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Production of NiTi via the FFC Cambridge Process

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The FFC Cambridge process is a direct electrodeoxidation process used to reduce metal oxides to their constituent metals in a molten $CaCl_2$ salt bath. NiTiO₃ was used as a precursor (the first stable oxide to form upon blending and sintering NiO and TiO₂ powders) and was successfully reduced using the FFC Cambridge process at 1173 K and a constant cell voltage of -3.1 V to produce a NiTi alloy. This work builds on the literature work [Chinese Science Bulletin, 51, 2535 (2006)] through: (i) a predominance diagram calculated to show the regions of phase stability throughout the usable potential window of the CaCl₂ salt; (ii) the investigation of a wide range of reduction times for a fixed cell voltage, elucidating several additional stable phases, to yield a complete and detailed reduction pathway. The reduction pathway for NiTiO₃ was identified through the analysis of a series of partial reductions, with fully reduced NiTi formed after a period of 24 h. The first stage of the reaction involved the rapid formation of Ni and CaTiO3. The reduction then proceeded via the formation of the intermediate compounds Ni3Ti and Ni2Ti4O. All the NiTiO₃ and Ni were consumed after a period of 6 h, while the intermediate compounds remained until the reaction was near completion. The experimental results related well to the thermodynamic predictions of the predominance diagram. A small variation in stoichiometry of the produced NiTi observed from the edge to the core of the samples was attributed to redeposition of Ti on the sample surface from the salt and a slightly Ti-rich NiTiO₃ precursor material. © 2008 The Electrochemical Society. [DOI: 10.1149/1.2987739] All rights reserved.

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NiTi alloys have high abrasion resistance, good elasticity, and possess shape memory properties. These materials have many important industrial and commercial applications, from actuators in air/spacecraft to damage-resistant frames for eyeglasses to use in biomedical implants and devices.

The main factor limiting their range of applications is the difficulty, and hence the cost, of their manufacture. Conventional manufacturing of NiTi is usually via one of three routes: high-temperature melting, high-energy ballmilling of mixed pure metals, or by powder metallurgy.^{1,2} These methods require a very large energy input, specialist equipment, high vacuum, and expensive high-purity Ti and Ni feedstock. For the last 50 years, Ti powder has been produced using the Kroll process (and to a limited extent by the Hunter process), a high-temperature batch method that involves the use of highly toxic chlorine to react with rutile to form TiCl₄. The TiCl₄ is then reacted with Mg and vacuum distilled to form Ti powder and an MgCl₂ by-product (which may be recycled through molten salt electrolysis). The production of Ni is also an energy-intensive electrolytic process that involves the production of sulfuric acid, which has potential health, safety and environmental issues.¹ Segregation in the manufacture of NiTi poses a significant challenge in hightemperature melting. The different densities and melting points of Ti and Ni cause segregation of Ni in the melt, thus necessitating remelting in the alloying process, which is both costly and time consuming.

Over the past decade, efforts have intensified to find a low-cost and more environmentally friendly alternative to the Kroll process. Of the dozen or so emerging processes to produce Ti powder, the Armstrong/ITP,³ and MER⁴ processes have received substantial U.S. government funding to develop pilot scale capabilities. The Armstrong/ITP process is essentially a continuous version of the Hunter process. It involves the injection of gaseous TiCl₄ into a flowing stream of molten Na, thus reducing and cooling it to produce Ti powder. The MER process employs carbothermic reduction of TiO₂ to produce TiO_{2-x} (where $x \approx 1$). An anode composed of carbon and this oxide is then constructed and is reduced to Ti via electrolysis.

Another competing process, and the focus of this paper, is the FFC Cambridge process.⁵ Over the last 7 years several companies have taken steps to commercialize the process, with the way currently being led in the U.K. by Metalysis. Other companies include BHP Billiton, British Titanium, Metalysis, Norsk Titanium, Timet, and QinetiQ. Worldwide the major players are Metalysis and Norsk Titanium, as the former has acquired the activities of QinetiQ and BHP Billiton.

