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HYDROMETALLURGICAL RECOVERY of MECHANOCHEMICALLY SYNTHESIZED Ti-Mg ALLOY POWDER FROM MILLED TiO$_2$-Mg POWDER MIXTURE

Tafadzwa Mushove

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witswatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering.

Johannesburg, 2010
DECLARATION

I hereby declare that this thesis submitted for the degree MSc Engineering (Metallurgy and Materials), at the Witwatersrand University, is my own original work and has not previously been submitted to any other institution of higher education. I further declare that all sources cited or quoted are indicated and acknowledged by means of a comprehensive list of references.

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Tafadzwa Mushove

17th day of March 2010
ABSTRACT

Ti-Mg alloy has desirable mechanical and other properties but is difficult to form by conventional ingot metallurgy. This work reports the results of a hydrometallurgical investigation on the recovery of Ti-Mg alloy powder synthesized from mechanochemical processing (MCP) of TiO$_2$ with Mg (15 wt.% beyond stoichiometric). The MCP synthesized alloy powder is intrinsically mixed with MgO and other oxides of Ti. The objective was thus to find a leachant that can leach out the by-products of the MCP process. Different inorganic and organic acid media, and their combinations, were used to try and recover a pure isolated Ti-Mg powder.

For comparison purposes, the dissolution of individual particulate polycrystalline MgO and TiO$_2$, and Ti-20Mg (obtained from milling blended elemental powders) was also investigated. The study indicated that separation with inorganic acids (HCl, H$_2$SO$_4$, and aqua regia) was not possible since as high as 80% of the milled Ti-Mg alloy powder was dissolving, yet the target TiO$_2$ was still undissolved under the same conditions. Recovery of Ti-Mg powder was not achieved with organic acids as well because MgO and TiO$_2$ showed marked resistance to dissolution and hence would contaminate the alloy powder. There was drastic co-dissolution of MCP TiO$_2$-Mg in combined HCl/organic acids while the TiO$_2$ resisted dissolution.
PUBLICATIONS AND PRESENTATIONS

DEDICATION

To Jefferson Kushinga

With all my love
ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to the following people for their kind help, support and encouragement throughout this study. I would like to thank my supervisor, Dr S. Ndlovu, for her valuable guidance, advice and support. I also want to thank my co-supervisors, Dr H.K. Chikwanda and Dr C. Machio, for their invaluable assistance during the course of this research work.

I am grateful to my colleagues Mr J Benson, Mr M Phasha, Mr S Bolokang and Ms G. Lesejane and the rest of my workmates from the Metals & Metal Processes in the CSIR for their assistance with the practicals and other technical aspects of my research. I am also indebted to the CSIR for providing the funding for this study.
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LIST OF ABBREVIATIONS

XRD : X-ray diffraction
M : Molarity
MCP : Mechanochemical processing
SEM : Scanning electron microscope
wt.% : Weight percent
at.% : Atom percent
CP : Commercially pure
L/S ratio : Liquid/Solid ratio
**MINERAL NAMES**

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CHAPTER 1

1.1 Background and Motivation

Titanium metal is the fourth most abundant structural metal in the earth’s crust, making up about 0.57 wt. %, and it is the ninth most abundant element (Sibum, 2003). Titanium and its alloys have been used in many applications particularly in the aerospace industry, because of their high strength (yield strengths range from 172 MPa for commercially pure [CP] titanium to above 1380 MPa for heat treated beta alloys), low density (between 4.43 g/cm\(^3\) and 4.85 g/cm\(^3\)), high strength-to-density ratio, and good corrosion resistance (Takeda, 2006; Leyens et al, 2003). Titanium primarily occurs as the minerals rutile (TiO\(_2\)), ilmenite (FeTiO\(_3\)) and sphene (CaTiSiO\(_5\)). Even though it is the ninth most abundant element in the earth’s crust (Sibum, 2003), the global production tonnage of metallic titanium was only 1.0x10\(^5\) tonnes in 2005, which was substantially lower than that of the common metals such as iron (Fe: 1.1x10\(^9\) tonnes in 2005) (Matsuoka, 2003).

Widespread titanium usage is prevented by its high production cost. The elevated cost is due to the current Kroll Process for refining titanium ore to titanium metal; the process is a labour intensive, multi-step, high temperature batch process with low productivity. Consequently, a new titanium production process with low cost and high productivity is required (Takeda et al, 2006). Studies are being conducted on direct reduction of rutile by more reactive metal reductants during mechanochemical processing (MCP). Direct reduction has the advantage that, apart from resulting in the formation of Ti alloys, it avoids the many expensive steps encountered in the Kroll process (Poulsen et al, 1983). Cheaper production of Ti metal aside, there is a need for lighter titanium alloys, especially to improve aircraft efficiency. It is recognized that a
density reduction is more effective in reducing aircraft weight than an increase in alloy strength (Wilkes et al, 1996). Density reduction can be attained by alloying Ti with lighter elements, e.g. Mg. Under equilibrium conditions, the solid solubility of magnesium in titanium is about 0.7 at.% at 890°C and much less (about 0.2 at.%) at 500°C (Wilson et al, 2001), which is significantly low.

1.2 MCP ‘far from equilibrium’ process for Ti-Mg alloy synthesis

The production of Ti–Mg alloys has its difficulties. For instance, conventional casting methods cannot achieve complete mixing of Ti and Mg because the boiling point of Mg (1090ºC) lies well below the melting point of Ti (1668ºC). Also, conventional casting, along with other processes like rapid solidification, and vapour quenching (Zhou et al, 1995) would require pure Ti made by the expensive Kroll process, which is a distinct disadvantage due to the cost of the Kroll Ti.

The challenges of producing Ti-Mg alloys by conventional methods have resulted in research into novel, far from equilibrium, processes of manufacturing Ti-Mg alloys. One such process is mechanochemical processing (MCP). The technology is a novel, solid-state process for the manufacture of metal powders, including metal alloy powders by ambient temperature reduction of a reducible metal compound by a reactive metal or metal hydride. Mg metal as a reductant is generating a lot of interest. Apart from producing Ti-Mg alloys when Mg is used in more than stoichiometric quantities (Poulsen et al, 1983), the element Mg has a density (1.74g cm\(^{-3}\)) which is lower than that of titanium (density 4.5g cm\(^{-3}\)). Accordingly, Ti-Mg alloys will exhibit appreciable density reductions compared to elemental Ti. Indeed, a 15% reduction in density has been reported for a Ti -11wt% Mg (Sun et al, 2002). Such a
density reduction could make Ti–Mg alloys attractive as replacements for present titanium alloys in applications like the aerospace industry where weight savings are important.

The MCP process is distinguished from competing technologies by the solid-state nature of the process that enables the formation of equiaxed nanoparticles, with a narrow size distribution and low levels of agglomeration (Mckormick et al, 1998).

The large departure from equilibrium possible in MCP leads to the attributes including extension of solubility levels of Mg in Ti. It also enables initiation of chemical reactions at much lower temperatures than those at which they would occur normally, leading to energy savings. In addition, it is a process that can be easily scaled up to commercial production (Koch, 1993).

The present research is focussed on separating Ti-Mg alloy powder synthesized from direct reduction of TiO₂ with Mg, using hydrometallurgical means. The Ti-Mg alloy powder was formed through reduction of TiO₂ by 15wt.% excess magnesium via mechanochemical processing (MCP). The other by-products of the MCP process are MgO, unreacted Mg, unreacted TiO₂ and incompletely reduced titanium oxides of the type TiₓOᵧ which require separation from the Ti-Mg alloy powder. The Ti-Mg alloy was synthesized by the CSIR and the process is thus protected by CSIR copyright; the role of this research was to focus on cleaning of the alloy rather than the alloy synthesis. It is hoped that once a cost effective beneficiation process is designed then titanium applications will become widespread.
1.3 Possible applications of Ti-Mg alloys

Possible Ti-Mg applications, by virtue of their lower densities and specific strengths (Sun et al., 2002), are given below:

1.3.1 Biomedical applications

The reason for the extended use of titanium and its alloys as implant biomaterials stems from their lower elastic modulus, their superior biocompatibility and improved corrosion resistance compared to the more conventional stainless steel and cobalt-based alloys (Nicula et al., 2007). Nanostructured titanium-based biomaterials with tailored porosity are important for cell-adhesion, viability, differentiation and growth. Newer technologies like foaming or low-density core processing were recently used for the surface modification of titanium alloy implant bodies to stimulate bone ingrowth and improve osseointegration and cell-adhesion, which in turn play a key role in the acceptance of the implants (Nicula et al., 2007). Examples of common biomedical devices include substitute heart valves and artificial hearts, artificial hip and knee joints, dental implants, internal as well as external fracture fixators, and skin repair templates. It is envisaged that Ti-Mg alloys will reduce the masses of these devices.

1.3.2 Aerospace applications

The use of Ti in the aerospace industry is among other reasons due to its lower density. As already noted in the Section 1.1, improved aircraft efficiency requires still lighter alloys and it is hoped that the introduction of Mg in Ti will produce novel alloys with a lower density and therefore that are suitable for making components in the aircraft industry (Wilson, 2001).
1.4 Problem Statement

Ti-Mg alloy powder has been produced by a mechanochemical process (MCP) through direct reduction of TiO$_2$ Mg. The MCP technique, however, also produces MgO, unreacted TiO$_2$, Mg and type TiO$_{1-x}$ oxides. It is required that the Ti-Mg alloy powder be isolated from the by-products of the MCP process by a hydrometallurgical process; in this context the Ti-Mg alloy is preserved while the by-products are leached out.

Various possible TiO$_2$/TiO leaching media have been investigated including sulphuric acid (Chun et al, 2007; Sole, 1999), hydrochloric acid (Chun et al, 2007; Imahashi et al, 1976) and organic acids such as ascorbic acid/oxalic acid in equi-molar concentrations (Mukherjee, 2005). The use of the test leaching media will be counter-balanced by the need not to dissolve the Ti-Mg alloy formed during the MCP process.

1.5 Objectives of the Study

The specific aims and objectives of this research are:-

- To derive a conceptual model for separating the Ti-Mg alloy from the waste oxides and unreacted metal powders.
- To optimize the Ti-Mg alloy powder separation process with respect to final recovery of a clean and pure Ti-Mg alloy.

1.6 Hypothesis

The premise of the work is that the Ti-Mg alloy powder will not be easily dissolved in the reagents that will be used to separate it from the by-products of the MCP technique.
1.7 Research Questions

The questions to be answered by this project are:

- Which one among the reagents that dissolves TiO$_2$ (and the other waste powders) would be more effective in meeting the aims and objectives of this study?
- Can the leach reagents be utilised in combination to achieve Ti-Mg isolation?
- What leach parameters (concentration, temperature, pulp density and leaching time) should be used during the leaching process to best achieve the objectives of leaching out the by products of the MCP process from the synthesized Ti-Mg alloy?

1.8 Dissertation Layout

This dissertation consists of five chapters. Chapter 1 provides the motivation for the research, the problem statement, and the overall objectives of this study. Chapter 2 contains the literature survey, which includes sections on mechanochemical processing (MCP) of Ti-Mg alloys and their possible uses. This chapter, however, predominantly dwells on dissolution literature of waste products of TiO$_2$-Mg milling in the MCP synthesis of the Ti-Mg alloy, along with possible organic and inorganic dissolution media. Chapter 3 (Experimental Procedures) describes the materials, methods and equipment used in this study. Chapter 4 looks at the results and discussion. The dissertation concludes in Chapter 5 with a summary of the research findings and recommendations. Appendices of detailed laboratory test results and references are also included.
CHAPTER 2

2.0 Literature Survey

This Chapter reviews the literature on the processing of Ti metal and the possible reagents that have been used to leach Ti ores. It also reviews the literature on metal oxide dissolution in acids and stability of Ti-Mg alloys in aggressive media.

2.1 The Kroll Process for Ti production

The Kroll process is a pyro-metallurgical industrial process used to produce metallic titanium through the formation of titanium tetrachloride from rutile, and its subsequent reduction with an active metal such as magnesium. Refined rutile (or ilmenite) from the ore is reduced with petroleum-derived coke in a fluidized bed reactor at 1000 °C. The mixture is then treated with chlorine gas, forming titanium tetrachloride (TiCl$_4$) and other volatile chlorides, which are subsequently separated by continuous fractional distillation. In a separate reactor, the TiCl$_4$ is reduced by liquid Mg (15-20% excess) at 800-850 °C in a stainless steel retort to ensure complete reduction:

\[
2\text{Mg}(l) + \text{TiCl}_4(g) \Rightarrow 2\text{MgCl}_2(l) + \text{Ti}(s)
\]  
(Eq 2.1)

The MgCl$_2$ in Eq. 2.1 can be further refined back to magnesium and chlorine which are recycled in the process. Complications for the process result from partial reduction of the titanium tetrachloride to its lower chlorides TiCl$_2$ and TiCl$_3$.

