Intermetallic compounds as oxygen evolving anodes for metal electrowinning : Electrochemical dealloying and effects of scale in practical electrochemistry

David E Williams School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand david.williams@auckland.ac.nz

Abstract

Electrochemical dealloying has recently been highlighted as a promising technique for developing active electrodes for water electrosplitting. Intermetallic compounds of a base metal with passive film-forming element are effective oxygen evolution anodes for metal electrowinning. Cobalt-silicon alloys and titanium-nickel intermetallics are demonstrated as examples and related to the proposed paradigm of electrochemical dealloying. These systems illustrate the effects of scale in practical electrochemistry, where 'scale' has multiple meanings: the transition to practise; formation of surface deposits; and the evolution of the interface in extended use. In the case of cobalt-silicon alloys, the microstructure of the metal is critical. A highly porous surface layer is developed, within which the active phase is 'nanostrands' of cobalt metal in 'nanoconfinement' within a slowlydissolving silicide matrix. Within the confined environment, a saturated solution of cobalt salt causes a salt film over the cobalt metal under which an oxygen-evolving cobalt anodic oxide is stabilised. In the case of TiNi, a nickel-rich surface forms over a thin titanium anodic oxide. Oxygen evolution occurs by field-assisted electron tunnelling to the surface nickel titanium oxide states. Field-driven ion migration both leads to these active states and leads to a slow dissolution of the metal. There is a useful range of composition between 51 and 55 wt% Ni (46 - 50 at %) which balances ductility against dissolution rate: excess titanium leading to a continuous phase of Ti₂Ni results in a very brittle material; separation of TiNi₃ leads to more rapid dissolution. In practise however, intrusion of oxygen during casting of large plates segregated Ti as the oxide Ti₄Ni₂O leading to separation of TiNi₃. The more rapid dissolution of this phase, in association with formation of MnO₂ from Mn salts present in plant electrolyte, led in association with oxidation of cobalt salts to deposition of an adherent surface scale under which the solution became strongly acidic. The accelerated anode dissolution led to an under-scale of TiO₂ which further increased acidification. Impractically rapid destruction of the anode resulted. The work illustrates how mass-transport and microstructure in the evolving interphase between electrode and electrolyte can interact in subtle ways important for practical application.

Introduction

Antharaj and Noda [1] recently published a review entitled "Electrochemical dealloying-assisted activity enhancement: The next big thing in water electrosplitting!". They describe electrochemical dealloying and leaching, particularly of intermetallics of Fe, Co or Ni, as a very promising strategy for decreasing overpotentials for water splitting, by increase of the surface area in the finely porous structure that may be developed by dealloying [2]. Antharaj and Noda note that the active phase for oxygen evolution in acid solution in these structures is likely the spinel oxides or oxyhydroxides of Co, Ni or Fe, and that the major effect is indeed the increase of electroactive surface area resulting

from leaching of components of the electrode material. They note however potential significant issues with this strategy, particularly the possibility of redeposition of leached components as an inactive entity on the anode, creating a hostile environment in the electrolyte solution that may promote catalyst corrosion. Here, a study of intermetallic compounds as anodes for oxygen evolution, specifically directed towards metal electrowinning, is presented. The generation of an active structure by electroleaching, and also by surface modification induced by the electrochemical reaction itself, is illustrated. The study highlights the issues posed by Antharaj and Noda, particularly the importance of scale in both its meanings: the deposition of scales on the anode surface developing a corrosive environment; and the translation from laboratory to practise introducing unexpected issues that led to failure of a promising approach.

Electrowinning of cobalt and copper from the liquor resulting from hydrometallurgical processing of ore or waste has long been practised [3]. A continual source of difficulty has been the selection of a suitable material for the anode. The requirements are insolubility, resistance to the mechanical and chemical effects of oxygen liberated on its surface, low oxygen overvoltage, and resistance to breakage in handling. The anode reaction may be chlorine or oxygen evolution [4]. An important factor is the composition of the electrolyte, specifically what species may be present depending on the purity of the feedstock, which in turn depends on the metal source and the process used to prepare it. Anode corrosion is critically important. Important factors are an economically acceptable rate of corrosion and spallation of the anode material and an acceptably low contamination of the cathode deposit that may result [4]. Whilst Ti-precious metal anodes as used in the chlorine industry (eg Ti-TiO₂-RuO₂) are acceptable with clean chloride electrolytes free of impurities, the corrosion rate in an acidic sulfate electrolyte, or in electrolytes containing components that can lead to the deposition of scales over the anode surface, such as Mn²⁺ leading to MnO₂, is too high for their use to be economical in those circumstances. Lead-based anodes are acceptable in sulfate electrolyte, but only if there are no traces of chloride present, for in that case anode corrosion leads to unacceptable contamination of the cathode deposit with lead. The majority of electrowinning facilities in conventional refineries indeed now use lead and lead alloy anodes. However anode effects in modern solvent extraction – electrowinning plants remain problematic [5]. With high current densities and high temperatures in electrolytes containing organics, a thick porous PbSO₄ layer forms on the anode, which eventually flakes off, particularly at the liquid-air surface, which is very turbulent and where an acid mist occurs. These particles get occluded into the cathode. These issues mean that there remains motivation to search for alternative anode compositions.