A schematic of the FFC Cambridge process cell is shown in Fig. 1. The process involves the progressive reduction of a TiO₂ cathode in a molten $CaCl_2$ salt bath. Oxygen is stripped from the TiO_2 at the cathode, and O^{2-} ions are transported via the salt to a consumable graphite anode. The oxygen combines with the anode and is evolved as CO or CO_2 .^{6,7} The cell is sealed and is continuously purged with Ar to generate an inert atmosphere. Ti alloys may be efficiently produced via the FFC Cambridge process by reducing precursors consisting of a mixture of the relevant metal oxides.⁸⁻¹⁰ This work will show that in the case of NiTi, an equiatomic, low-oxygen product may be produced through the reduction of NiO-TiO2 mixed precursors

Successful production of NiTi via the FFC will avoid the costly melting and remelting steps employed in the conventional manufacturing routes. The process allows the production of near-net-shape



Figure 1. Schematic of the FFC Cambridge process.

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products with very few prereduction processing steps. Also, the flexibility of the process means that small batches of high-value, nonconventional, and specialized alloys may be made economically.

Many researchers have attempted to identify the underlying electrochemistry and the reduction pathway for the reduction of TiO_2 to Ti metal.^{5,11-14} This system is now fairly well understood. However, the reduction of NiO-TiO2 mixed precursors to form NiTi has received relatively little attention.¹ Previously, Zhu et al. performed a series of experiments concerning the reduction of NiTi. Their investigations concerned (i) the effect of electrolysis voltage on the reduction product (fixed time), and (ii) the effect of reduction time on the product (fixed voltage). Both sets of experiments examined six individual voltages and reduction times, respectively. This work describes the successful production of low-oxygen equiatomic NiTi via the FFC Cambridge process using a similar methodology to that used in Ref. 1. It builds on the work of Zhu et al. as follows: (i) The calculation of an electrochemical predominance (Littlewood) diagram to show the regions of phase stability throughout the entire range of possible electrode potentials for the CaCl₂ salt, from 0 V applied voltage, to the breakdown voltage (defined as the voltage required for deposition of Ca at unit activity in the salt). This diagram encompasses additional thermodynamically stable phases that have not been considered in Ref. 1. This diagram represents a significant contribution to the solution electrochemistry of the system. As to the authors' knowledge, this is the first such diagram to be calculated for the Ni-Ca-Ti-Cl-O system. (ii) The investigation of a wider range of reduction times for a fixed cell voltage, thus elucidating a more complete and detailed reduction pathway, with the help of the results of (i). (iii) The further experimental verification of the "3-phase interline" mechanism proposed for sample metalliza-tion by Chen et al.¹⁵ and Deng et al.¹⁶ The results of this work have also been compared with and validated against studies to investigate the initial oxidation of NiTi for biomedical applications.^{17,18}

Experimental

Pellet precursor production .- The starting material for all of the experiments performed was the commercially available NiTiO₃ powder (procured in micrometer powder form from Pfaltz & Bauer, Inc.). This source was chosen over mixing individual batches of NiO and TiO₂ manually in the interests of repeatability of the experiments (the same batch of powder was used for all experiments). The as-received powder was ground in a mortar and pestle together with a small amount of distilled water, which acted as a binder for the initial stages of pellet production. One gram of the powder per pellet was placed in a 13 mm diameter die and subjected to a uniaxial compressive pressure of 222 MPa for 60 s. The compacted pellets were then drilled by hand with a 3 mm diameter hole to allow them to be attached to the CP-Ti cathodic current collector. They were then placed in an alumina crucible and subjected to the following sintering schedule: ramp at 3 K min⁻¹ in air to 1373 K; hold for 3 h; furnace cool.

Electrochemical reductions.— The electrochemical cell used in all the reduction experiments is shown schematically in Fig. 2. The reduction cell is constructed from Inconel with a water-cooled steel top plate (SFL Instron). The cell is housed in a vertical programmable tube furnace (SFL Instron). The molten CaCl₂ salt is contained in a grade 2 CP-Ti crucible of diameter 89 mm o.d., a wall thickness of 10 mm, and a height of 200 mm. The precise design of the reaction vessel has been described fully elsewhere.¹⁹

The CaCl₂ was in the form of dehydrated granules (Fluka) and was placed in the crucible and allowed to thermally equilibrate at 373 K. The CaCl₂ was then heated under an Ar atmosphere (BOC Pureshield at 200 mL min⁻¹) at a rate of 0.1 K min⁻¹ to 573 K. The Ar was oxygen gettered by passing over heated Ti turnings. The CaCl₂ was then held at 573 K for a period of 5 h. This process was to ensure that the salt was completely dry prior to heating to the working temperature. The temperature was then increased to the working temperature of 1173 K at a rate of 3 K min⁻¹.



