sub> powder from washing in DMSO and magnetic collection is shown in (d). The elemental composition was confirmed by inductively coupled plasma – atomic absorption spectroscopy (ICP–AAS) analysis.

of controlling uniformity in the composition of an alloy produced by the FFC Cambridge process. This is largely because the distribution of the alloying elements in the compounded precursor is uniform at the atomic level within a short distance. Thus, once the oxygen atoms are removed at appropriate potentials, these closely arranged alloying atoms can react quickly to form the desired alloys or intermetallics.

The importance of the pre-compounding step can be also appreciated when producing  $LaNi_{5-x}M_x$  hydrogen storage alloys (powders).<sup>54, 55</sup>  $La_2O_3$  is a hygroscopic oxide and can react spontaneously with molten  $CaCl_2$ , which challenges the usual method of preparing the oxide precursor, and maintain its integrity in the molten salt during electrolysis. By pre-compounding (sintering) the  $La_2O_3$  powder mixed well with the NiO powder at elevated temperatures in air, formation of several co-oxide phases may be achieved, including  $LaNiO_3$  (< 1000°C),  $La_4Ni_3O_{10}$  and  $La_3Ni_2O_7$  (1100–1250°C), and/or La<sub>2</sub>NiO<sub>4</sub> (> 1300°C). These co-oxide phases are all very stable in air and molten CaCl<sub>2</sub>, ensuring success in the follow-on electrolysis. The precompounding step can also be applied to make LaNi<sub>5-x</sub>M<sub>x</sub> hydrogen storage alloys (powders) with three or more components so that their charge/discharge performance can be improved. The as-produced electrolytic LaNi<sub>5-x</sub>M<sub>x</sub> powders possessed fairly reversible activity in alkaline electrolyte for hydrogen storage, as evidenced in Fig. 2.8(a) by the cyclic voltammograms of the electrolytic powder of LaNi<sub>4</sub>Co.<sup>55</sup> Figure 2.8(b) compares the discharging capacity of



2.8 (a) Cyclic voltammograms<sup>55</sup> and (b) discharge capacity variation versus the number of charge/discharge cycles (60 mA g<sup>-1</sup>, 1.45 V/0.90 V)<sup>54</sup> of the indicated electrolytic LaNi<sub>5</sub>-type powders measured in 6.0 M KOH at 25°C. (c) A schematic comparison of the conventional process and the FFC Cambridge process for making LaNi<sub>5-x</sub>M<sub>x</sub> powders; superscripts indicate original references in Zhu *et al.*<sup>54</sup>



2.8 Continued

the electrolytic LaNi<sub>5</sub> powder with two multi-component LaNi<sub>5-x</sub>M<sub>x</sub> samples prepared by electrolysis of the pre-compounded precursors. Note that the theoretical electrochemical hydrogen storage capacity for charging LaNi<sub>5</sub> to LaNi<sub>5</sub>H<sub>6</sub> is 371.9 mAh g<sup>-1</sup>, which is not too far from the maximum discharging capacities measured for the electrolytic LaNi<sub>5</sub> and LaNi<sub>4</sub>Co powders. Fig. 2.8(c) illustrates the flowcharts of the conventional and the FFC Cambridge processes for making the LaNi<sub>5</sub> powders, showing clearly the advantages of the FFC approach: simple, direct and energy efficient.<sup>54,55</sup>

## 2.5 Conclusions and future trends

Since the publication of the original patent in 1999, the FFC Cambridge process has attracted great attention in both the industry and academia. While its commercial development is beyond the scope of this chapter, the prospects for using this new process to produce metal powders, particularly pre-alloyed powders, are introduced in terms of the principles and the technological advantages compared with existing industrial processes. In particular, research on the FFC Cambridge process has so far succeeded in production of most tested pure metal, binary and ternary alloy powders with

accurate control of the elemental composition and low energy consumption. Many of these developments offer great versatility and flexibility to meet application needs. On the other hand, this chapter also offers analyses of the technical challenges ahead of the optimisation and commercialisation of the FFC Cambridge process, and possible solutions. It is obvious that the space allocated here is insufficient to give a more comprehensive review of the literature on this new process for making metal powders. Nevertheless, it is hoped that this chapter may stimulate and be of some assistance to readers with interests in making wider investigation and further development of the FFC Cambridge process for production of metal powders, particularly in demonstrating its great technological potential in the post-fossil era.

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