The resulting porous metallic titanium sponge is purified by leaching or heated vacuum distillation. The sponge is jack hammered out, crushed, and pressed before it is melted in a consumable electrode vacuum arc furnace. The melted ingot is allowed to solidify under vacuum. It is often remelted to remove inclusions and ensure
uniformity. These melting steps add to the cost of production, and hence the ultimate product cost. Titanium is about six times as expensive as stainless steel (Gerdemann, 2001).

Figure 2.1: Flowchart for the Kroll process (Kroll, 1940)

The major advantage of the Kroll process is its ability to produce high-purity titanium with low oxygen content. However, the reduction process is a labour-intensive, batch-type process and its productivity is low. More fundamentally, the process does not allow for the production of alloy powders. The production of alloy powders directly from the titanium ores or titanium oxide can greatly assist in reducing the production
cost of titanium alloys. Consequently, a new titanium production process with low cost and high productivity is required (Takeda et al, 2006).

2.2 Mechanochemical Processing

Mechano-chemical processing (MCP) is a term applied to the simultaneous chemical processing to induce oxidation-reduction reactions and chemical refinement processes through solid state reactions. It is also used for mechanical alloying of powder materials to produce metallic alloys, for instance, Ti-Mg alloys. Mechanical alloying is a powder metallurgy process in which alloying is obtained from repeatedly welding, fracturing and rewelding of powder particles through high energy mechanical milling. All these processes occur through solid state reactions. This is enabled by the energy of impact of the milling media on the reactants which effectively substitutes for high temperature so that solid state reactions can be carried out at room temperature (Froes et al, 2004; Mckormick et al, 1998). There are various theories in literature of how the alloy powder forms (Lai et al, 2002; Welham et al, 1999; Wilkes et al, 1996; Sheibani et al, 2007; Mckormick et al, 1998; Suryanarayana, 2004).

The principal attributes of mechano-chemical processing with respect to the present research include ultrafine powder production, extension of solubility limits, refinement of the matrix microstructure/nano-grain formation, synthesis of novel crystalline phases, the possibility of alloying difficult-to-alloy elements and scalability (Mckormick et al, 1998).
2.2.1 MCP in the synthesis of Ti-Mg alloys

A possible method for the manufacture of Ti–Mg alloys is mechanochemical milling of rutile with more than stoichiometric quantities of Mg powders. There are two basic processes that would be expected to take place in the mechanochemical processing (MCP) of Ti-Mg alloy powders from ball milling of rutile and magnesium. The first process is the reduction of rutile to titanium monoxide (TiO) followed by further reduction of the monoxide to metal by Mg which itself changes to magnesium oxide (MgO) (Welham, 1998). The reduction to Ti metal takes place when stoichiometric Mg quantities are used as shown by the Equations 2.2 and 2.3 below. It is possible that sub-stoichiometric oxides form especially given the fact that the milling process is chaotic in nature.

\[
\text{TiO}_2 + Mg \rightarrow TiO + MgO \quad \text{(Eq 2.2)}
\]

\[
\text{TiO} + Mg \rightarrow Ti + MgO \quad \text{(Eq 2.3)}
\]

\[
Ti + Mg \rightarrow Ti - Mg \quad \text{(Eq 2.4)}
\]

For synthesis of Ti-Mg alloys, more Mg than the stoichiometric quantity is added to the TiO₂. The stoichiometric Mg is all oxidised to MgO, while the excess quantity goes towards formation of Ti-Mg alloy (Welham, 1998). In this scenario, the summed up chemical equation for the process (from Eq 2.2 – 2.4) would be expressed as Equation 3.5:

\[
\text{TiO}_2 + 3Mg \rightarrow Ti - Mg + 2MgO \quad \text{(Eq 2.5)}
\]

The reduction and alloying processes depicted in Eq 2.5 occur chaotically, because of the random nature of the mechanochemical milling process. Thus reaction depicted in
Eq 2.5 may not go to completion. As such, excess Mg generally boosts the probability of synthesizing a sizable proportion of the Ti-Mg alloy.

2.3 Hydrometallurgical removal of waste powders.

The Ti-Mg alloy powder formed from the MCP of TiO$_2$ and Mg (Eq. 2.5) has to be separated from the other products of the process. This can be achieved through direct solubilisation in suitable reagent/s which should have very little effect, ideally none at all, on the dissolution kinetics of Ti-Mg alloy. Various organic and inorganic acids will be investigated as possible waste powder dissolution reagents.

Of all the waste powders produced, incompletely reduced TiO$_2$ (because it has higher surface energy relative to MgO) will probably be the most difficult to solubilize, and hence the emphasis will be on it. Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is created (Kiejna et al, 2006). It is presumed that the other waste powders will prove to be relatively easy to dissolve. TiO is expected to generally dissolve in media which dissolves TiO$_2$ because it is less stable than TiO$_2$ thus making it more amenable to dissolution by any media which attacks the more stable TiO$_2$.

2.3.1 Metal oxide dissolution

Dissolution is the solvation of a solid by an aqueous chemical solution. It involves the use of a lixiviant which is brought into contact with a material to be dissolved (Kim, 2004). When an oxide is dissolved, the O$^{2-}$ incipiently coordinated to cations in an oxide layer will be replaced by H$_2$O, OH$^-$ or other ligands when the cations are transferred into solution. The key to identifying the overall rate of reaction lies in
understanding the factors that affect the elementary steps. The following steps are well-known:-

- mass transport of solutes (H$^+$, OH$^-$, ligands) to the oxide surface;
- surface attachment of the solutes (adsorption or surface complex formation);
- various surface chemical reactions (inter-lattice transfers, etc.);
- detachment of products from the surface;
- mass transport of dissolved products into the bulk of the solution.

The general principles governing the mechanisms and kinetics of dissolution of oxides are not sufficiently known particularly because single oxides have seldom been intensively studied, and the range of conditions for the individual oxides varies from one author to the next in literature (Fedorockova et al, 2008).

Many oxides are difficult to dissolve in mineral acids or chelating agents, for kinetic rather than thermodynamic reasons. The rate of dissolution of metal oxides in dilute acids may be affected by a large number of factors relating to both the solute and to the solvent. As already stated, current theories of the dissolution of ionic oxides predict that the dissolution rate should have an inverse exponential dependence on solution pH. These theories are concerned with situations in which dissolution rates are not governed by diffusion in the solution but are controlled by solid-liquid interactions in the interphase region (Jones et al, 1981).

Dissolution reactions are characterized as hydrolysis, alkaline, acidic, or oxidative and reductive leaching. The lixiviant in solution may be acidic or basic in nature. The type and concentration of the lixiviant is normally controlled to allow some degree of selectivity for the species that are to be solubilised. In the dissolution process,
oxidation potential, temperature, and pH of the solution are important parameters, and are often manipulated to optimize dissolution of the desired species into the aqueous phase (Kim, 2004). The process of leaching can be complicated by secondary reactions, such as precipitation, adsorption, or formation of complexes. The dissolution of mineral components and the behaviour of dissolved components is controlled by the system variables like pH, and the concentrations of the dissolved species. The sections that follow are going to review the literature on dissolution of the oxides that need to be solubilised in the current project.

2.3.1.1 Dissolution of MgO

The dissolution of MgO in acid is controlled by the chemical reaction of MgO with H\(^+\) ions at the liquid-solid interface, while the dissolution rate of MgO crystals depends on the nature of the crystals and their surface orientation and on the temperature and concentration of the acid used (Sangwal, 1980). The dissolution of MgO in inorganic acids (HCl, HNO\(_3\) and H\(_2\)SO\(_4\)) is a liquid–solid reaction in which no solid product is formed. The overall MgO dissolution process may be controlled by chemical reaction or by external mass transfer. It involves the diffusion of H\(^+\) ions through the liquid film at the liquid–solid interface to the surface of the solid particles, surface chemical reaction and diffusion of liquid products of the reactions from the interface through the film to the bulk liquid. The stoichiometry of the reaction between MgO and hydrogen ion in solution is represented by Eq. 2.6.

\[
MgO(s) + 2H^+(aq) \Rightarrow Mg^{2+} + H_2O(l) \tag{Eq. 2.6}
\]

The surface chemical reaction involves the transfer of magnesium cations and the oxygen anions from the solid to the solution, in which the cations will be hydrated. The transfer of the anions will involve protonation or hydroxylation reactions at the
surface of the solid, to form water (Raschman et al., 2006; Fedorockova et al., 2008). The overall rate can be controlled by diffusion of dissolved reactants/products or by the surface reaction, depending on the reaction conditions.

Many authors (Raschman et al., 2006; Fedorockova et al., 2008) have shown that the empirical rate law $r = k [H^+]^n$ for MgO dissolution exhibits a fractional rate order $n$ which is compatible with kinetic theories, and is indicative of a process controlled by surface reaction. However, there are situations when the application of different theoretical approaches results in identifying various potential rate-controlling steps for identical reaction conditions, with no clear basis for discrimination between these alternatives (Fedorockova et al., 2008).

The rate of MgO dissolution is insensitive to the concentration of dissolved cation; the dissolution rate increases as the concentration of magnesium ($Mg^{2+}$) ions in solution increases during dissolution of the first few monolayers of the oxide. MgO is relatively easily solubilised (Jones et al., 1981; Fedorockova et al., 2008). Although the reaction order for $H^+$ ions seems not to be affected by the type of acid used, the activation energy of the reaction in common inorganic acids changes in the order $HCl \leq HNO_3 < H_2SO_4$. The higher values of activation energy obtained for $H_2SO_4$ could indicate that the surface chemical reaction is controlled by different reactions between surface anions and protons created by dissociation of $H_2SO_4$ (Fedorockova et al., 2008).

Varying the concentration of $HCl$ acid from 1.0 to 5.3 M has been found to decrease the dissolution rate of MgO (Raschman et al., 2006). When MgO is introduced in an inorganic acid the dissolution rate increases rapidly despite a decrease in $H^+$ concentration in solutions with low $Mg^{2+}: H^+$ molar ratios (Raschman et al., 2006).
For MgO particles in acetic acid solution, the principal chemical reactions and the corresponding equilibrium equations are listed as follows:

\[
CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \quad (\text{Eq. 2.7})
\]

\[
MgO + 2CH_3COO^- + 2H^+ \rightleftharpoons Mg^{2+} + 2CH_3COO^- + H_2O \quad (\text{Eq. 2.8})
\]

\[
MgO + 2H^+ \rightleftharpoons Mg^{2+} + H_2O \quad (\text{Eq. 2.9})
\]

\[
MgO + H_2O \rightleftharpoons Mg^{2+} + 2OH^- \quad (\text{Eq. 2.10})
\]

Acetic acid (Eq. 2.7) is a weak organic acid with a small equilibrium constant of about 1.8x10^{-5}. Dissolution of MgO in acetic acid (Eq. 2.8), can be finished in a reasonably short period of time, with the major salt produced being the water-soluble magnesium acetate which would turn into tetrahydrate, Mg(CH_3COO)_2 .4H_2O, after saturation (Chung et al, 2008).