Figure 2. Schematic of FFC reduction cell.

The final stage of preparation was pre-electrolysis of the CaCl₂ to remove any impurities present in the salt that could contaminate the reduction product. This was done through pre-electrolysis using a grade 2 CP-Ti rod as the working electrode and a graphite anode (10 mm diameter Tokai Carbon EC4) and applying a cell voltage of -2.8 V for typically 90 min. Pre-electrolysis was deemed complete when a sufficiently low background current was observed (typically 80–120 mA at -2.8 V).

The sintered NiTiO₃ precursor pellet was attached to the CP-Ti current collector and slowly lowered into the molten CaCl₂ to minimize thermal shock effects. A voltage of -3.1 V was applied across the two electrodes. This voltage was approximately 0.1 V greater than the voltage required for the deposition of Ca at unit activity in the salt. The voltage was gradually raised so as to keep the current around 500 mA. This was to ensure that all phase changes in the reduction pathway were allowed to take place, and that those requiring a larger voltage. Samples were reduced for periods of 1, 3, 6, 12, and 24 h. One sample was also exposed to the salt with no applied voltage for 600 s to observe the reduction products produced.

Analysis techniques.— Following reduction, samples were cleaned for 20 min in an ultrasonic bath in water to remove any residual salt and allowed to soak for a period of 16 h. They were then prepared for analysis using standard metallographic techniques. The samples were characterized using backscattered electron imaging (BEI), X-ray energy-dispersive spectroscopy (X-EDS) using a JEOL 840A scanning electron microscope (SEM), and a Gemini field emission gun SEM (operated at 20 keV), each fitted with an Oxford Instruments X-EDS unit. All samples were characterized through X-ray diffraction (XRD) using a Phillips PW 1710 diffractomter with a Cu K α radiation source and a Ni filter. Phases were identified by using indexing information obtained from the International Centre for Diffraction Data.

Results and Discussion

Partial pellet reductions at constant voltage.— Figure 3 shows a summary of the results obtained from XRD analysis performed on each of the products of the series of partial reductions. The trace for



Figure 3. Summary of XRD traces of partial reductions.

the as-sintered pellet shows a good match for the NiTiO₃ standard. The analyses performed allow the main stages of reduction from the NiTiO₃ precursor to NiTi to be defined as follows:

600 s with no applied potential (Fig. 4a). The outer surface of the NiTiO₃ pellet has reduced to form CaTiO₃, elemental Ni, and residual NiTiO₃. The edge layer consisted of Ni surrounded by a CaTiO₃ matrix. The core consisted of isolated Ni, CaTiO₃, and the remaining NiTiO₃.

1 h reduction (Fig. 4b).— 1 h marks the appearance of the Ni₃Ti and Ni₂Ti₄O phases in addition to all the phases present in the 600 s sample. The sample is notably layered with the remaining NiTiO₃ concentrated on the sample edge, and a larger volume fraction of elemental Ni regions can be observed throughout. The edge layers appear more porous and the core is consolidated. Ni₂Ti₄O is thought to be an ordered solid solution of O in Ti₂Ni¹⁸ and is the first oxide formed upon oxidation of NiTi. This suggests that reduction occurs from the surface and progresses to the core; as Ni₂Ti₄O is the most "advanced" reduction product at this stage of reduction, it is segregated to the edges of the sample.

3 h reduction (Fig. 4c).— The layered structure has further developed into three distinct layers with the surface being more porous than the inner layers. The Ni_2Ti_4O and the remaining $NiTiO_3$ are concentrated on the edge, the CaTiO₃ and the Ni_3Ti share the mid-



Figure 4. BEI images, XRD traces, and phases present in partially reduced NiTiO₃ precursors removed at specific intervals during the reduction process: (a) 600S at the open-circuit potential, (b) 1 h, (c) 3 h, (d) 6 h, (e) 12 h, and (f) 24 h.