An older technology, used successfully before the development of modern solvent extraction methods for electrolyte purification was the use of cast silicon alloys of Cu, Co and Fe. 'Duriron' is a highly corrosion resistant alloy, of nominal composition silicon ~14.2 wt. %, carbon ~0.8 wt. %, balance iron. It is used for its resistance to sulfuric acid environments. An initially high corrosion rate in boiling sulfuric acid decreases to low values over 10's of hours [6]. It has been successfully used as anodes for impressed current cathodic protection [6, 7], showing low anode consumption in acid, alkali, and sea water environments even at high current densities. The cast microstructure is complex; phases Fe, Fe₃Si, Fe₅Si₃ and FeSi are all expected [8]. Rather high corrosion rates have however been reported (~10% of the total current [9]). Vacuum arc melted Fe₃Si has been proposed as the anode electrode plate in the acid pickling of stainless steel, in strong nitric acid [10]. Corrosion rates in this demanding application were also relatively high, ~ 13g/(m² h) . In electrowinning the corrosion of Fe into the electrolyte led to a loss of current efficiency and Duriron in this application was replaced by copper silicide containing Pb [11]. This material was extremely brittle and was replaced by cast Co-Mn-Si alloy [12].

Kuhn et al[13] described the electrochemical corrosion behaviour of Cu, Co and Ni silicides in both sulfate and chloride electrolytes. They stated that the oxygen current was a minor fraction of the total current for all alloys tested and that the expected reduction in corrosion current at the highest potentials, due to transpassivation, was scarcely perceptible. Kuhn and Shalaby [14] suggested that the phase that was electroactive for oxygen evolution was a cobalt orthosilicate, formed within a μ m-scale thickness surface film developed by anodic polarisation at high potential. Shein et al [15-17] showed, for cobalt silicides in sulfuric acid solution, a significant diminution of corrosion current with respect to Co and a transpassive range, presumably oxygen evolution. They described a selective dissolution of Co with formation of an SiO₂ anodic film.

An alloy of composition (wt %) Co(11.5 - 13)Si(4-6)Mn was successfully used for many years for electrowinning of copper, in Chile, and of cobalt, in the DRC and Zambia, because chloride contamination of the electrolyte militated against the use of Pb anodes. The microstructure is complex and similar to the cast iron silicon alloys, and the anodic polarisation behaviour is also similar [18]. The original description of the cobalt silicide anodes was that Mn addition acted to decrease the oxygen evolution overpotential [12]. At temperatures above 30°C, adherent, heavy deposits of MnO₂ together with some cobalt oxide were formed on the anodes and it was assumed that this was the electroactive phase [12]. This alloy being brittle with high oxygen evolution overpotential, the increase of which over time to an unacceptably high value determined the useage life of the anode, provided the motivation for exploring other intermetallic compounds that could also be non-contaminating anodes. Recent work has revisited silicide anodes, prepared by powder metallurgy as porous forms [1, 19]. The powder metallurgy preparation of porous silicides of Fe, Mn or Co has been described by Shen et al [19]. These were multiphase materials: the iron silicide contained Fe₅Si₃, FeSi and Fe₃Si. A highly porous structure developed over 24 hr of anodic polarisation. The corrosion rate during oxygen evolution during this time was very low (scale of μ g/Ah). A surface oxide of Fe₂O₃ – SiO₂ formed. However, long-term performance was not presented. Intermetallic compounds of titanium with base metals (Fe, Co, Ni, Cu, Mn) have seemed to offer a particularly promising combination of relatively low oxygen overpotential with relatively low corrosion rate. Guenani et al [20] have described the preparation of Ti-Ni anodes by compressing mixed powders of Ti and Ni then sintering at a low temperature (500°C) in order to partly sinter and strengthen the compact whilst avoiding the formation of the Ti-Ni intermetallic compounds. In 1 M NaOH these electrodes showed low oxygen evolution overpotential; the presence of a Ni(II)-Ni(III) redox couple at the electrode surface was indicated. Wang et al [21] describe oxygen evolution on TiMn₂ prepared by powder metallurgy, in dense and porous forms. The dense form had oxygen evolution overpotential similar to that for the TiNi intermetallics but with rather larger Tafel slope; for the porous form, overpotential was, as expected, significantly lower. However, thick surface oxide scales of MnO_2 , Mn_3O_4 overlaying TiO₂ formed and anodes failed (significant increase of cell voltage) after 3.5 month (porous) or 6 month (dense) of continuous operation. Development of a deposit of MnO₂ that is electrochemically active for oxygen evolution seems to require a specific methodology, otherwise the scales formed are simply detrimental [22].