2.3.1.2 Dissolution of TiO_2/TiO

The ease of dissolution of TiO_2/TiO appears to depend on phase. TiO_2 exists in three main phases which are anastase, brookite and rutile. It is generally considered that at low pressures only rutile has a true field of stability; anastase and brookite form as metastable phases (Banfield et al, 1993). Solution-phase preparation methods for TiO_2 generally favour the anastase structure. This is because the surface energy of anastase is lower than those of rutile and brookite (Reyes-Coronado et al, 2008). Surface energy quantifies the disruption of intermolecular bonds that occurs when a surface is created. Dissolution of TiO_2 (indeed any material) disrupts its bonds, and therefore consumes energy. Therefore the higher the surface energy, the more resistant a particular solid is to dissolution.
Literature Survey

Literature (Van Humbeeck, 2009) has shown that dissolution of TiO$_2$ films in electrolytes free of aggressive fluoride (F-) ions takes place uniformly all over the oxide surface, and not as a localized attack. The dissolution will essentially be chemical, with a dissolution rate exhibiting a first order dependence towards the protons concentration at low pH. Dissolution of TiO$_2$ films in acidic electrolytes is depicted by Eq. 2.11 where the hydroxide compound rapidly dissociates in acidic media (Van Humbeeck, 2009)

$$TiO_2 + H^+ + H_2O \Rightarrow Ti(OH)_3$$  \hspace{1cm} (Eq. 2.11)

Titanium monoxide (TiO) is a lower oxide of Ti that is unstable at 700–800 K. During its synthesis, and under controlled partial oxygen pressure, it can dissociate to form either Ti$_2$O, Ti$_3$O$_2$ or Ti$_2$O$_3$. TiO contains 16.7 at.% vacancies in the titanium and oxygen sublattices (Valeeva et al, 2001), making it a high energy state phase. The configuration of the force field around vacancies ensures rapid shrinking of the lattice in the direction away from its centre. This leads to sub-micropitting when the atoms nearest the vacancies dissolve away (Gutman, 1998). Therefore it is expected that TiO should generally dissolve in media which dissolves TiO$_2$ since it is less stable than TiO$_2$ (Valeeva et al, 2001; Gutman, 1998, El-Hazek et al, 2007).

2.3.2 Reagents for leaching TiO$_2$

Various possible TiO$_2$ leaching media have been reported in the literature including sulphuric acid, hydrochloric acid (Chun et al, 2007), organic acids (Mukherjee, 2005) and aqua regia. Aqua regia is a mixture of nitric acid and hydrochloric acid in the volume ratio 1:3 (Bachman, 1999). It is expected that TiO should also dissolve in media which dissolves TiO$_2$. This is because, as noted above, TiO is less stable than
TiO$_2$ and is expected to be rapidly attacked by any media which attacks the more stable TiO$_2$.

The choice of the leaching reagent in this project will be based on the possible effects to be avoided, such as dissolution of the Ti-Mg alloy powder. One of the aims of this project will be to clarify the sensitivity of the Ti-Mg alloy towards dissolution and to optimize the leaching conditions to avoid the undesirable chemical reactions as well as to develop a cheap and technologically feasible method of separating the Ti-Mg alloy powder from the waste powders.

2.3.2.1 Sulphuric acid leaching

TiO$_2$ dissolves when it comes into contact with H$_2$SO$_4$, titanium going into solution as positively charged ions. The precise compositions of the aqueous species that form are controversial, particularly because of difficulties in achieving thermodynamic equilibrium in these systems. In acid media, at pH less than 1.3 in the absence of complex forming reagents like SO$_4^{2-}$ ions, titanium dissolves to form monomeric divalent cations (assumed to be TiO$_2^{2+}$) (Sole, 1999). The dissolution of TiO$_2$ is enhanced by mechanical pretreatment which increases the lattice strain and surface area of oxide particles (Sasikumar et al, 2007).

The dominant species during the dissolution of TiO$_2$ in sulphuric acid is TiOSO$_4$.2H$_2$O, represented more accurately as Ti(OHO)$_3$(HS)$_4$. This structure consists of an infinite zigzag of –Ti-O-Ti-O- chains where titanium is octahedrally coordinated by two bridging oxygen atoms, an oxygen atom from each of three sulphate ions, and
one water molecule. Species such as TiOSO$_4$, [TiO(SO$_4$)$_2$]$^{2-}$ and [TiO(SO$_4$)$_4$]$^{4-}$ also form (Eqs 2.11 – 2.13) with increasing sulphate concentration (Sole, 1999).

\[
\text{TiO}^{2+} + \text{SO}_4^{2-} \rightarrow \text{TiOSO}_4 \quad \text{(Eq. 2.12)}
\]

\[
\text{TiOSO}_4 + \text{SO}_4^{2-} \rightarrow \text{TiO(SO}_4)_2^{2-} \quad \text{(Eq. 2.13)}
\]

\[
\text{TiO(SO}_4)_2^{2-} + 2\text{SO}_4^{2-} + 2\text{H}^+ \rightarrow \text{TiO(SO}_4)_4^{4-} + \text{H}_2\text{O} \quad \text{(Eq. 2.14)}
\]

Polymerized titanium (IV) species exist in aqueous sulphate media (from H$_2$SO$_4$) and the maximum polyions concentration occurs at sulphuric acid concentrations of 1.4 to 1.6M. At higher concentrations; the polymeric species are destroyed and at 5 to 8M monomeric species predominate. The rate of TiO$_2$ dissolution increases with sulphuric acid concentration up to 14M since the concentration of hydrogen cations peaks there. Optimum extent of TiO$_2$ dissolution can reach 87% (Sole, 1999).

There are problems of hydrolysis when lower acid concentrations (1.5M- 4M) of free sulphuric acid) and high temperatures (90–110°C) are used. For instance, in 4M sulphuric acid the hydrolyzed product has a compact structure and is strongly adherent preventing further dissolution of the un-reacted rutile. In contrast, in 0.9M acid solutions, the hydrolyzed product will be poorly compacted and dissolution could continue. In both cases the hydrolysis product is thought to be rutile TiO$_2$ (Chun et al, 2007). It therefore appears that with sulphuric acid leaching of TiO$_2$, the acid concentration should be kept within certain limits to avoid formation of solid products which may contaminate the Ti-Mg powder alloy.

Literature also reports on the use of reagent mixtures based on H$_2$SO$_4$ to dissolve TiO$_2$. Some of these reagents were concentrated H$_2$SO$_4$ mixed with (NH$_4$)$_2$SO$_4$, and concentrated H$_2$SO$_4$ mixed with HF (Korn et al, 2002). For H$_2$SO$_4/(\text{NH}_4)_2\text{SO}_4$, 0.4g of
TiO$_2$ was dissolved in 16ml of concentrated H$_2$SO$_4$ with 0.06M (6.4g) of ($\text{(NH}_4\text{)}_2\text{SO}_4$). The mixture was heated for 30 minutes at 250°C to effect complete dissolution of the sample (Korn et al, 2002). With H$_2$SO$_4$ in HF, a 4g oxide sample was digested in 10ml of concentrated HF and 16ml of concentrated H$_2$SO$_4$ and the mixture was heated to 200°C until evolution of SO$_3$ fumes. The mixture was then cooled before adding 10 ml of concentrated HF, followed by heating to 200°C until SO$_3$ fumes were evolved. After cooling, the above procedure was repeated continuously until complete decomposition was effected at about 4 hours (Korn et al, 2002). The above two procedures are very aggressive and are meant for total decomposition of TiO$_2$, without much regard to preservation of anything else that could be intermixed with the oxide. For this research work the above procedures would have to be modified and made less aggressive because of the need to preserve Ti-Mg alloy powder.

2.3.2.2 Hydrochloric acid leaching

When titanium oxide and or its compounds are introduced to hydrochloric acid, Ti$^{4+}$ ions form initially but may hydrolyze back to titanium dioxide (El-Hazek et al, 2007). The hydrolysis occurs when Ti$^{4+}$ concentration is greater than 10$^{-3}$M and when the concentration of hydrogen ions is less than 0.5M as can happen with a relatively low initial acid/ilmenite mole ratio. At a high acid to rutile ratio, the Ti(IV) concentration in solution may never reach the threshold concentration required for hydrolysis. High leach temperatures lead to rapid hydrolysis resulting in the precipitation of TiOCl$_2$ and TiO$_2$ in the pores of the particles. At lower temperature or at higher initial acid to rutile mole ratios, the hydrolysis reaction does not proceed as rapidly and this results in the formation of TiOCl$_2$ fines in the leach solution. The TiOCl$_2$ may be hydrolyzed to TiO$_2$ if the acid concentration decreases significantly. Thus, with hydrochloric acid,
there should be accurate control of parameters like acidity and acid/solid ratio to avoid hydrolysis (El-Hazek et al, 2007).

Addition of phosphate and fluoride to hydrochloric acid and or using alcoholic hydrochloric acid solutions has been found to enhance the leaching of ilmenite/rutile. For instance, leaching of ilmenite with 6M HCl and 0.5M methanol–water (CH₃OH-H₂O) mixture at 110°C and solid/liquid ratio (S/L) of 0.02 g/mL results in the dissolution of 91% Ti compared to dissolutions of 53.5% Ti in 6M HCl alone (Olanipekun, 1999).

It appears that the optimum conditions for TiO₂ leaching in hydrochloric acid involve working with 12M acid with a solid/liquid ratio of 1/20 at 80 °C for 2.5 h, using ore ground to – 200 mesh size. This has a dissolution efficiency of 95% (El-Hazek et al, 2007). As a leachant, hydrochloric acid allows comparatively easier recovery of the useful free acid from its waste solution. In addition, the recovery of a number of metal ions by liquid–liquid extraction from hydrochloric acid solutions is considerably easier than that from sulphuric acid medium (Olanipekun, 1999).

2.3.2.3 Aqua regia leaching

Aqua regia is formed from a freshly prepared mixture of concentrated nitric and hydrochloric acids, in a volumetric ratio of 1:3 respectively. It is a highly corrosive, fuming yellow or red solution. It was so named because it can dissolve noble metals gold and platinum, although titanium, tantalum, iridium and osmium are able to withstand it. Neither constituent acid will do so alone, because, in combination, each acid performs a different task. Nitric acid is a powerful oxidizer, which will dissolve a metal element forming cations (M⁺⁺). The hydrochloric acid provides a ready supply
of chloride ions (Cl\textsuperscript{-}), which react with the metal cations to produce chlorometal anions, also in solution.

2.3.2.4 Organic acid leaching

TiO\textsubscript{2} dissolves in organic reducing reagents namely ascorbic acid, oxalic acid and l-cysteine. Studies indicate that a maximum of about 45% TiO\textsubscript{2} can be dissolved by ascorbic acid in 4 hours when oxide/acid molar ratio is 1/2 (Mukherjee, 2005). With oxalic acid and ascorbic acid in equi-molar concentrations, dissolution of TiO\textsubscript{2} is up to 60% in 2.5 hours. The dissolution rate was found to be 50% in 1 hour when cysteine was added (Mukherjee, 2005). Organics need to be added to TiO\textsubscript{2} in mixtures if better dissolution rates are to be realized (Mukherjee, 2005). This could pose problems when an acid regeneration step is necessary since the different organic acid components may respond differently to the regeneration reagent(s) employed.

2.3.3 Stability of Titanium and its alloys in aggressive media

Titanium element is characterized by a very negative standard redox potential ($E^\circ=-1.63$ V/S.H.E. Ti\textsuperscript{2+}/Ti\textsuperscript{4+}). However, it has a high chemical stability due to the formation of a very resistant and protective oxide layer on its surface. The oxide layer forms from the rapid oxidation of Ti to Ti\textsuperscript{4+} ions, which in acids, exist only as titanyl ions (Ti(OH)\textsubscript{2}\textsuperscript{2+}) even at pH values below 1. Beyond that, they evolve into Ti(OH)\textsubscript{4}, which precipitates and dehydrates, resulting in the most stable form TiO\textsubscript{2} which is the main component of the passivating layer. The phenomenon of passivation is a guarantee of excellent resistance to corrosion in various electrolytic media (Fovet et al, 2001).
Ti-based alloys are usually very resistant to some organic acids, e.g., acetic and lactic acid, but can be corroded by others such as formic acid and citric acid. However, aerated solutions often suffice to inhibit corrosion of unalloyed Ti in the stronger organic acids, such as formic, lactic and citric. The dissolution of titanium is known to be extremely slow even in aggressive media such as HCl or H\textsubscript{2}SO\textsubscript{4}, for example. However, titanium does dissolve in concentrated hydrofluoric acid (HF) (Schmidt et al, 2006). Ti shows marked resistance to corrosion and pitting in seawater and oxidizing chloride solutions. Pitting can be observed on Ti surfaces under anodic polarization in bromide containing aqueous solutions, mainly in HBr media (Schmidt et al, 2006).

### 2.3.3.1 Dissolution of Ti-Mg alloys

The titanium-magnesium alloys exhibit high negative values of corrosion potential and substantial corrosion rates during anodic polarization. The character of the anodic process on such a pseudoalloy is determined by the influence exerted by its magnesium component, and is unaffected by the presence of the titanium skeleton. Titanium has good corrosion resistance and passivity which, in principle, should be transferable to Ti-Mg alloys in order to improve their corrosion resistance. The incorporation of titanium in these alloys gives rise to a self-healing corrosion layer and reduced galvanic potential (Dias et al, 2002).