Figure 5. Ni–Ti phase diagram.²⁰

layer, while Ni and $CaTiO_3$ are present in the core. CaO is also evident in the XRD trace and is thought to be entrapped by unreduced $CaTiO_3$.

6 h reduction (Fig. 4d).— The main difference in the 6 h reduction is the loss of the elemental Ni and remaining NiTiO₃, and the first appearance of NiTi. The quantities of Ni and NiTiO₃ have decreased throughout the reduction to this point, while the quantities of Ni₃Ti and CaTiO₃ have increased. It is likely that the remaining Ni was consumed to form Ni₃Ti, and the NiTiO₃ formed further CaTiO₃, liberating Ni to form more Ni₃Ti. The stoichoimetry of the NiTi formed varied from the edge of the pellet to its core. The Ti-rich NiTi observed at the pellet edges is thought to be due to Ti redeposition from the salt. The porosity of the edge layer remains the same as for earlier times in the reduction pathway, while the mid and core layers are more consolidated than before.

12 h reduction (Fig. 4e).— The same phases present in the 6 h reduction are also present in the 12 h reduction. However, the quantity of NiTi has increased at the expense of a drop in the quantity of Ni₂Ti₄O. Overall the porosity of the sample has increased in all layers due to shrinkage caused by the removal of oxygen from the structure.

24 h reduction (Fig. 4f).— After a period of 24 h, the sample is fully reduced. The pellet consisted solely of NiTi with small isolated regions of Ti₂Ni. No CaO is observed in the final reduction product. The pellet is notably reduced in size compared to that corresponding to shorter reduction times. The midlayer is consolidated, while the edge and core layers are porous. The reason for the formation of Ti₂Ni can reasonably be attributed to the starting material being slightly Ti-rich. Figure 5 (Ref. 20) shows that the NiTi phase field is almost a vertical line along the 50:50 atom %, so that even a small excess of Ti will cause Ti₂Ni formation.

The presence of CaO in the core of partially reduced samples has been observed in Ref. 1 and has been attributed to the rapid formation of CaTiO₃ in the initial stages of reduction. This results in an increased CaO concentration in the liquid phase in the porous regions of the pellet until saturation and eventual precipitation of solid deposits occurs. The CaO may become entrapped until reduction of the perovskite proceeds, at which point the CaO may redissolve into the salt and leave the pellet.¹

Figure 6 shows a line scan through a profile of the pellet. It can be seen that the majority of the pellet consists of almost equiatomic NiTi, while the edges of the pellets appear Ti-rich. The stoichiometry of the NiTi formed in the 6, 12, and 24 h reduced samples varied from the edge of the sample to the core. Ti-rich NiTi at the pellet edge, and NiTi closer to the 50:50 atom % ratio existed at the mid and core layers. The most likely cause of the Ti-rich surface



Figure 6. X-EDS line scan through cross section of a fully reduced NiTi pellet: (a) BEI image showing points of line scan and (b) results of X-EDS analysis.

layers of the pellet is that although most of the TiO_2 goes to form $CaTiO_3$ as shown in Reaction 1, a small quantity is able to dissolve into the salt¹

$$\operatorname{Ca}^{2+} + \operatorname{TiO}_{2-r} + O^{2-} \to \operatorname{CaTiO}_{3-r}$$
 [1]

Ti has a limited solubility in CaCl₂, but when the salt is polarized to sufficiently negative potentials, the Ti will come out of solution and deposit on the surface of the pellet, producing the Ti-rich regions as observed.

The reason for the initial rapid formation of CaTiO₃ can be attributed to the fact that at the beginning of the reduction there is a large surface area of NiTiO₃ available, allowing rapid reduction and release of O^{2–}. The rate of O^{2–} production exceeds the rate at which it can diffuse away in the bulk melt. This in turn leads to the rapid initial formation of CaTiO₃ (as per Reaction 1). This acts as a blocking layer to further reduction until more negative potentials are reached, thus slowing the rate of reduction. Initial formation of CaTiO₃ is rapid, despite the very low initial concentration of CaO in the salt.