Sedriks et al studied the electrochemical behaviour of Ti-Ni alloys and intermetallics in acidified chloride solution [23]. The introduction of Ti₂Ni, by alloying titanium with nickel, greatly facilitated the overall cathodic reaction. Anodic polarization showed that the introduction of Ti₂Ni in the alloy generates a surface which is passive. Lu and Srinivasan [24] studied oxygen evolution on Ti-Ni intermetallic compounds in 30 wt% KOH at 80°C. For TiNi and TiNi₃ the Tafel slope was similar to that observed on Ni. On TiNi₃ the oxygen overpotential was very similar to that for Ni; on TiNi it was a little greater. The behaviour was assumed due to the presence of a surface layer of NiOOH. Ti₂Ni showed a high Tafel slope and oxygen evolution overpotential; the behaviour was assumed due to

the presence of an anodic barrier layer. Paleolog et al [25] studied the anodic oxidation kinetics and electrochemical properties of the passive surfaces of Ti, Ni, and Ti-Ni alloys in neutral and alkaline Na₂SO₄ solution. They indicated that the anodic oxide growth on Ti-Ni alloys proceeds by a law similar to that observed on pure Ti. As in other work, for compositions containing TiNi, oxygen evolution approached the rate observed on Ni. The ferrocyanide oxidation reaction was also facilitated. They interpreted that the metal immediately adjoining the oxide is enriched with nickel, and the zone bordering on solution approaches TiO₂ in its composition. The reduction of the thickness of the outer film part with the increase of Ni content in the alloy results in a facilitated anodic oxidation of solution ions. A current due to passive film growth was evident on Ti₂Ni prior to oxygen evolution [26, 27]. On the passive film the rate of the ferrocyanide oxidation was consistent with that expected for tunnelling through a thin insulating layer [27] [28]. X-ray photoelectron spectroscopy showed that the passive layer on Ti₂Ni was TiO₂, enriched in Ni at the metal-film interface [26]. TiNi in air spontaneously forms a thin passivating layer of TiO₂ ; at the oxide-film interface, the metal is enriched in Ni [29, 30].

The present paper presents the results of two studies, of the Co-Si-Mn alloy and of TiNi as oxygenevolving anodes, that are shown to be examples where the active interphase is generated as a consequence of electrochemical leaching. Taken together, they illustrate how mass-transport and microstructure in the evolving interphase between electrode and electrolyte can interact in subtle ways important for practical application. The Co-Si-Mn alloy is shown to be a Co anode, protected from excessive corrosion by the development of the interphase, in turn related to the alloy microstructure formed on solidification during manufacture. The TiNi anode develops an electrocatalytic layer of Ni-Ti oxyhydroxide on the outer surface of a passive film. Despite great promise in the laboratory, this material failed in practise because the developing interphase promoted corrosion, again in turn related to contaminant phases formed during manufacture.

Methods

Materials for small-scale laboratory investigation were prepared by non-consumable arc melting from a tungsten electrode under argon on a water-cooled copper crucible. The charge comprised coarse lumps of pure metal or master alloy because powders were blown out of the crucible by the arc. The resulting button (approx. 50 g) was inverted and remelted five times. The specimens had oxygen content 0.1 to 0.2 wt%. Titanium was commercial grade purity wire (IMI 130). Nickel was sulfur-free strip containing 0.06 wt% Co, 0.1 to 0.5 wt% Fe, ~10 ppm S. Cobalt and silicon were BDH laboratory reagent grade. Cast Ti-Ni alloy plates (15 x 20 cm) for larger scale investigation were prepared by induction melting in air with a rudimentary argon gas cover, before pouring into sand moulds. They carried a surface scale of titanium oxide with nickel-enriched metal immediately underneath which was ground off before use. They had a bulk oxygen concentration of 0.6 to 0.8 wt %. Anodes for plant trial were made by a simple scaleup of this process. They were 1 m² area and had oxygen concentration typically 1.7 wt%. A used Co-Mn-Si cast anode, composition Co14Mn6Si, was obtained in 1978 from the electrowinning plant at Rokana, Zambia.

A number of commonly available metallographic sample mounting materials were tested for their resistance to hot acid solutions. Diallylphthalate appeared completely resistant and was used throughout to mount samples for electrochemical study. The mounted sample, exposed area 5 cm², with electrolyte-facing surface polished was either ground on the back to expose the metal then the mounting clamped against the flat face of a standard 25mm diameter glass flange joint that formed the electrochemical cell, using a titanium backing plate, viton O-ring and spring-loaded clamp, or had a stainless steel screw through the mounting into the back of the sample, tightened against a Ti backing plate and sealed with O-rings against a glass flange. The reference electrode was

Hg,Hg₂SO₄,Na₂SO₄(aq) , (SSE): E_H = 660 mV (20°C). For measurement at elevated temperature, the reference electrode was maintained at room temperature and any thermoelectric potential difference developed in the Luggin capillary was ignored. The current amplifier for the potentiostat had both linear and logarithmic output. For corrosion rate measurement, either the electrolyte was sampled at intervals or the solution flowed at constant rate of 8 mL/min through a cell of volume 8 mL and samples were collected for analysis every 1 min: Ni and Co by atomic absorption spectrophotometry; Ti colorimetrically by addition of excess H_2O_2 to the acid solution [31]. Corrosion rate was also determined gravimetrically following extended operation. Corrosion rate , also called 'wear rate', is here expressed as amount corroded / charge passed (mg/Ah) or equivalently as current assuming dissolution valency 2 for Ni and Co and 3 for Ti .