The anodic dissolution of titanium-magnesium composites is characterized by independence of electrochemical reactions. In tests in a KOH solution, the Ti-Mg composites exhibited high corrosion resistance: Their rates of dissolution in the whole component concentration range did not exceed 0.03 mm/yr (Frantsevich et al, 1993). Ti-Mg alloys are novel materials; research into these is still centred on their synthesis.
Consequently, literature on corrosion tests of Ti-Mg alloys in HCl, H$_2$SO$_4$, aqua regia and the organic acids is still scarce.

2.3.4 Influence of mechanical activation on dissolution

The influence of mechanical activation on dissolution of finely milled minerals has recently attracted attention. Mechanical activation introduces physicochemical changes like phase transformations, structural defects, strain and changes in the surface characteristics of minerals, which in turn enhance the dissolution rate and/or extent of dissolution (Sasikumar et al, 2007).

There are three ways in which dissolution is enhanced. Oxygen vacancies, brought about by the chaotic nature of the mechanical activation, are among the primary chemically active defects on the surface of reducible transition metal oxides. These act as direct adsorption sites, and also as electron donor sites thus modifying the surface electronic structure and thus the surface chemistry (Wendt et al, 2005). They are also high energy sites, because they possess force fields which predispose the nearest atoms in the vicinity of the vacancies to dissolution leading to micropitting (Gutman, 1998).

The formation of line defects, called dislocations, during mechanochemical processing can also affect dissolution. Like the vacancies mentioned above, dislocations also are associated with stress fields, which make them high energy sites, and therefore more reactive. The effect of dislocations can however be tempered in the presence of impurities. On the one side, when the impurities segregate at the dislocations, their mechanochemical activity decreases because of stress relaxation
(therefore, ‘old’ dislocations are more difficult to etch) (Gutman, 1998). On the other hand, the extent of dissolution may increase because a change of the chemical composition of the region of exit of the dislocation may reduce their corrosion resistance (Gutman, 1998).

2.3.5 Benefits of leaching out waste powders

Ti-Mg alloy is a high value product with a potentially lower density and has potential to be used in the aerospace, biomedical and marine industries. By definition high value products are those which are difficult to make, are made from expensive precursors or have a high energy cost in manufacture (Welham, 1999). Value addition for the Ti-Mg alloy can be achieved by simplifying the route of synthesis through using MCP rather than conventional ingot metallurgy (or other complex far from equilibrium processes), for instance, to ensure increased solid solution of Mg into Ti (Gerdemann, 2001). It can also be achieved by using TiO$_2$ powder, which is a relatively low cost precursor, as a starting material in the mechanochemical process rather than using elemental Ti from the expensive Kroll Process (Takeda, 2006).

Mechanochemical processing (MCP) of TiO$_2$ and Mg to synthesize Ti-Mg alloy forms a number of by products. MCP is a process which is scaleable to commercial production quantities, unlike certain other “far from equilibrium” processes (Koch, 2003). Thus, to realize full benefits from the process, it is imperative that the waste products of MCP are separated from the synthesized Ti-Mg alloy powder.
CHAPTER 3

3.0 Experimental Procedures

3.1 Introduction

This chapter describes the techniques used in this project. It starts by describing the techniques used to characterize the powders used, followed by the hydrometallurgical procedures used to recover the Ti-Mg alloy.

3.2 Test powders

The TiO$_2$-Mg powder samples used for the hydrometallurgical separation project were supplied by the CSIR and most specific parameter details of the milling aspect are thus protected by CSIR copyright. The TiO$_2$-Mg powder samples were continuously milled for 32 hours. The total masses mixed were 80g TiO$_2$ and 60g Mg; this translated to 15 wt.% excess Mg, relative to the stoichiometric Ti produced from complete reduction of TiO$_2$. The Mg powder was 15% more than stoichiometric quantity to increase the proportion of the Ti-Mg alloy thus synthesized. The powders were also characterized for phase and particle size distribution, before the hydrometallurgical separation procedures.

Elemental Ti-20(wt.%)Mg milled powders and polycrystalline commercial rutile (TiO$_2$) and magnesium oxide (MgO) were also subjected to the reagents used in the separation procedures. The Ti-20Mg alloy was synthesized from mechanical alloying of blended elemental Ti and Mg from another CSIR project, itself also protected by CSIR copyright. The objective was to determine the dissolution of individual particulate polycrystalline MgO and TiO$_2$, and Ti-20Mg and use their dissolution behaviour and extrapolate it on the dissolution of the MCP synthesized powders. The
Experimental Procedures

TiO$_2$ and MgO were not pre-milled. The alloy Ti-20Mg was obtained from mechanical alloying of blended elemental (BE) Ti and Mg powders, and is distinct from the alloy obtained from the MCP process which is intimately mixed with other by products.

In total four different categories of powders were used in this research; namely milled TiO$_2$-Mg, Ti-20Mg (from blended elemental powders), as well as commercial TiO$_2$ and MgO. It is the milled TiO$_2$-Mg powder mixture that generates the species MgO, Ti-Mg and unreacted TiO$_2$ and Mg; this mixture will, henceforth, be referred to as TiO$_2$-Mg to differentiate it from Ti-20Mg from BE powders and commercial TiO$_2$ & MgO powders.

3.3 Powder Characterisation

3.3.1 X-ray Diffraction (XRD)

TiO$_2$-Mg powders mechanochemically processed (MCP) for a duration of 32 hours (including an unmilled TiO$_2$-Mg, Ti and Mg) were taken for phase analysis by XRD to determine the phases present and, more importantly, to ascertain the relative degree to which the reduction and alloying had progressed. Leached powder residues were also taken for XRD analysis to determine the phases, and their relative intensities, that resisted dissolution. Analysis of the residue phases should, therefore, give an indication of those phases that would have largely dissolved in the individual leach reagents.

The phase compositions of the powders were determined using XRD analysis. An X'Pert Pro MPD, Philips PW1710 diffractometer with a graphite monochromator and Cu Kc radiation was used. The copper XRD tube was excited using voltage and anode
current of 40kV and 20mA respectively, and step-scanning measurements were done in the range from 10 to 70° $2\theta$, with a step of 0.02° $2\theta$ and a counting time of 1s per step.

### 3.3.2 Particle size analysis

Particle Size Analysis (PSA) was carried out with a Malvern Particle Size Analyzer MS2000, based on the principle of laser diffraction. A Microtrac Bluewave Analyzer was also used. Powder particles, each sample about 10 milligrams, were suspended in a dispersant (water) and an ultrasonic agitator before a monochromatic laser beam is projected through the suspension. The powder particles scatter the laser beam at an angle that is inversely proportional to their size. The angular intensity of the scattered light is then measured by a series of photosensitive detectors (Figure 3.1). The map of scattering intensity versus angle is the primary source of information used to calculate the particle size. Particle size analysis (PSA) was carried out on pre-milled blended powders, and the milled powders. Residues powders after leaching were not particle size analyzed.

![Schematic diagram of the laser diffraction measurement](image-url)

**Figure 3.1: Schematic diagram of the laser diffraction measurement**
3.3.3 Morphological characterisation of MCP powders

The morphology of both pre-milled and milled samples was investigated using a Jeol JSM-6300F scanning electron microscope (SEM) at an accelerating voltage of 15 kV. The samples were coated with carbon to enhance conductivity, and hence achieve better resolution of the micrographs. The morphology of the unmilled and milled TiO$_2$-Mg helps to explain the progress of reduction and/or alloying; composition becomes homogenous and there will be no distinction between the initial powders (Lai et al, 2002).

3.4 Hydrometallurgical experiments for recovery of MCP synthesized Ti-Mg alloy powder

The separation of the waste constituents (by-products TiO, MgO; and incompletely reduced oxides of Ti and Mg) from the Ti-Mg alloy powder was done through direct dissolution in suitable organic and inorganic acids/reagent(s). The inorganic reagents used were sulphuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), aqua regia, concentrated H$_2$SO$_4$ with hydrofluoric acid (HF), and concentrated H$_2$SO$_4$ with ammonium sulphate. The inorganic reagents were equi-molar oxalic/ascorbic acids, and equi-molar l-cysteine/ascorbic acids. These inorganic and organic acids named above gave good dissolution of TiO$_2$, a difficult to dissolve phase from Literature (Chun et al, 2007; Sole, 1999; Imahashi et al, 1976; Mukherjee, 2005).

The dissolution experiments were carried out in a Julabo SW23 Shaking Waterbath (Figure 3.2), equipped with a removable shaking carriage that accommodates up to 11 round bottomed, graduated flasks. The shaking frequency is adjustable from 20 to 200 rpm. The flasks openings were sealed with aluminium foil to minimize spillage of
contents and evaporation of the leaching reagents during the agitated, heated leach runs. The waterbath setup was placed in a fume cupboard.

The dissolution experiments were performed in 250 ml flat bottomed flasks. For each run, 200 ml of acid solution of predetermined molarity was charged into a flask and heated to the required temperature. Thereafter, powder sample was added to the flask and the contents were stirred at a constant speed. The leach parameters were temperature 90°C (for inorganic acids) and 60°C (for organic acids), stirring speed of 200rpm and liquid/solid ratio of 100ml/1g. The high liquid/solid ratio was meant to decrease the viscosity of the slurry and consequently the mass transfer resistance in the acid-powder particle interface.

The molarities used for sulphuric acid (H$_2$SO$_4$), hydrochloric acid (HCl), aqua regia were 0.1M, 0.5M, 0.9M and 1.3M while 0.025M, 0.05M, 0.075M and 0.1M were used equi-molar oxalic/ascorbic acids, and equi-molar cysteine/ascorbic acids. The molarity of equi-molar cysteine/ascorbic acids was extended to 0.8M in order to understand its effect better. The mixtures of inorganic reagents were based on concentrated H$_2$SO$_4$ with a morality of 3M, 4M, 5M and 6M mixed with 0.06M ammonium sulphate, and with 0.1M hydrofluoric acid.
The duration of leaching was 40 minutes for inorganic acid and 2.5hrs for organic acids. At the end of each dissolution experiment, the individual residues were filtered, washed with distilled water and dried. These residues were subsequently weighed, and, for each leach solution, the percent residues were plotted against concentration to give dissolution graphs (Appendix D). They were also analysed for phases by XRD as described in Section 3.3.1.

**Figure 3.2 Setup of the Julabo SW23 dissolution apparatus**
CHAPTER 4

4.0 Results and discussion

4.1 XRD characterisation of powders

The XRD patterns of the TiO$_2$-Mg blended powder, MCP TiO$_2$-Mg, and Ti-20Mg from blended elemental powders are shown in Figure 4.1. This figure also shows the patterns of unmilled elemental Ti and Mg, and Ti-20Mg milled for 32 hours.

\[ \text{\textbullet TiO}_2 \quad \text{\square Mg} \quad + \text{MgO} \quad * \text{Ti-Mg} \quad ' \text{Ti} \]

Figure 4.1: X-ray diffraction patterns of the TiO$_2$-Mg powder mixtures milled for various durations
The intensities of TiO$_2$ and Mg peaks reduced while the peaks broadened, from the initial TiO$_2$-Mg powder to that milled for 32 hours, indicating a reduction in the grain size. A new peak, determined as being that of MgO could be seen, indicating that the reduction reaction was mechanically activated. The observation of the formation of MgO and the lowering in peak intensity of TiO$_2$ and Mg (Figure 4.1) on the XRD patterns suggests a typical oxidation-reduction reaction that involves displacement of Ti from TiO$_2$ by Mg, resulting in formation of MgO as indicated by Eq. 4.1

$$\text{TiO}_2 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgO} \quad \text{(Eq. 4.1)}$$

The enthalpy of formation for 2MgO is -1204kJ which is about four times lower than that of TiO$_2$ (-315kJ), so that the reaction as mentioned in Eq. 4.1 is a forward single step reaction (Shankar et al, 2003).