The formation of elemental Ni in the initial stages of the reduction was observed. This may be due to the creation of a galvanic cell between the Ti current collector and the NiO in the pellet precursor. When the NiO and the Ti are placed in contact with each other, the Ti will preferentially oxidize to TiO₂ and the NiO will be reduced to Ni. This is because the TiO₂ has a lower Gibbs free energy than NiO and is hence the more stable oxide ($\Delta G_{NOO}^0 = -133.576 \text{ kJ/mol}$, while $\Delta G_{TIO_2}^0 = -732.128 \text{ kJ/mol at 1173 K}^{21}$). This effect is exacerbated by the porous morphology of the sample, allowing this ef-

fect to not only be evident at the sample surface but be distributed throughout the sample to its core. This is evident from Fig. 4, where elemental Ni is clearly visible both at the pellet edge and core for reduction times up to 1 h.

The above observations are largely in agreement with several published works on the oxidation/deoxidation of NiTi.^{1,17,18,22} Both Firstov and Zhu predict Ni will come out of solution as the first reduction product. Zhu also observed the formation of CaTiO₃ along with the Ni (Firstov was oxidizing NiTi in air). Both Firstov and Churpina suggested that TiO₂ would form along with the Ni as the first reduction products.

It can clearly be seen from Fig. 4 that reduction occurs through progressive layers. The low-magnification images clearly show a layered structure up to the 12 h reduction. After 24 h the structure is almost entirely NiTi, and the layers visible are due to different levels of porosity through the pellet. This is in agreement with the "3phase interline" mechanism (described fully elsewhere) proposed by Chen et al.¹⁵ for the reduction of Cr_2O_3 in $CaCl_2$, and Deng et al. who reduced AgCl to Ag in KCl and SiO₂ to Si in CaCl₂.¹⁶ Metallization starts initially at the point of 3-phase contact (the "3-phase interline") between the charge transfer at the Ti electrode, the CaCl₂ electrolyte, and the NiTiO₃ precursor pellet. Contact at this point is the only point initially where reduction can take place, as the NiTiO₃ is an insulator. As metallization takes place, the area of 3-phase contact is increased as the conductive metallized layer grows. Initially the reduction front proceeds along the top and bottom edges of the pellet. The diffusion rate of oxygen out of the pellet is lower through the metallized layer than through the unreduced NiTiO₃. When both the top and bottom surfaces become metallized, the layers join along the edge of the pellet due to the preferential diffusion of oxygen out of the NiTiO₃. It can be seen from Fig. 4 that the metallized layer is porous, enabling the electrolyte to penetrate into the pellet and oxygen is able to diffuse out, albeit at a reduced rate than in the initial stages. Reduction then proceeds from the conductive edges of the pellet toward the core. The final areas of the pellet to form NiTi are those at the center of the pellet. This is because the passage of the electrolyte and oxygen is limited to some extent by the consolidated metallized layers surrounding the core.

The difference in the rates of metallization from the initial stages (outermost surface) compared with the latter stages (core regions) has an important effect on the phases formed. The rapid initial reduction occurring at the surface accounts for the large quantity of CaTiO₃ that forms (initially concentrated at the pellet surface) via Reaction 1. Figure 4 shows that the porous metallized layer can be observed fully formed after only a 1 h reduction, and the formation of consolidated metallized midlayers can be clearly seen from 3 h onward in the reduction.

The reason for the difference in porosity through the sample cross section is that as reduction proceeds from the pellet edge to its core, the most reduced species will form first near the edge. Oxygen accounts for 31% of the mass of the NiTiO₃. Therefore as material is reduced, the porosity of the structure will increase, followed by the sintering together of the remaining structure. The sintering process involves self-diffusion of material, which occurs at a much higher rate in metals than in oxides. Therefore, regions that have been metal for the longest period of time will sinter to a greater degree than newly metallized layers. This accounts for the consolidated outer layers (first to metallize) and the more porous core; as the core is the last to metallize, it will also be the least sintered. The immediate surface layer is Ni-depleted and is therefore more porous than the midlayers.