Results and Discussion

1. Cobalt-manganese-silicon alloy

Figure 1 shows cross-sectional micrographs of the surface of a commercial cobalt-silicon-manganese anode after months of plant service in Zambia. Indeed there is a Mn-rich surface scale. Underneath this is a finely-textured porous corroded layer of metal. As the surface scale and corroded surface metal layer were progressively ground away, the oxygen overpotential measured in 1.5M H₂SO₄ electrolyte decreased and active dissolution features characteristic of cobalt metal appeared.



Figure 1 Cobalt-manganese-silicon anode materials after plant use. (A) a micro-structured corroded surface layer is formed; (B) on the outer surface, a manganese-rich scale is deposited; (C) progressive grinding away of the surface layers decreases the oxygen overpotential ($1.5 \text{ M H}_2\text{SO}_4$ electrolyte, 22°C).

Figure 2 compares the electrochemistry of the freshly ground alloy with that of Co metal. Pure Co metal shows (Fig 2A) with increasing anode potential, the characteristic voltammetry of dissolution through a salt film followed by passivation underneath the salt and oxygen evolution on this passive layer. Oxygen evolution was accompanied by a slow dissolution of cobalt, with current density about 10% of that due to oxygen evolution; the dissolution current at 300 A m⁻² corresponded to a wear rate of 90 mg / Ah. Saturation of the solution with CoSO₄ significantly diminished the cobalt dissolution current density. The Co-Si-Mn alloy showed similar features (Fig 2B). Corrosion of this

alloy resulted in diminution of the current density due to dissolution through the salt film. Over time, the corrosion rate during oxygen evolution fell from a value similar to that for pure Co to a much lower value, less than 10 mg/Ah (figure 2C). Previous literature had not shown the transpassive dissolution of cobalt . Here, it was found that the geometry of the cell was important: with the electrode horizontal and facing upwards, salt-film formation and the transpassive evolution of oxygen was indeed observed. With this electrode geometry, at constant current the electrode potential could oscillate between values corresponding to active dissolution and values corresponding to oxygen evolution, because the salt concentration and density gradient established as cobalt sulfate was formed near the electrode surface served to stabilise the salt film. This gradient was dispersed when oxygen evolution occurred on the passive cobalt oxide film underneath the salt film, leading to dissolution of the salt film and re-occurrence of active dissolution.

The microstructure of the Co-Mn-Si alloy is complex: fig 2D. The Co-Si phase diagram [32] shows three mutually immiscible intermetallic compounds: Co₂Si, CoSi and CoSi₂. There is a eutectic at 12 wt% (22 mol%) Si, between Co and Co₂Si. There are ten ternary phases in the Co-Mn-Si phase diagram [33], including Co₂MnSi, Co₃Mn₃Si₂, CoMnSi, and Co₃Mn₁₂Si₅. As a cast plate solidifies from the melt, the first material to solidify would be a mixture of Co, Co₂Si and Co₂MnSi. As this material forms, the melt in contact with it is enriched in Si and depleted in Co and Mn, causing the first-formed Co to be encapsulated in Si-rich phases, with detailed microstructure dependent on the cooling rate. The microstructure of a large cast plate revealed by etching shows the consequences: 'nanostrands' of Co encapsulated in Co₂MnSi and in Co₂(Mn)Si and Co(Mn)Si₂ where the detailed phase structure is unresolved. The porous surface layer formed in anode operation comprises the silicide phases.



Figure 2. Comparison of the electrochemistry of cobalt-manganese-silicon with that of metallic cobalt. (A) With increasing anode potential, Co metal shows (i) active dissolution; (ii) formation of a salt film and diffusion-limited dissolution through this; (iii) passivation under the salt film (depassivation on the reverse scan); (iv) oxygen evolution on the passive surface, with significantly diminished dissolution current (plotted as points: (v) - that shows similar potential dependence to oxygen evolution. Saturation of the solution with CoSO₄ greatly diminishes the dissolution current.

(B) Co-Mn-Si shows the same voltammetric features as Co metal; after a period of oxygen evolution, the dissolution current is diminished. (C) Corrosion rate of Co-Mn-Si (initially polished) under oxygen evolution as a function of time. (D) Microstructure of Co-Mn-Si (electrolytic etch; 10% oxalic acid, 1 sec, 2 A cm⁻²)