### 4.1.1 Proportion of Ti-Mg synthesized

The extent of the reduction of TiO$_2$ by Mg was evaluated from the Eq. 4.2 (Lai et al, 2002):

$$D = \left( \frac{I(\text{TiO}_2)}{I(\text{TiO}_2) + I(\text{MgO})} \right) \times 100 \quad \text{(Eq. 4.2)}$$

where I is the intensity of the diffraction peaks of MgO and TiO$_2$. The initial TiO$_2$ peak intensity was 1625 while the final MgO peak intensity was 250. Therefore, the reduction of TiO$_2$ at the optimised MCP duration was evaluated from Eq. 4.2 to be 90%. The assumption in using Eq. 4.2 was that there was no formation of substoichiometric oxides of Ti and, from XRD data (Fig 4.1), there was no evidence of Ti$_x$O$_y$ substoichiometric oxides. Lastly, the degree of crystallinity was assumed to be the same in all phases present in the milled powder.
Thus, 10% of the TiO\textsubscript{2} remained unreduced at the end of the milling process and the rest took part in the mechanochemically induced reduction and alloying. Stoichiometric quantities of TiO\textsubscript{2} and Mg powders were mixed (Eq. 4.1) and the maximum theoretical amount of free Ti formed was calculated. Total reduction of the TiO\textsubscript{2} was assumed. It was on the basis of the maximum amount of Ti that can be theoretically formed that the mass of 15wt.% excess Mg was calculated. The sum of the excess Mg (Eq. 4.3) and the stoichiometric TiO\textsubscript{2} and Mg (Eq. 4.1) formed the precursor powder blends mechanochemically processed (MCP) for different durations.

\[
\text{TiO}_2 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgO} \quad \text{(Eq. 4.1)}
\]

\[
\text{Ti} + 15\text{wt.}%\text{Mg} \rightarrow \text{Ti} - \text{Mg} \quad \text{(Eq. 4.3)}
\]

The expected products (MgO and Ti-Mg) and their masses, assuming the reaction goes to completion, are 80.6g MgO and 55.1g Ti-Mg alloy. All the excess Mg was expected to go into solution with Ti to form the Ti-Mg alloy powder. However, this was not entirely the case as the XRD pattern of the MCP powders showed evidence of oxides of Ti. The reduction reaction did not go to completion.

However, it was shown using Eq. 4.2 that only 90.4% reduction of the initial TiO\textsubscript{2} mass was achieved. The remaining TiO\textsubscript{2} phase was essentially unchanged after milling for 32 hours, except for refinement of the particle sizes (Figure 4.4). Hence, of the 79.9g TiO\textsubscript{2} added, 72.2g (90.4%) was reduced by the reductant Mg. From this, and using proportion calculations, it was found that the masses of products at 90.4% reduction were 72.9g MgO and 43.3g Ti. The amount of Mg in the MgO product is 43.9g; thus the difference of 11.9g (from the 55.8g initially added) went towards mechanical alloying with free Ti from the reduction process. The amount of free Ti at
90.4% TiO₂ reduction was calculated to be 43.3g such that the total mass of Ti-Mg alloy synthesized was 55.2g.

The constituents in the mechanochemically processed product and their respective masses are 7.7g unreduced TiO₂, 72.9g MgO and 55.2g Ti-Mg alloy. This translated to weight percentages of 5.6%, 53.7% and 40.7% respectively. Thus at 32 hours of milling 40.7% Ti-Mg alloy powder is synthesized (Appendix A2). The proportions of the various constituents in the milled powder are shown in Table 4.1.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Unreacted TiO₂</th>
<th>Ti-Mg alloy</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>5.7</td>
<td>40.7</td>
<td>53.7</td>
</tr>
<tr>
<td>Constituent mass, (g) {from 2g samples}</td>
<td>0.114</td>
<td>0.814</td>
<td>1.07</td>
</tr>
</tbody>
</table>

4.1.2 Morphological evolution of MCP powders

Figure 4.2 gives the morphologies of the MCP TiO₂-Mg powders; the perfectly spherical particles in Figure 4.2(a) are TiO₂ while the irregular platy particles in Figure 4.2(b) are Mg. There was a discernable size difference between the Mg and TiO₂ powders, with the former being coarser.
(a) TiO$_2$  
(b) Mg

Figure 4.2: SEM micrographs of the individual starting powders

Figure 4.3: SEM micrograph of TiO$_2$-Mg powders milled for different durations.

The Mg powder particles lost their initial morphologies which were replaced by a globular morphology while the TiO$_2$ powder particles were indistinguishable from the Mg (Figure 4.3). It is possible that the TiO$_2$ particles, which are expected to be brittle, already fractured and were lodging themselves into the soft Mg particles (Mckormick et al, 1998). Higher magnifications revealed that the globular particles themselves were agglomerates of smaller particles that appeared to be welded together. This evolution of morphology is in line with the ball milling process which proceeds through repeated welding, fracturing and rewelding of powder particles, (Mckormick et al, 1998).
4.1.3 Particle Size Analysis

Figure 4.4 shows the particle size distribution of the TiO$_2$-Mg powder mix mechanochemically processed for 32 hours.

![Particle size distribution of TiO$_2$-Mg powder milled for 32 hours](image)

**Figure 4.4: Particle size distribution of TiO$_2$-Mg powder milled for 32 hours**

The MCP TiO$_2$-Mg powder mix was composed of the particles with a $d_{50}$ of 8.6 microns. The steep gradient of the distribution curve indicates that the powder had a narrow size range, with a $d_{10}$ and a $d_{90}$ of 2.5 and 21 microns, respectively. The narrowing of the size range was a direct result of mechanochemical processing, where steady state sizes are achieved due to the balance between fracturing and rewelding. This is typical of milling operations. Unmilled TiO$_2$-Mg powder had a much wider particle size ranges (Appendix B8, Table B1 and Figure B1).

4.2 Hydrometallurgical recovery of MCP synthesized Ti-Mg alloy powder

The synthesis of Ti-Mg alloy through direct reduction of TiO$_2$ with excess Mg during MCP formed by-products which included MgO, unreacted TiO$_2$ and minute quantities of Mg (Eq. 2.4). The value product, Ti-Mg alloy powder, has to be recovered from its
intimate mixture with the by-products of mechanochemical reduction. Dissolution experiments were carried out to separate the mechanochemically synthesized Ti-Mg powder alloy from the waste powders.

Figure 4.5: XRD spectra of TiO$_2$-Mg milled for 32 hours

Figure 4.5 shows the XRD patterns of processed TiO$_2$-Mg powder mix. The peaks of incompletely reduced TiO$_2$ are visible as well as the peaks for the products of milling which are Ti-Mg alloy and MgO. The spectra also shows the strength (hence the relative abundance of each constituent) of the peak intensities relative to each other. As indicated by the spectra, MgO and the Ti-Mg alloy are the major phases and they occur at seemingly overlapping 20 values of 36.5, 42.5 and 62°.
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The MgO peaks are seen to be more intense than any other peak implying that MgO had become the main phase, with TiO$_2$ peaks being the second most prominent peaks on the pattern. The new phases (MgO and Ti-Mg) had broader, less intense peaks indicating that their crystallinity was low. It is possible that the crystallinity of TiO$_2$ was higher hence it got to be the second most prominent phase. It has been shown that while 2 wt.% of a material can be detected if the particle size range is 26 -38 microns, 25wt.% is required if the particle size range is 0.05 – 1 microns (Shankar et al, 2003).

Thus, that TiO$_2$ has a prominent peak could have been a consequence of fracturing dynamics and particle size, as well as the relative abundance of phase. However, from particle size analysis (Figure 4.4), the $d_{50}$ of 9 microns is a lot larger than the 0.05 – 1 micron range. This, in effect, meant that the individual peaks intensities in Figure 4.5 had more to do with the relative abundance of the respective phases, and a lot less to do with fracturing dynamics of the powder species therein.

In the dissolution experiments conducted, the liquid/solid ratio used was 100ml/1g. The ratio was deliberately made high and is ideal, from the viewpoint of fundamental kinetic analysis, to decrease the viscosity and consequently the mass transfer resistance in the acid-powder particle interfaces (Sasikumar et al, 2007). Lower ratios are only more realistic from an industrial and scale up point of view. Further, the acid will be sufficient to react evenly with each and every constituent in a given powder without affecting the dissolution or lack thereof of the other constituents. Thus, it can be assumed that the dissolution behaviour of independent commercially pure TiO$_2$ will be comparable to that of incompletely reduced TiO$_2$ intimately mixed with Ti-Mg alloy and MgO in the milled TiO$_2$ mixture, from the mechanochemical process. The dissolution of the milled components is bound to be slightly higher, though, because of dissolution enhancement brought about by mechanical activation (Gutman, 1998).
4.2.1 Effect of leaching in dilute sulphuric acid

Figure 4.6 shows the results of the leaching experiments performed using H$_2$SO$_4$. The masses of the residues are given in Table D1 in Appendix D. About 40% MgO was dissolved at the lowest acid concentration and all the MgO was subsequently dissolved in acid concentrations of 0.5M and beyond.

![Figure 4.6 Effect of H$_2$SO$_4$ concentration on the leaching of the individual powders](image)

For TiO$_2$, slightly less than 30% dissolved at 0.1M sulphuric acid with about 40% dissolving as the concentration was increased to 0.5M. However, a further increase in acid molarity was accompanied by a sharp reduction in the proportion of dissolved TiO$_2$. The amount of dissolved oxide then levelled off at about 20% at higher acid molarity. The low dissolution of titanium in acid concentration higher than 0.5M is probably due to hydrolysis, polymerization and precipitation of titanium ions in solution (Sasikumar et al, 2007). At acid concentrations below 1.5M, the hydrolyzed
product will be poorly compacted and dissolution could continue although more slowly. The hydrolysis product is thought to be rutile TiO$_2$ (Chun et al., 2007). Sulphuric acid isolation of the Ti-Mg alloy powder is not viable as it is being solubilised faster than the wastes (TiO$_2$) in the concentration ranges studied. The curve for TiO$_2$-Mg does not rise as the TiO$_2$ curve in the range 0.5-1.3M; there is no correlation between the masses leached in both curves. This apparent lack of dissolution congruency (common elements or compounds in the two powders dissolving at the same rate) could be due to the species common to both powders being in different ratios (Welham, 1998). Amount of oxides of Ti in MCP TiO$_2$-Mg could have been insignificant to cause any curve changes similar to those in the TiO$_2$ curve. This observation could imply that species other than incompletely reduced TiO$_2$ (Ti-Mg and MgO) were the ones predominantly dissolving while unreduced TiO$_2$ in MCP TiO$_2$-Mg was largely resistant.

About 20% of the independent Ti-20Mg dissolved at 0.1M H$_2$SO$_4$ with the dissolution increasing with increasing acid concentration until there was only 11.7% left at 1.3M. About 53% of the MCP TiO$_2$-Mg powder dissolved in 0.1M H$_2$SO$_4$: this is much higher than the amount of TiO$_2$ that dissolved for the same concentration. The dissolution rate decreased with increasing acid concentration and, above 0.9M, the amount of powder dissolved became independent of the acid concentration. This was reminiscent of the behaviour of the TiO$_2$ oxide at higher acid molarity.

The similarity in dissolution behaviour between TiO$_2$ and processed TiO$_2$-Mg at higher acid concentrations could imply that incompletely TiO$_2$ was now one of the dominant phases left in TiO$_2$-Mg after other phases had been largely leached out. This
was supported by the XRD pattern (Figure 4.7) of TiO$_2$-Mg leached at 0.5M which was already showing that TiO$_2$ peaks (along with peak intensities) were more dominant than those of other phases. It is apparent that in the acid concentration range used, the MCP TiO$_2$-Mg residue decreased from 47.7\% to 17.2\% and this went way below the theoretically calculated Ti-Mg proportion of 40.7\% (Table 4.1). The value shows that the Ti-Mg alloy phase dissolved to a big extent.

![XRD pattern](image)

**Figure 4.7** XRD pattern of milled TiO$_2$-Mg residue leached in 0.5M H$_2$SO$_4$.

Figure 4.7 shows the XRD pattern of mechanochemically processed TiO$_2$-Mg residue leached at 0.5M H$_2$SO$_4$. The pattern shows that dissolution did not appear to be proportional to the initial masses of the respective constituents in the milled mixture. However, it is apparent that the TiO$_2$ peaks have become the most prominent after
leaching, while before, they were the second most prominent. It is possible other phases in the milled TiO$_2$-Mg were dissolved at higher rates than TiO$_2$.

TiO$_2$, which constituted only 5.7% of the whole mixture, was still present in the pattern at 0.5M sulphuric acid even though only 25% (Figure 4.6) of the initial TiO$_2$-Mg residue remained undissolved. Meanwhile, independent polycrystalline MgO was completely dissolved at 0.5M (Figure 4.6). This implied that the MgO in milled TiO$_2$-Mg was all leached out as well, and this can be corroborated by the lack of MgO peaks in the XRD patterns of the powder milled at 0.5M H$_2$SO$_4$.

The leaching of TiO$_2$ powder showed peak dissolution of 39% at 0.5M in the acid range 0.1-1.3M. Literature has shown that dissolution of TiO$_2$ can get as high as 65% in H$_2$SO$_4$ (Sasikumar et al, 2007) albeit with more aggressive parameters which will not augur well for the synthesized Ti-Mg alloy in MCP TiO$_2$-Mg powder blend.