Figure 7 illustrates the layered reduction progression. The figure shows a detailed profile of the 12 h pellet from the edge to the core. XRD scans have been taken of the pellet surface (lightly ground to move any contaminants from the salt), the mid, and core layers. Corresponding BEI images and X-EDS analysis have also been performed at each stage.

The XRD analyses show a highly metallized surface layer and midlayer with a mixed ceramic and metal core. The porous surface



Figure 7. Phases identified in the 12 h reduction product: (a) summary of XRD traces and (b) SEM backscattered images and X-EDS identified phases.

layer is composed of NiTi (Ti-rich). The midlayer was more consolidated and again consisted of NiTi (closer to an equiatomic Ni:Ti ratio). The core layer consisted of isolated regions of Ni_3Ti surrounded by a CaTiO₃ matrix. A notable observation from the XRD traces is that the NiTi peaks appear wider on the pellet edge trace than in the core. This is likely due to the variation in chemistry observed in these layers.

TiO₂ was not observed in this work or in Zhu's work. It is feasible that in this work and Zhu's the rate of O^{2-} generation within the pellet exceeded the rate at which it could be transported to the anode in the bulk melt. This would cause the formation of the pervoskite CaTiO₃, as observed in many works on the reduction of rutile.^{8,9,12,19,23} A possible reaction to form the perovskite is shown in Reaction 1.¹

The perovskite phase is considered undesirable during reduction as it reduces the porosity of the pellet, thus impeding salt ingress to the core, and entrapping CaO. It also lowers the conductivity of the sample.⁸ Reaction 1 would also explain why we fail to see the lower oxides of Ti as predicted by Firstov.¹⁷

After 1 h of reduction, the formation of Ni₂Ti₄O and Ni₃Ti are also observed. The quantity of both of these phases continues to increase until 6 h into the reduction. After this time, the amount of Ni₃Ti begins to decrease in preference to the formation of NiTi. The quantity of Ni₂Ti₄O remains steady until around 12 h into the reduction, after which it gradually decreases to form NiTi. This is largely in agreement with Chuprina's observations on the initial oxidation (final reduction) products of NiTi, where the remaining Ni₃Ti and Ni₂Ti₄O combine in the following reaction to form NiTi¹⁸



Figure 8. Isothermal section at 1173 K for Ti–Ni–O.²²

$$Ni_{3}Ti + Ni_{2}Ti_{4}O + 2e^{-} \rightarrow 5NiTi + O^{2-}$$

The final reduction product after a 24 h reduction is a pellet that is almost entirely equiatomic NiTi with isolated regions of Ti_2Ni that are most likely due to a small Ti excess in the starting material. Ni₂Ti₄O may reduce to form Ti₂Ni under Ti-rich conditions via the following reaction¹⁸

$$Ni_2Ti_4O + 2e^- \rightarrow 2Ti_2Ni + O^{2-}$$
[3]

This is further supported by Fig. 8,²² which shows that NiTi has a narrow homogeneity range of approximately 2 atom % Ni and can dissolve about 4 atom % O. Thus a slight variation from the equiatomic chemistry would result to promote the formation of a second phase, whether that be a Ti-rich Ti₂Ni or an Ni-rich Ni₃Ti phase.

Predominance diagrams.— Predominance diagrams are valuable tools to aid in the characterization of new electrochemical systems. The diagrams are analogous to Pourbaix diagrams that show regions of stability as a function of pH. Littlewood²⁴ applied this concept to molten salt systems, with electrode potential on the ordinate, but replacing the abscissa with pO^{2-} (negative log of oxide ion activity in the melt). The most reduced species lie to the bottom of the diagram, with the most oxidized on the top. The detailed construction of these diagrams is described fully by Dring et al., and by Littlewood et al. in the seminal paper on the subject.²⁴ Figure 9 shows the calculated predominance diagram for the Ca–Ti–Ni–O–Cl

system. This diagram is, to the authors' knowledge, the first such diagram to be calculated for the system and represents a significant advance in the understanding of its solution electrochemistry. Predominance diagrams are derived from purely thermodynamic principles and do not take into account the kinetics of the system. Ni_2Ti_4O has been omitted from the diagram due to insufficient thermodynamic data.