The anode behaviour can be simply interpreted. The active anode is not the surface coating of MnO₂ but is the metallic cobalt present in the solidified eutectic mixture. A very finely porous structure, comprising the silicide matrix, forms as the metallic cobalt dissolves. Previous work, in not resolving the cobalt 'nanostrands' has misinterpreted the composition of the surface layer and in not observing the passivation of Co under a salt film has missed the important point about the way the microstructure enables development of a dynamically evolving interface which leads to electroactivity with low corrosion rate. Thus, within the finely porous structure that develops over time, a saturated solution of cobalt sulfate is formed and the Co metal becomes passivated underneath the consequent salt film. Oxygen evolution occurs on this passivated Co surface. The active anode is stabilised by 'nanoconfinement' consequent upon the microstructure developed by casting. The increase over time of anodic overpotential for oxygen evolution is due to the increase of electrolyte resistance within the porous structure as the active Co phase progressively and slowly dissolves. The 'depolarising' effect of Mn is to cause the silicide matrix to dissolve under anodic polarisation rather more rapidly than would the pure Co₂Si, enlarging the pores and resulting in somewhat lower ohmic resistance. Consistent with these ideas, if the alloy was chill-cast – cooled rapidly from the melt by first arc-melting the constituents within a small water-cooled copper crucible - then the eutectic microstructure was unresolvable; corrosion rate was higher and oxygen overpotential lower than for the sand-cast alloy plate. However, chill-casting resulted in an extremely brittle material: the intermetallic compounds are very brittle. The presence of larger nanostrands of cobalt metal in the sand-cast alloy serve to interrupt crack propagation and so improve the mechanical properties.

2. Titanium-Nickel intermetallic compounds

In preliminary scanning of the properties of intermetallics, oxygen evolution at fairly low overpotential was found to be a phenomenon common to intermetallic compounds of valve metals with Fe, Co, Ni and Cu. For a given base metal, the order of oxygen overpotential at fixed current density was generally AI < Ti < Zr < Ta, Nb with corrosion rate the inverse. For a given valve metal, the order of oxygen overpotential was generally Co < Ni < Cu < Fe. The Ti – Ni system seemed particularly advantageous form the point of view of both oxygen overpotential and corrosion rate as well as cost. The Ti-Ni phase diagram shows three mutually immiscible intermetallic compounds : Ti₂Ni, TiNi and TiNi₃, with the TiNi phase showing a small range of composition [34]. Arc-melted (chill-cast) material in the range 40 to 55 wt% Ni shows irregular nodules of TiNi surrounded by Ti₂Ni : figure 3. The Ti₂Ni compound is extremely brittle (Charpy impact energy [35] < 1 J); TiNi is somewhat ductile (Charpy impact energy ~ 50 J). With sufficient TiNi, a continuous network of this phase is formed throughout the material. Cracks propagating through the material could therefore be blunted and stopped. A material with adequate impact strength is found in the range 51-55 wt% Ni (46 - 50 at %). Figure 4 compares the voltammetry of Ni with that of the intermetallic compounds. In 1.5M H₂SO₄ the intermetallics showed a suppression of active dissolution, a passive range and oxygen evolution with overpotential ~ 0.9 V, in the order TiNi₃ < TiNi < Ti₂Ni. The current showed hysteresis; with potentiostatic or galvanostatic steps the current or potential relaxed to a steady state over a time scale of up to 1 hr, depending on acidity and temperature (significantly

faster at higher temperature and acidity). A potentiostatic step applied to a TiNi electrode from the rest potential into the regime of oxygen evolution showed, following the a fast spike due to double layer charging, a current peak, rising on a time scale of 10 s and then relaxing on a time scale of a few minutes. Rapid scans from different potentials showed (figure 4B) reduction of surface species formed under oxygen evolution, and the electrode behaving in the passive range before oxygen evolution as a large capacitor (\sim 70 μ F cm⁻²). Under oxygen evolution and at 70°C the interfacial capacitance determined by AC impedance measurement was even larger: $200 - 300 \ \mu F \ cm^{-2}$. Under oxygen evolution at higher potential, the Tafel slope for metal dissolution was very similar to that for oxygen evolution and dissolution rates of Ni and Ti were the same as their mole ratio in the metal whilst before the onset of oxygen evolution, the dissolution current for Ti exceeded that for Ni and indeed at higher temperature became the same as the total current (Figure 4C). Nickel dissolution rates at room temperature were (mg/Ah): Ni, 60; TiNi₃, 60; TiNi, 4; Ti₂Ni, 3. With increase of nickel content above 55 wt%, TiNi₃ separates and the dissolution rate correspondingly increased markedly, thus giving a preferred range of composition of 51 – 55 wt% Ni, having adequate impact strength and acceptably low corrosion rate and oxygen overpotential [36]. The corrosion rate under oxygen evolution was strongly dependent on acidity and temperature: figure 4C, figure 5. A small substitution of Ta for Ti significantly decreased the corrosion rate at elevated temperature and acid concentration. Substitution at this level did not alter significantly the overpotential for oxygen evolution. Nb substitution had a similar effect though not as marked. The corrosion rate increased linearly with concentration of trace fluoride (approximately doubled in the presence of 50 ppm F⁻). Sulfate anion also accelerated the corrosion rate under oxygen evolution: 0.23 mg/Ah of Ni in 1 M $HClO_4$ compared with 3.4 mg/Ah of Ni in 1 M H_2SO_4 at room temperature.