4.2.2 Effect of leaching in concentrated sulphuric acid (with enhancers)

Figure 4.8 shows the leach behaviour of the powders with variation in the concentration of H$_2$SO$_4$ (enhanced with 0.1M HF). TiO$_2$ had a constant dissolution of slightly below 40% across the whole concentration range. Ti-20Mg residue was at 40% initially before it gradually decreased to almost 1% at 6M acid concentration, while MgO was completely dissolved in all concentrations.
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Figure 4.8: Effect of leaching in concentrated H$_2$SO$_4$ with HF

Figure 4.9 shows the XRD patterns of TiO$_2$-Mg powder leached in 0.5M H$_2$SO$_4$ (enhanced with 0.1M HF). The patterns indicated that the TiO$_2$ was resistant to dissolution since its peaks became the more dominant ones after leaching.

Figure 4.9 XRD pattern of milled TiO$_2$-Mg residue leached in 0.5M H$_2$SO$_4$ (with 0.1M HF)
Figure 4.10: Effect of leaching individual powders in concentrated H$_2$SO$_4$ with (NH$_4$)$_2$SO$_4$

Figure 4.10 shows the extent of dissolution in relation to increase in the concentration of H$_2$SO$_4$ (enhanced with 0.06M (NH$_4$)$_2$SO$_4$). The results show that TiO$_2$ dissolution, which was virtually constant and fluctuated slightly at 33%, was independent of concentration in the acid range investigated. There was reduced dissolution of TiO$_2$-Mg and Ti-20Mg powders at elevated reagent concentrations. Their respective residues gradually increased with increase in acid concentration; TiO$_2$-Mg was 36% at 3M and it got to be 47% at 6M, while Ti-20Mg was 16% and ended up being 40% at 6M. Independent, polycrystalline MgO completely dissolved across all the molar concentrations used.
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\[ \text{TiO}_2 \quad \text{Mg} + \text{MgO} \quad \ast \text{Ti-Mg} \]

Figure 4.11 XRD pattern of milled TiO\(_2\)-Mg residue leached in 0.5M H\(_2\)SO\(_4\) (with 0.06M (NH\(_4\))\(_2\)SO\(_4\))

Figure 4.11 shows the XRD pattern of the MCP TiO\(_2\)-Mg powder residue leached in 0.5M H\(_2\)SO\(_4\) (with 0.06M (NH\(_4\))\(_2\)SO\(_4\)). Just like the patterns of powders leached with H\(_2\)SO\(_4\) (HF), Figure 4.11 shows that the TiO\(_2\) phase became the more dominant after leaching. This indicated that TiO\(_2\) was more resistant to dissolution compared to other phases; it was intimately mixed with in the MCP TiO\(_2\)-Mg powder.

Leaching of powders in concentrated H\(_2\)SO\(_4\) with 0.1M HF (Figure 4.8), and in concentrated H\(_2\)SO\(_4\) with 0.06M (NH\(_4\))\(_2\)SO\(_4\) (Figure 4.10) showed that TiO\(_2\) was largely undissolved in both leach media. The degree of dissolution of TiO\(_2\) in both H\(_2\)SO\(_4\)/HF and H\(_2\)SO\(_4\)/(NH\(_4\))\(_2\)SO\(_4\) was virtually the same. It follows that the individual
additions of HF and (NH₄)₂SO₄ to concentrated H₂SO₄ leach media did not have any effect on the dissolution properties of TiO₂.

Concentrated H₂SO₄ with 0.1M HF cannot be satisfactorily used to isolate Ti-Mg alloy from MCP TiO₂-Mg powders because the oxides of Ti did not show much amenability to dissolution. There was about 60% (Figure 4.8) undissolved polycrystalline TiO₂ which is unacceptably high. The independent alloy (Ti-20Mg) was completely dissolved at higher acid concentrations which showed that the Ti-Mg alloy in the MCP TiO₂-Mg would not be spared dissolution as well.

4.2.3 Effect of leaching in hydrochloric acid.

The fraction of each individual powder extracted vs. concentration plots for the different HCl concentrations are given in Figure 4.12. Concentration of the leachant has a significant effect on the leaching of the TiO₂-Mg and MgO powders whose residues drastically decreased with increase in HCl concentration. The proportion of TiO₂-Mg residue decreased to about 35% at 0.5M concentration after which it tapers off and finally gets to about 22% remaining at 1.3M hydrochloric acid. This translates to a mere 0.44g from the initial 2g sample. From theoretical calculations (Appendix A2), Ti-Mg is 40.7% of the milled TiO₂-Mg powder blend. This means that, at 1.3M, almost half of the calculated proportion of Ti-Mg alloy powder from the mechanochemical process has been leached out.
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Figure 4.12: Effect of HCl concentration on the leaching of the individual powders.

From Figure 4.12, proportion of the TiO$_2$ residue at each acid concentration gradually decreased from slightly over 80% at 0.1M to just over 60% at 1.3M. In no case was the fraction of TiO$_2$ dissolved more than 40%. Clearly, the initial unprocessed TiO$_2$ was not readily amenable to hydrochloric acid dissolution at the acid concentration range under consideration. This is probably due to hydrolysis and precipitation reactions of Ti ions in solution, and reactions usually set in at elevated temperatures and at specific acid concentrations for prolonged periods of leaching (Sasikumar et al, 2007). Hydrolysis of Ti ions is favourable at higher temperatures (>70 °C), longer leaching time (>45 min) and at acid concentrations lower than 8M (<8M HCl) (Sasikumar et al, 2007). It is the hydrolysis of dissolved Ti which makes dissolution of TiO$_2$ in hydrochloric acid very difficult.
It is possible that TiO$_2$ precipitated from Ti ions in hydrolysed TiOCl$_2$ species. The entire precipitation reaction occurs accompanied by the hydrolysis of TiOCl$_2$ and via the formation of an intermediate hydroxide (Eq. 4.4):

$$TiOCl_2 + 2H_2O \Rightarrow TO(OH)_2 + 2HCl \quad \text{(Eq. 4.4)}$$

The intermediate then disintegrates to give a TiO$_2$ precipitate and water (Eq. 4.5).

$$TiO(OH)_2 \Rightarrow TiO_2 + 2H_2O \quad \text{(Eq. 4.5)}$$

![XRD pattern of milled TiO$_2$-Mg residue leached in 1.3M HCl acid](image)

**Figure 4.13: XRD pattern of milled TiO$_2$-Mg residue leached in 1.3M HCl acid**

The XRD spectra for some of the leach residues corresponding to HCl leaching is presented in Figure 4.13 which shows patterns of TiO$_2$-Mg leached in 1.3M HCl acid. Initially, before leaching, the top three peaks’ intensities are all above 100 with the overlapping MgO/Ti-Mg peak at 2$\theta$ 36.5° being the most prominent (Figure 4.5).
However, after leaching, the MgO/Ti-Mg peak became less pronounced and the TiO$_2$ peak at 25° got to be the most pronounced. Other lesser peaks of insufficiently reduced and undissolved TiO$_2$ also became more prominent at the 1.3M leach run.

Although the MgO phase was leached in 40 minutes of leaching, the dissolution of TiO$_2$ rutile phase was found to be low even at the end of the leaching run. The TiO$_2$ phase has become the most prominent on the XRD patterns of TiO$_2$-Mg leached at 1.3M (Figure 4.13). This most likely indicated that other phase components in MCP TiO$_2$-Mg, namely MgO and Ti-Mg, had largely dissolved in the leach media. At the same HCl, independent polycrystalline MgO was completely dissolved while 30% of the independent Ti-20Mg alloy from elemental powders remained undissolved (Figure 4.12). The deduction is that, after leaching in 1.3M, the mechanochemically processed TiO$_2$-Mg powder contained TiO$_2$ and some bit of Ti-Mg alloy as evidenced by the presence of these phases on the XRD patterns (Figure 4.13).

4.2.3.1 Cyclic leaching with 0.1M HCl

At 0.1M HCl, there was very little dissolution of the TiO$_2$-Mg (3%). This was lower compared to the TiO$_2$ and MgO (16% and 26%, respectively), which needed to be leached out of the milled mixture. It was postulated that the pattern at 0.1M acid concentration, where more TiO$_2$-Mg was undissolved compared to TiO$_2$ and MgO, could be maintained by subsequent cyclic leaching runs at the same conditions. Cyclic leaching is the process where a powder is leached, filtered, dried and re-leached for a number of cycles under the same leach conditions. The amount of incompletely reduced oxides of Ti (and MgO) was envisaged to incrementally dissolve at each cyclic leach of the milled TiO$_2$-Mg mixture, without affecting the value Ti-Mg alloy
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(in the milled TiO$_2$-Mg) to a larger extent. For purposes of comparing the dissolution behavior under the cyclic leaching, polycrystalline MgO and TiO$_2$ were also leached under the same conditions.

The results of cyclic leaching in HCl at 0.1M are shown in Figure 4.14. At the first cyclic run, TiO$_2$-Mg residue was 97% while those of TiO$_2$ and MgO were 82% and 73%, respectively. However, there was more of TiO$_2$ (57%) residue than any other leached powder at the end of the cyclic leach runs, the next most abundant residue was Ti-20Mg with 52%. The milled TiO$_2$-Mg dissolved more and more until the last run when it had the lowest residue left compared to the other powders. Its value at the third and final run was a drastically low at 33% and, at this point there was no need to continue the cyclic leaching runs, further cyclic leach runs only dissolved the TiO$_2$-Mg further without much effect on the TiO$_2$ powder.

The amount dissolved depends on the initial quantity of the dissolving phase, and the kinetics of dissolution. A lower initial quantity will result in a lower dissolved mass, which means a higher residue. For MCP TiO$_2$-Mg and using the Lai equation (Eq. 4.2), the starting Ti-Mg and MgO proportions were high, being 40.7% and 53.7%, respectively. These calculated proportions are just indicative; they are not absolute. It is the proportion of Ti oxides which is low at 5.7%. Only 3% of the TiO$_2$-Mg mixture dissolved; this could indicate that the initial mass of the dissolving phase is low. In the three cyclic leaching runs, TiO$_2$ residue reduced from 82% to 57% while MgO was from 73% to 42%. For the same conditions processed TiO$_2$-Mg decreased from 97% to 33%. Recovery of Ti-Mg alloy powder would prove difficult since the MCP TiO$_2$-Mg was dissolving at a faster rate compared to the by-product powders.
The XRD patterns of the TiO$_2$-Mg residues leached in HCl (Figure 4.13) continue to show the presence of TiO$_2$. Thus, it would appear that the low initial dissolution was because of low kinetics of dissolution rather than on the relative quantities of the powder constituents in the MCP TiO$_2$-Mg. It therefore follows that dissolution at lower concentrations was mainly of MgO and the Ti-Mg alloy.

Figure 4.14: Cyclic leaching of the individual powders at 0.1M HCl

It is not possible to use cyclic leaching with HCl (Figure 4.14) to isolate Ti-Mg alloy powder as every other mechanochemically processed TiO$_2$-Mg powder constituent, with the exception of TiO$_2$, was largely dissolving. In this case, cyclic leaching is more or less similar to leaching for a more prolonged duration at the same parameters. Thus, HCl cannot be used to separate the synthesised Ti-Mg alloy powder from the waste powders.
4.2.4 Effect of leaching in aqua regia

The dissolution of the various powders in aqua regia is shown in Figure 4.15. TiO$_2$-Mg showed gradual dissolution from 20% at the initial 0.1M acid concentration to 70% at 1.3M. All the MgO was completely dissolved at concentrations of 0.5M to 1.3M. TiO$_2$ did not show appreciable dissolution as only about 22% was dissolved at 1.3M. For Ti-20Mg, 38% was dissolved at 0.1M concentration. Thereafter, the amount of Ti-20Mg residue gradually increased with increased aqua regia concentration until it tapered off at about 90% at 1.3M.

Figure 4.15: Effect of aqua regia concentration on the leaching of the individual powders.