The ideal reduction route would be one that avoids the formation of the perovskite CaTiO₃, as it is undesirable for the reasons mentioned earlier. However, this is unlikely to be achievable in this system due to the porous nature of the pellet structure. The concentration of the O^{2-} ions within the pores of the pellet is dependent on the rate of reduction of the material surrounding them. Thus, if a large quantity of material has undergone a phase transformation as part of the reduction pathway, large quantities of O^{2-} ions will be ejected into the surrounding pores. This will cause the local concentration of O^{2-} to become very high compared to that in the bulk salt. Thus, the system will be driven locally to the far left of the predominance diagram, causing the almost inevitable formation of CaTiO₃. This effect is exacerbated by the fact that despite efforts to remove all contaminants from the CaCl₂, some oxide will always exist in the electrolyte.

A typical melt will have a pO^{2-} of 3 at 1173 K. Such behavior has been observed by several researchers.^{8,9,19} The system does not reduce in an ideal manner (i.e., vertically down the diagram from the NiTiO₃ field) but rather progresses down and left. This is an example of the predominance diagram failing to take into account the kinetics of the system.

The diagram has been validated by the experimentally observed results. The NiTiO₃ transforms into elemental Ni and TiO₂ (which rapidly transforms to CaTiO₃ as a result of Reaction 1), followed by the formation of Ni₃Ti at the expense of the Ni, and eventually the formation of NiTi.

Conclusions

 $\rm NiTiO_3$ pellet precursors have been successfully reduced to form NiTi using constant voltage electrolytic reduction in a molten CaCl₂ bath at 1173 K. The reduction pathway has been characterized using a combination of SEM, X-EDS, and XRD analysis methods. The reduction pathway identified is shown in Fig. 4 and is in agreement with research conducted on the oxidation and reduction of NiTi^{1,17,18}

Reduction occurs in a layered fashion, with the first reduction reactions occurring at the points of 3-phase contact between the electrolyte, Ti electrode, and the NiTiO₃ pellet precursor. Reduced species then spread along the outer surfaces of the pellet before proceeding to the core upon completion of the reduction.





The stoichiometry of the NiTi produced varies from the pellet edge to the pellet core, remaining more Ti-rich at the edge of the pellet due to redeposition of Ti from the electrolyte. Broadening of the NiTi XRD peaks has been observed due to the variation in NiTi stoichiometry and possible oxygen inclusion.

The final reduction product after 24 h under reducing potential is a NiTi pellet with a porous edge structure, a consolidated midlayer, and a porous core. Trace amounts of Ti_2Ni were observed due to the precursor NiTiO₃ being slightly Ti-rich, thus pushing the system into the two-phase region of NiTi + Ti_2Ni .

A predominance diagram was constructed for the Ca–Ti–Ni– O–Cl system to help optimize processing routes to produce low oxygen content NiTi under controlled conditions. The reduction pathway identified in this study agrees with the phases predicted in the predominance diagram.

The presence of CaO was a result of entrapment of salt in the core of the pellet during reduction due to the rapid formation of CaTiO₃ in the initial stages. The perovskite inhibits movement of the CaO to the bulk melt until it is reduced in the later stages of reduction. No CaO is observed in the final 24 h reduction product.

The predominance diagram also suggests that it would be virtually impossible to avoid the formation of the perovskite during reduction. If the rate of O^{2-} production is higher than the rate at which it may be removed from the pellet into the salt, the local O^{2-} concentration will become very high in the pores of the pellet as the surrounding material is reduced. This forces the reduction pathway to the left (low pO^{2-}) of the diagram during reduction. Also, impurities present in the electrolyte mean that the salt will begin with a pO^{2-} of around 3 at 1173 K.

This work has demonstrated the potential to use the FFC Cambridge process to produce homogeneous NiTi in a single-step, nonmelt electrolytic process, avoiding the problems of segregation of Ni in the melt. The reduction pathway has been characterized and a predominance diagram constructed. The results from this work will greatly aid the scale-up of this NiTi processing route to an industrial level. Imperial College London assisted in meeting the publication costs of this article.

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