Steady-state Tafel lines had a significantly smaller slope than Tafel lines determined by short potentiostatic steps, to an extent dependent on the temperature: figure 6. The steady state Tafel line for TiNi in 1.5 M H_2SO_4 had slope increasing from 58 mV/decade to 110 mV with increasing potential; at 70°C it was 110 mV (Figure 4C, figure 6). The Tafel slope determined from potentiostatic transients at 20°C increased from 160 to 240 mV with increasing potential; at 70°C it increased from 140 to 200 mV.



Figure 3. Microstructure of Ti53Ni arc-melted (chill cast). The nodules have composition TiNi and the material surrounding them has composition Ti₂Ni.



Figure 4 (A) Comparison of potentiodynamic voltammetry of Ni and of titanium-nickel intermetallic compounds; 23°C, 200 mV / min. (B: Inset) potentiodynamic scan at 100 mV/s with variation of anodic reversal potential following initial scan to +1.5V SSE at 10 mV / s (C) total current and corrosion current under oxygen evolution, for TiNi at 22°C (potentiodynamic scan at 10 mV / min) and 70°C (potentiostatic step, 9 min / step). Corrosion current derived by solution analysis and assuming z = 3 for Ti, z = 2 for Ni . Electrolyte: 1.5 M H₂SO₄.



Figure 5. Nickel dissolution rate, W_{Ni} , from TiNi and Ti_{0.48}Ta_{0.2}Ni under oxygen evolution (300 A m⁻²) as a function of acidity and temperature. [H₂SO₄] + [Na₂SO₄] = 1 mol dm⁻³ for concentrations < 1 mol dm⁻³.



Figure 6. Steady state and transient Tafel lines for TiNi in 1.5 mol dm⁻³ H₂SO₄ electrolyte. (A) exemplar potentiostatic transients used to determine the transient Tafel line; $\Delta E = +/- 24$ mV, E = +1.4 V SSE, 70°C. (B) steady state (points) and transient (lines) Tafel plots at 20°C and 70°C; at the centre of each transient Tafel line is the steady state point from which the transient was determined.

XPS showed, on a sample following polarisation under oxygen evolution, signals for Ti and O characteristic of a layer of TiO_2 , as well as signals characteristic of the presence on the surface of $Ni(OH)_2$. There was no signal from metallic Ni . A short Ar^+ etch brought up the signal for Ni metal. Whilst the Ni signal is likely due to Ni incorporated within the anodic oxide both at the solution interface and near to the metal, a possible artifact is that Ni hydroxides could have been simply adsorbed or precipitated on the surface as a consequence of Ni being dissolved from the metal.

In contrast to the behaviour with respect of oxygen evolution, the redox reaction of ferriferrocyanide on TiNi in sulfuric acid solution was very irreversible. Occurring below the anode potential for oxygen evolution, the behaviour was that expected for tunnelling through a space charge barrier in a thin passive film [28, 37]: figure 7. The behaviour was similar to that shown in the literature for Ti₂Ni[26, 27] and for passive Ti [38, 39].



Figure 7 Cyclic voltammetry of 10 mM $K_4Fe(CN)_6$ in 1.5 M H_2SO_4 at 22°C on a TiNi electrode. Scan rate 13 mV / s. The start potential is marked with a dot and the direction of scan with the arrows.

The results presented above show that a passivating anodic oxide is formed on TiNi prior to oxygen evolution: the potentiostatic and potentiodynamic results are consistent with the nucleation and growth of a passivating layer whose thickness changes in response to change in electrode potential. The results in the literature indicate that this is TiO_2 in which case, Ni would be enriched in the immediate subsurface below the oxide as the film grows. The acceleration of dissolution by fluoride and sulfate in solution is consistent with the anodic film under oxygen evolution conditions being dominantly TiO_2 : sulfato and fluoro complexes of Ti(III) and Ti(IV) would promote dissolution.

There are two possible interpretations of the results: that the passive oxide cracks at higher electrode potential [40] exposing the metal on which forms the nickel oxyhydroxide oxygen evolution catalyst and from which Ni dissolves; or that Ni is transported through the passive film along with Ti, by high field ion migration. The marked drop in dissolution rate relative to oxygen evolution rate for TiNi compared with Ni indicates the second model. Furthermore, the comparison of transient and steady-state Tafel lines has a simple explanation if the passive layer thickness changes slowly in response to change of electrode potential whilst the current due to tunnelling through the film changes immediately. In that model, dissolution is driven by the potential difference across the film-solution interface; the total potential drop from metal to solution is divided between that across the film and that across the solution interface. At sufficiently high electrode potential drop across the film leading to an increase in that across the interface [28]. Khan and Schmickler [41] described electron transfer between solution species and an oxide -covered metal film where the oxide had localised band gap electronic states. For an anodic process, the system changed from direct elastic tunnelling between metal and solution to tunnelling from