The situation with aqua regia was the same as for H$_2$SO$_4$; at no point was there dissolution of MCP TiO$_2$-Mg being more than the dissolution of TiO$_2$. This leachant, which is strongly oxidising, has shown that it cannot be used to effect the separation
of Ti-Mg from the processed powder mixture. Aqua regia is a corrosive, fuming yellow liquid whose fumes and yellow colour are caused by reaction of HNO₃ acid with HCl acid to form nitrosyl chloride (NOCl), Cl₂, and water. Both Cl₂ and nitrosyl chloride are yellow-colored and volatile. The nitrosyl chloride further decomposes to nitric oxide, NO, and chlorine. It is possible that some of these species formed are precursors and intermediates to those species which are favourable for hydrolysis hence the TiO₂ resistance to aqua regia dissolution. The rise in the residue amount of Ti-20Mg powder with increasing acid concentration is thus probably due to hydrolysis. Figure 4.16 shows the XRD pattern of the MCP TiO₂-Mg powder leached in 0.9M aqua regia. The pattern confirmed what the dissolution graph showed (Figure 4.15): TiO₂ was not amenable to much dissolution in the media used, and it thus became the most dominant phase after leaching despite it being only 5.7% initially.

![TiO₂ Mg + MgO * Ti-Mg](image)

Figure 4.16: XRD pattern of milled TiO₂-Mg residue leached in 0.9M aqua regia
4.2.5 Effect of leaching in oxalic/ascorbic acids

The variation of powders residues with acid concentration after leaching with equimolar oxalic/ascorbic acids is shown in Figure 4.17.

![Figure 4.17: Effect of oxalic/ascorbic acid concentration on the leaching of the individual powders](image)

Polycrystalline TiO$_2$ did not show much dissolution in equimolar oxalic/ascorbic acids. The least dissolved phase was MgO, with a residue of about 90% at the lowest acid concentration. There was XRD evidence showing that the MgO exposed to the equimolar oxalic/ascorbic acid reagent was probably converted to Mg(OH)$_2$ (Fig 4.18).

The proportion of TiO$_2$ dissolved was virtually constant and independent of the leach media concentration. The TiO$_2$ residues on the whole acid concentration range fluctuated at around 80%. On the other hand, TiO$_2$-Mg, Ti-20Mg and MgO dissolved
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Initially but gained mass with increasing acid molarity. MgO gained more mass than other powders with about 150% residue at the final acid concentration of 0.2M. TiO<sub>2</sub>-Mg had a residue of 121% at the final acid concentration investigated while Ti-20Mg gained mass up to 117% before tapering off slightly at the end. Mechanochemically processed TiO<sub>2</sub>-Mg, MgO and Ti-20Mg had very little dissolution at low acid strength before they started steadily gaining residue mass to values beyond 100% with increased acid concentration. These three powders have Mg in common; Mg combined with O<sub>2</sub> in MgO (in both crystalline MgO and milled TiO<sub>2</sub>-Mg), and alloyed to Ti (in both MCP TiO<sub>2</sub>-Mg, and Ti-20Mg).

Independent polycrystalline TiO<sub>2</sub> did not have Mg in it, and all its residues were under 100%. Thus, only the Mg bearing powder phases gained in residue masses beyond 100%. This was most likely because of the Mg<sup>2+</sup> ions (from the dissolved Mg bearing phases) in the equimolar oxalic/ascorbic acid mixture were hydrolysing to Mg(OH)<sub>2</sub>. XRD analysis of the residues (Fig 5.18) showed the presence of Mg(OH)<sub>2</sub>; the Mg in both the oxide and the Ti alloys probably went into solution as Mg<sup>2+</sup> cations before being quickly hydrolysed to Mg(OH)<sub>2</sub>. Elemental Mg metal was also subjected to the equi-molar oxalic/ascorbic acid reagent as the other powders. The Mg residue also steadily gained in residue mass beyond 100% as the reagent concentration was increased confirming that, indeed, the gain in mass was because of the Mg ions (Eq 3.5) reacting to form Mg(OH)<sub>2</sub> precipitate. Indeed, XRD analysis of elemental Mg leached in 0.15M concentration (Appendix C11) showed the presence of Mg(OH)<sub>2</sub> phases, over and above those of undissolved Mg.

\[
MgO(s) + 2H^+ (aq) \rightarrow Mg^{2+} + H_2O(l) \quad \text{(Eq. 3.5)}
\]
\[ Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s) \]  

(Eq. 3.5)

The high propensities of mass gain in these leached powders seem to indicate that the conditions were optimum for maximum hydrolysis of the Mg leached from the oxide, and from the alloy matrix. Figure 4.18 shows the XRD spectra of the mechanochemically processed TiO\textsubscript{2}-Mg powder mixture leached in 0.15M oxalic/ascorbic acids. The peaks of incompletely reduced oxides of Ti are visible although they are not the most dominant. There was presence of Mg(OH\textsubscript{2}) as shown by the labelled peaks. No MgO was detected in the XRD analysis; all the oxide had probably hydrolyzed to Mg(OH\textsubscript{2}).

\[ \bigcirc \text{TiO}_2 \; \bullet \text{Mg} \; \blacktriangleleft \text{Mg(OH)}_2 \; \blacklozenge \text{Ti-Mg} \]

Figure 4.18: XRD spectra of milled TiO\textsubscript{2}-Mg residue leached in 0.15M ascorbic/oxalic acids
The results indicated that leaching in oxalic/ascorbic acids is impossible because the phases of interest, those that need to be leached out (MgO and TiO$_2$), are having the least tendency to dissolve. As a result, oxalic/ascorbic acid mixture cannot be used to effectively isolate Ti-Mg alloy from the waste powders as it leaches out the Mg in the alloy matrix, and it does not result in good dissolution of TiO$_2$. Literature of TiO$_2$ dissolution in organics showed that a maximum dissolution of 60% in 2.5 h was obtained in equi-molar concentrations of oxalic acid and ascorbic acid (Mukherjee et al, 2005). No leach parameters were given in the literature apart from the leach duration.

4.2.5 Effect of leaching in equimolar cysteine/ascorbic acids

Milled powder samples, as well as the polycrystalline TiO$_2$ and MgO leached in equimolar cysteine/ascorbic acids in the range 0.025 to 0.8M are shown in Figure 4.19.

![Figure 4.19: Effect of equimolar cysteine/ascorbic acids on the leaching of the individual powders](image-url)
The dissolution of TiO$_2$ and Ti-20Mg showed a sharp increase on moving from a concentration of 0.025M to 0.05M. 32% TiO$_2$ and 42% Ti-20Mg dissolved at 0.05M acid. Beyond 0.05M there was a drastic increase in the masses of TiO$_2$ and Ti-20Mg residue retained. The TiO$_2$ gradually dissolved with increase in the equimolar concentration until about 29% residue was left at 0.8M. On the other hand, Ti-20Mg began to show marked resistance to dissolution beyond 0.05M with the residue proportion gradually picking up with increase in the equimolar concentration until it was about 75% at 0.8M. On the other hand, MCP TiO$_2$-Mg and MgO showed gradual decrease of their residue proportions with increase in the equimolar concentration. Mechanochemically processed TiO$_2$-Mg, from which 51% MgO and 6% incompletely reduced TiO$_2$ (total 57%) (Table 4.1) need to be leached out, was drastically dissolved until only 9% residue remained. MgO steadily dissolved until 13% MgO residue remained after leaching in 0.8M cysteine/ascorbic acids.

The powder most resistant to dissolution, TiO$_2$, showed considerable dissolution with increased leach media concentration up 0.8M where 71% of it dissolved. Literature (Mukherjee et al, 2005) on dissolution of TiO$_2$ in organics has dissolution up to 60% percent; leach equipment and parameters were not given. Cysteine/ascorbic acid proved to be the best possible reagent for leaching out substantial proportions of TiO$_2$ while, at the same concentration, avoiding considerable losses of the Ti-Mg alloy due to inadvertent co-dissolution. About 76% recovery of the Ti-Mg powder was achieved by leaching with equimolar cysteine/ascorbic acids. This was, however, with contamination of 20%MgO (min.) and 4% TiO$_2$ (min.) at 0.8M.
Equimolar cysteine/ascorbic acid showed a lot of potential in separation of Ti-Mg from the MCP TiO\textsubscript{2}-Mg. At lower acid concentrations, more of the MCP TiO\textsubscript{2}-Mg is retained at concentrations 0.025 and 0.05M than any other powder. A lot more independent TiO\textsubscript{2} dissolved at these same concentrations, particularly at 0.05M. It is postulated that the oxides of Ti from the milled TiO\textsubscript{2}-Mg mixture can be separated from the synthesized Ti-Mg alloy through leaching at 0.05M for a number of repeated leach cycles. However, an unacceptably high proportion (11%) of the milled TiO\textsubscript{2}-Mg will be dissolving at each leach cycle, assuming results of subsequent leach runs will be consistent with those obtained at 0.05M equimolar cysteine/ascorbic acid.
Inevitably, a considerable proportion of the value Ti-Mg alloy will end up being leached out along with the other waste powders during subsequent leach cycles. This is corroborated by the leaching curve of independent Ti-20Mg (from blended elemental powders) which showed that 42% of the powder dissolved at 0.05M concentration. Not much MgO (29% at 0.05M) was dissolved despite the fact that it is a relatively easy oxide to dissolve. Thus MgO will be retained in each leach cycle and, at the end, an unacceptably high proportion will be retained in the final Ti-Mg alloy.

To counter the unacceptable loss of MCP TiO$_2$-Mg (11%) during each postulated cyclic leaching run, the duration of leaching was decreased to 1 hour for all powder samples. It was expected that all the curves in Figure 4.19 between 0.025M and 0.05M (where TiO$_2$-Mg residue was more than those of other powders) would generally shift upwards at reduced leach duration so that as much MCP TiO$_2$-Mg residue as possible would be initially retained. Cyclic leaching would then be performed on these powders leached at low duration (where more milled TiO$_2$-Mg residue is expected to be retained). It is envisaged that this would limit the dissolution of the processed TiO$_2$-Mg (and hence Ti-Mg alloy powder therein) on subsequent cyclic leach runs while leaching more of the waste powders with each pass.

Table 4.2 shows the results of leaching in 0.05M equi-molar cysteine/ascorbic acids at different durations. Initially, the powders were leached for 2.5 hours and the results indicated potential for separation. Thus, the powders were then leached for a less duration to maximise on that potential.
Table 4.2 Leaching in 0.05M cysteine/ascorbic acids at 2 different durations

<table>
<thead>
<tr>
<th>Powder</th>
<th>% residue at 2.5hrs</th>
<th>% residue at 1hr</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>68.3</td>
<td>81.9</td>
<td>13.6</td>
</tr>
<tr>
<td>Ti-20Mg</td>
<td>58.3</td>
<td>70.1</td>
<td>11.8</td>
</tr>
<tr>
<td>TiO$_2$-Mg</td>
<td>87.1</td>
<td>66.5</td>
<td>-20.57</td>
</tr>
<tr>
<td>MgO</td>
<td>70.8</td>
<td>77.5</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Table 4.2 shows that the residues of TiO$_2$, Ti-20Mg and MgO increased when the leaching duration was decreased to 1 hour. TiO$_2$ had the largest residue weight gain of 14%, with MgO with the least weight gain of about 7%. On the contrary, TiO$_2$-Mg residue decreased to 67% down from 87% on moving to the lower duration. The potential for separation by cyclic leaching was lost on moving to the lower leach duration as even more of the MCP TiO$_2$-Mg powder mixture went on to be dissolved, contrary to expectations.

4.2.6 Leaching in combined HCl and equimolar cysteine/ascorbic acids

HCl and equi-molar cysteine/ascorbic acids showed potential of Ti-Mg isolation at 0.1M concentration (Figures 4.12 and 4.19). This means that, at this concentration, both leach reagents show desirable tendencies of dissolving, to a larger extent, the undesirable waste products while the TiO$_2$-Mg remains largely unaffected. It was decided to try and combine these desirable tendencies in one reagent by mixing HCl and equi-molar cysteine/ascorbic acids on a 50/50 mol.% basis.
Figure 4.21 shows the variation of powder residue with concentration of combined HCl and equi-molar cysteine/ascorbic acids. The leaching behaviour of MgO and TiO$_2$-Mg powders samples showed substantial decreases in their respective leach residues with increased leach media concentration. The extent of dissolution of MgO increased until all the sample was dissolved at combined acid concentration of 0.75M. With MCP TiO$_2$-Mg powder mixture, the dissolution curve gradually tapered off until there was about 23% residue left at 0.75M acid.