localised states in the oxide with increase of overpotential: the current density increased to a limit then became constant. In the present case the effect would be that Ni may then be oxidised at the film-solution interface, generating the catalytic sites for oxygen evolution. The results would then be interpreted in terms of field-assisted tunnelling of electrons through a thin passive surface oxide from surface states [42]. A reasonable assumption is that these are associated with Ni oxyhydroxide, and could be formulated as defect states in the titanium oxide. The strong potential dependence of charge stored in these surface states would account for the very high interfacial capacitance at oxygen evolution potentials. These states are specifically associated with oxygen evolution. The potential dependence of the rates of oxygen evolution and of corrosion is very similar, implying that corrosion occurs as dissolution from the same surface defects that mediate oxygen evolution, and is maintained by high-field ion transport through the surface oxide. The surface oxide thickness would be determined by the balance between dissolution and formation rate, and would be expected to be dependent on temperature and acidity, as observed. The steady state Tafel slope would reflect the potential dependence of both the oxide thickness and the surface reaction rate; the transient Tafel slope would show the potential dependence of the surface reaction rate only. Thus an important factor in the behaviour would appear to be the transport of Ni through the anodic film; presumably this is promoted by Ni enrichment in the metal, which would occur progressively with increasing electrode potential. The trigger for oxygen evolution would then be the appearance of a sufficient concentration of Ni in defect states at the outer film surface.

Song et al [43] described the generally accepted mechanism for the oxygen evolution reaction on an oxide surface, which essentially retains the original formulation of Lu and Srinivasan [44]: in the first step, oxidation of a hydroxide anion adsorbed in an active site gives an adsorbed hydroxyl radical. Coupled proton and electron removals then give an activated adsorbed oxygen atom, which may then, in proton-coupled electron transfers, give first adsorbed hydroperoxide then oxygen, or may combine directly to give oxygen. Damjanovic and Jovanovic [45] formulated the active site on the anodic oxide on Pt as an oxygen vacancy with the reactions driven through the anodic film by fieldassisted tunnelling [46]. Boddy developed these ideas for oxygen evolution on semiconducting TiO₂ again invoking formation of a surface oxygen vacancy as a key step [47]. For the case of the TiNi intermetallic compound, the surface states active for oxygen evolution, and also the sites from which the metal ions dissolve can be formulated as an oxygen vacancy defect complex: speculatively an oxygen vacancy associated with Ni(III) and Ti(III) in the lattice, written V_0 Ni_{Ti} Ti_{Ti}. That is, the charge compensation for the oxygen vacancy is spread across neighbouring cations, partially oxidising Ni and partially reducing Ti. Substitution of a small amount of Ta for Ti would result in Ta injection into the anodic film. Ta(V) substitution in the film would suppress oxygen vacancies; the beneficial effect of Ta substitution on the corrosion rate thus has a natural explanation if oxygen vacancies are indeed critical sites for reaction.

This formulation finds support in recent computational modelling. Heydari et al [48] have computed the formation energy for a bridging oxygen surface vacancy and the electronic energy states associated with it for Ni-doped TiO₂. The charge-compensating metal ion (Ni_{Ti}['] and Ti_{Ti}[']) are most favourably found near the oxygen vacancy, and this defect complex is surface-segregated as indeed a simple electrostatic model would show [49]. Dissociative adsorption of water was predicted to occur on the defect. The Ni impurity in association with an oxygen vacancy provided localised states in the band gap [50]. The assumption then is that these localised states are the sites for electron transfer from the dissociatively adsorbed water molecule, leading successively to hydroxyl, oxygen and hydroperoxide radicals.

3. Cast Ti-Ni alloy anodes in practise

The results presented above indicated that an anode with composition around Ti53Ni would be promising for use in cobalt electrowinning, particularly with a small substitution of Ta or Nb for Ti. The electrowinning cell liquor for full-scale trials was a sulfate electrolyte containing typically Co ~ 40 g/L, Ni ~ 1 g/L, Mn ~ 1 g/L, Ca ~ 0.6 g/L, Mg ~ 5 g/L and trace fluoride (100 – 150 ppm; likely present as colloidal CaF₂). The solution fed into the cells had pH ~ 6 and temperature ~ 50 – 60 °C. It was heated further, to 70 – 80°C, and acidified , to ~ 10 g/L H₂SO₄ (0.12 M) by the passage of the cell current and by the anode reaction evolving oxygen. The expected wear rate from the studies reported above was ~ 2 mg / Ah. However, laboratory tests of small cast plates in a mixture made up to have comparable composition to the cell liquor gave wear rates between 3 and 15 mg/Ah; plant trials of full-size plates gave rates of 17 – 21 mg/Ah. After 5 months plant service, anodes corroded through at casting defects (figure 8) and broke. They were covered with a heavy scale which was crystalline and layered: black over pink and white with intense white material in blisters .



Figure 8 (A) fragment of anode plant, broken off during plant service. (B) cross-section showing corrosion at casting defect. (C) cross-section showing layered structure of scale and almost complete loss of metal thickness.

There were two reasons for the failure. Firstly, the data on the basic electrochemistry of the intermetallic compounds was obtained using materials carefully prepared by arc-melting under argon in a water-cooled crucible: hence chill-cast. Materials for commercial trials were prepared by induction melting under argon and casting into sand moulds with an argon gas cover. These cast plates contained oxygen, to an amount dependent upon their size. Cast plates for laboratory trials were small : 12×20 cm and contained typically 0.6% oxygen; those for commercial trials were $\approx 1 \text{ m}^2$ and contained typically 1.7% oxygen. Figure 9 shows the microstructure of these materials. Particularly for the large cast plates it is dominated by angular crystals, evidently formed first during the solidification and identified as the oxide Ti₄Ni₂O. This oxide, a solid solution of oxygen in Ti₂Ni, segregates a significant amount of Ti and leads to the separation of TiNi₃ [51], a highly corrodible phase. This phase also efficiently segregated Nb added to the alloy so the expected benefit was not obtained.



Figure 9 Microstructure of cast plates. (A) small laboratory plate, containing ~ 0.6% oxygen.; (B) large cast plate from plant trial, containing ~ 1.7% oxygen, showing angular precipitates typical of oxide and having composition Ti_4Ni_2O .

The second reason for the failure was the formation of an extremely adherent scale. The solution would acidify underneath the scale and as a consequence the corrosion rate would rise. Underneath the scale, the solution would become saturated in Ti(IV) leading to precipitation of TiO_2 and hence further thickening of the scale. Blisters containing an intensely white product underneath a black scale were indeed observed. The formation of scale and enhancement of corrosion could potentially become self-accelerating. Scale formation and wear rate had a complex dependence on temperature, temperature cycling and solution composition (Table 1). For the formation of an adherent scale whose properties led to surface acidification and corrosion enhancement, the presence of both Co^{2+} and Mn^{2+} in the electrolyte seemed to be necessary. With Co^{2+} alone, at high temperature an unusual and adherent scale was formed. In the presence of Co^{2+} and Mn^{2+} the oxides of Co(III) and Mn(IV) were possible reaction products.

solution	temperature								
	50 – 60 °C		70 – 80°C		Daily cycle 20°C to 80°C				
	Wear	Scale	Wear	Scale	Wear	Scale			
	rate	appearance	rate	appearance	rate	appearance			
	mg/Ah		mg/Ah		mg/Ah				
Na ₂ SO ₄	low	-	low	-					
CoSO ₄	low	-	12	Adherent,					
40 g/L				shiny black					
				under flaky					
MnSO ₄	low	Flaky, non-	low	Flaky, non-					
1 g/L		adherent		adherent					
CoSO ₄ +	4 - 10	Yellow, thin	3 - 9	Shiny,	15 - 24	Yellow,			
MnSO ₄		and coherent		coherent,		thick,			
40 g/L Co, 1		over black		black at		coherent			
g/L Mn				lowest wear		and flaking,			
				rate		over black			
Simulated					10 - 13	Adherent			
plant						yellow			
electrolyte									

40 g/l Co, 1			scale over
g/L Mn, 9 g/L			black
MgO, 1 g/L			
Ca(OH) ₂ , 0.3			
g/L CaF ₂			

Table 1 Scale appearance and total wear rate (gravimetrically determined) for small Ti53Ni castanodes in laboratory tests.

Conclusion

The cobalt silicide example has shown the importance of microstructure and the development of the interphase over time in developing an active surface by electrochemical dealloying, and has highlighted one aspect of electrochemical dealloying as a strategy for development of robust and active oxygen evolution electrodes [1] : the increase of overpotential with time due to increase of ohmic drop within the leached layer and within surface scales. It also illustrates the importance of mass transfer within the developed microstructure in sustaining an environment which maintains stability and activity of the electroactive phase. The microstructure of the material plays a critical role for both of these effects and it would seem that achieving an appropriate balance between mass transport to sustain the catalyst and ohmic drop to minimise overpotential may be non-trivial. The TiNi example also illustrates how an electrocatalytic surface can develop as a result of an electrochemical transformation. However, this example also emphasises the importance of surface scales in promoting anode corrosion. These scales may not appear in laboratory trials but instead appear in practise at scale because of subtle differences in solution composition or anode operating procedure or practical manufacture. Such issues will continue to be of importance as scaleup of electrochemical water splitting proceeds.

These examples have illustrated the importance of the dynamics of the interphase region, where the configuration of the interphase, its extent, porosity and tortuosity, dynamically evolving and closely coupled to transport in the electrolyte, is critical. They have also illustrated the subtlety of scale, in the sense that deposits determine conditions in the interphase boundary layer, and that the constituents can interact in unexpected ways reminiscent of the colloid chemistry controlling electrophoretic deposition. The subtlety of scale in the sense of transition to practise has also been illustrated, where unanticipated effects can lead to significant practical difficulty.

Acknowledgment

This work was executed in the research laboratories of IMI Titanium, Kynoch Works, Birmingham, UK, in 1977-79, under the general supervision of Mr J.R.B. Gilbert. Experimental work was done in collaboration with Mr J.M.Fisher, Mr K.K.Verma and Mr S.J Warden, with technical assistance of Mrs M.M.Finglass. XPS measurements were made at ICI Plastics. The work is now published by permission of IMI plc.

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