TiO$_2$ and Ti-20Mg powders did not show much dissolution at the acids concentrations investigated. TiO$_2$ residue amount fluctuated at 80%. For Ti-20Mg, the residue slightly increased from 85% at lower acid concentration to about 87% at 0.3M before slightly reducing to 69% at the final acid concentration.
Figure 4.22: XRD spectra of milled TiO$_2$-Mg residue leached in combined HCl and equi-molar cysteine/ascorbic acids

Figure 4.22 shows the XRD spectra of MCP TiO$_2$-Mg powder leached in combined HCl and equimolar cysteine/ascorbic acids. The TiO$_2$ peaks are strong in the pattern; it showed that the oxide did not dissolve much despite it having the least theoretical proportion in the milled TiO$_2$-Mg (5.7%, Table 4.1). Other peaks of MgO and Ti-Mg, prominent before leaching, were now greatly reduced in intensity and all became lower than those of TiO$_2$. More of Ti-Mg and MgO in the milled TiO$_2$-Mg mixture dissolved ahead of the oxides of Ti. The desirable tendencies from both individual leach reagents appear to have been lost when they were combined into one reagent. The combined HCl and equi-molar cysteine/ascorbic acids simply became more aggressive; and dissolved a great deal of the MgO as well as the MCP synthesised Ti-Mg in the milled TiO$_2$-Mg mixture (Figure 4.21). Only 23% of TiO$_2$-Mg remained as
residue yet theoretical calculations indicate that there is 40.7% Ti-Mg alloy. Thus it is not possible to isolate Ti-Mg alloy using combined HCl and equi-molar cysteine/ascorbic acids as the leach reagent.

4.3 Summary of discussion

Chapter 4 described and discussed the results of hydrometallurgical recovery of MCP synthesized Ti-Mg alloy powder from the intrinsically mixed by-product powders. It was the objective of this research to dissolve out these by-products in different organic and inorganic acids to remain with a clean Ti-Mg alloy powder residue.

Inorganic acids (HCl, H_2SO_4 and aqua regia) were not able to effect recovery of the synthesized Ti-Mg alloy. Incompletely reduced TiO_2, from the CSIR copyrighted MCP process, was largely resistant to dissolution in the inorganic acids. For the same conditions, the other powders (Ti-20Mg, MgO and TiO_2-Mg) were dissolving to a great extent effectively meaning the synthesized Ti-Mg was also being lost due to co-dissolution.

Two acid combinations were used for recovery of synthesized Ti-Mg alloy powder in organic acids, namely equi-molar oxalic/ascorbic acids and equi-molar cysteine/ascorbic acids. The oxalic/ascorbic acid combination was found ineffective in Ti-Mg alloy powder recovery. TiO_2 powder was very resistant to dissolution across all the concentration ranges. The other powders namely MgO, Ti-20Mg and TiO_2-Mg (Mg was common to all of them), all gained in mass with increased concentration. This was because of hydrolysis of the Mg component to Mg(OH)_2.
There was some degree of success in dissolving of TiO₂ in cysteine/ascorbic acids combination. Most of the TiO₂ was dissolved at higher concentrations. However, milled TiO₂-Mg was drastically dissolved for the same leach parameters while MgO, which dissolved with ease in inorganic acids, was not completely dissolved even at higher concentrations. This in point of fact meant that the cysteine/ascorbic acids combination was not able to effect recovery of the synthesized Ti-Mg alloy powder as there was high co-dissolution of the alloy powder as well as contamination from the incompletely dissolved MgO and TiO₂.
CHAPTER 5

5.0 Conclusions and Recommendations

5.1 Conclusions

It was noted that the high cost of Ti metal is due to the current Kroll Process for refining titanium ore which is a labour intensive, multi-step, high temperature batch process with low productivity. Literature also illustrated that there is need for lighter titanium alloys for instance in biomedical applications, and in aerospace applications. Consequently, and for this particular research work, mechanochemical processing (MCP) of TiO\textsubscript{2} with 15wt.% excess Mg was done to produce a Ti-Mg alloy (which is lighter than Ti metal), and should be relatively cheaper since Ti bearing precursor (rutile) is not from the expensive Kroll process. The MCP technique, however, resulted in the production of a Ti-Mg alloy powder which was intimately mixed with other powders like MgO, unreacted TiO\textsubscript{2} and minute amounts of unreacted Mg. The thrust of this project was to hydrometallurgically recover the Ti-Mg alloy powder through the selective dissolution of the waste and/or unreacted powders from the MCP process.

Sulphuric acid, hydrochloric acid, equimolar ascorbic acid/oxalic acids, equimolar l-cysteine/ascorbic acids were used in the dissolution work. The dissolution periods were fixed while the concentrations of the different leach media were manipulated to create conditions favourable for the dissolution of the by products of the MCP process, and the preservation of the Ti-Mg alloy powder.
5.1.1 Dilute inorganic acids

Dilute inorganic acid dissolution of waste by-products of the MCP process to recover a clean Ti-Mg alloy proved unsuccessful since TiO$_2$ was resistant to dissolution while Ti-20Mg and TiO$_2$-Mg were virtually dissolved out. The dilute acids used were H$_2$SO$_4$, HCl and aqua regia.

In the concentration ranges used, (0.1 – 1.3M across all three dissolution media), unreacted TiO$_2$ waste powder did not dissolve out to a larger extent as envisaged in the research postulation. Thus 16 – 36% TiO$_2$ dissolved in HCl, 20 – 39% in H$_2$SO$_4$, and 13 – 21% in aqua regia. This means that under the same conditions, and on the milled TiO$_2$-Mg powder, at least 61% of the unreacted TiO$_2$ remain undissolved in all the three leach reagents. However, the other waste powder (MgO), showed ease of dissolution as it was completely leached out in all three reagents at medium to higher concentrations.

For the Ti-20Mg alloy synthesized from blended elemental (BE) powders, the dissolution percentage ranges were 10 – 69% in HCl, 20 – 88% in H$_2$SO$_4$, and 11 – 31% in aqua regia. The control alloy powder was dissolving rather drastically where TiO$_2$ showed marked dissolution resistance. MCP processed TiO$_2$-Mg (which contains MgO (53.6 %), unreduced TiO$_2$ (5.7 %) and Ti-Mg alloy (40.7 %): Appendix A2) had heavy dissolution percentages in all the dilute inorganic acids considered. These were 3 – 78% in HCl, 53 – 83% in H$_2$SO$_4$, and 20 – 70% in aqua regia. As the theoretical proportion of Ti-Mg alloy in milled TiO$_2$-Mg was calculated to be 40.7%, this effectively meant the alloy also dissolved substantially. This is supported by the drastic dissolution of the control Ti-20Mg from mechanically alloyed BE powders.
5.1.2 Concentrated sulphuric acid with enhancers

Concentrated $H_2SO_4$ separately mixed with two dissolution enhancing reagents, namely $0.1M$ HF and $0.06M$ $(NH_4)_2SO_4$ was used for dissolution of the powders in the range $3M – 6M$.

$TiO_2$ showed marked dissolution resistance in both reagents. For $H_2SO_4$ (with $(NH_4)_2SO_4$), $35 – 38\%$ was dissolved; while for $H_2SO_4$ (with HF), $37 – 39\%$ was dissolved in the concentration range considered. This followed that the final product from MCP processed and leached $TiO_2$-Mg had a lot of contamination from the undissolved $TiO_2$. On the contrary, both Ti-20Mg alloy and MCP processed $TiO_2$-Mg showed severe dissolution in both reagents ($59 – 100\%$ Ti – 20Mg in $H_2SO_4$ with HF, $59 – 97\%$ $TiO_2$-Mg in $H_2SO_4$ with HF; $60 – 84\%$ Ti – 20Mg in $H_2SO_4$ with $(NH_4)_2SO_4$, $53 – 64\%$ $TiO_2$ – Mg in $H_2SO_4$ with $(NH_4)_2SO_4$). As the proportion of Ti-Mg alloy in milled $TiO_2$-Mg is $40.7\%$, severe dissolutions of this level meant that it was the alloy to be preserved and recovered which dissolved rather than the $TiO_2$. MgO was completely dissolved in all the concentration ranges across both reagents. Thus the overall scenario with concentrated $H_2SO_4$ with dissolution enhancers was that the leached product will be contaminated with $TiO_2$ unreduced during the MCP process, and that there will be unacceptable losses of the value Ti-Mg alloy powder through its inadvertent co-dissolution. Concentrated $H_2SO_4$ with dissolution enhancers cannot, therefore, be used to efficiently and successfully recover Ti-Mg alloy powder from the waste products of the MCP process.
5.1.3 Equimolar organic acids

Equimolar cysteine/ascorbic acids, and equimolar oxalic/ascorbic acids were the two organic acid combinations used in the Ti-Mg powder recovery leach experiments. MgO is generally easy to dissolve relative to other oxides in other reagents. However, equimolar cysteine/ascorbic acid could not leach it all out; only 27 – 87% MgO was dissolved in the concentration range investigated. With equimolar oxalic/ascorbic acids, MgO residue proportion actually increased with increased concentration due to hydrolysis to the hydroxide. Consequently, Ti-Mg product from either of these leach reagents will be expected to be heavily contaminated with the oxides/hydroxides of magnesium.

Another waste powder, unreduced TiO$_2$, was not totally leached out in either leach media. There was some degree of success on leaching the TiO$_2$ (71% leached out) in cysteine/ascorbic acids but 90% of TiO$_2$-Mg was also dissolved at the same parameter. This TiO$_2$-Mg contained 40.7% Ti-Mg alloy (Appendix A2), so this effectively meant Ti-Mg alloy powder also co-dissolved to a larger extent. This was also supported by the independent Ti-20Mg from alloyed BE powders which showed a large dissolution of 16 – 41% under the same organic acid concentration range.

Equimolar organic acids, therefore, can not effectively be used to separate MCP synthesized Ti-Mg alloy from the waste products. The alloy will inevitably be contaminated to a great extent, and a substantial amount will be lost through unintended co-dissolution.
5.1.4 Combined inorganic/organic acids

HCl freshly mixed with equimolar cysteine/ascorbic acids on a 50% basis was used for the MCP synthesized Ti-Mg hydrometallurgical separation, in a concentration range 0.075 – 0.75M. HCl and equimolar cysteine/ascorbic acids had individually shown some potential for Ti-Mg alloy powder recovery from waste powders.

TiO$_2$ was not dissolved to a big extent as only 17 – 22% was leached out in the concentration range investigated. MgO showed little ease of dissolution at low concentrations with only 21 – 59% dissolved, which eventually got to 100% dissolution at 0.75M. In the same concentration range, the control Ti-Mg alloy powder did not show much dissolution (15 – 31%), while TiO$_2$-Mg inadvertently dissolved to a large extent (1 – 77%).

5.2 Summary of conclusions

From the study carried out on recovery of MCP synthesized Ti-Mg alloy powder using organic and inorganic acids it was concluded that:

- Recovery of the alloy with inorganic acids (HCl and H$_2$SO$_4$, and aqua regia) was not possible since as high as 80% of the milled Ti-Mg alloy powder was co-dissolved, yet TiO$_2$ was still undissolved for the same conditions.
- Recovery of Ti-Mg powder was also not achieved by leaching with organic acids; the species MgO showed marked resistance to dissolution and hence would contaminate the alloy powder.
- Isolation of the Ti-Mg alloy powder using combined HCl/organic acids was not effective; TiO$_2$ resisted dissolution while there was drastic co-dissolution of MCP TiO$_2$-Mg (and hence the alloy therein).
Conclusions & Recommendations

- Ti-Mg alloy powder was not recovered using concentrated H$_2$SO$_4$ with dissolution enhancers. The leached product was contaminated with TiO$_2$ unreduced during the MCP process. There was also unacceptable loss of the value Ti-Mg alloy powder through its inadvertent co-dissolution.

5.3 Recommendations

- It is recommended to optimise the MCP process to generate a powder with the least amount of insufficiently reduced TiO$_2$.

- It is recommended to investigate on cyclic leaching with different leach reagents. Different reagents attack the powders differently, some more (or less) drastically than others. It could be possible to select a variety of leach reagent combinations and durations which will leave the pure Ti-Mg alloy while maximizing dissolution of the waste powders.

- Sequential dissolution of the waste powders in different leach media is recommended. Some leach media like inorganic acids (H$_2$SO$_4$, HCl and aqua regia) were good at dissolving out MgO, while others like cysteine/ascorbic acids were effective in dissolving TiO$_2$ to a great extent (71%). Combining the potentially effective reagents to form one reagent did not work as evidenced by the results from HCl mixed with equimolar cysteine/ascorbic acids on a 50% basis. Thus, sequential dissolution using the more promising reagents is envisaged to incrementally remove all the waste powders while preserving the value Ti-Mg alloy powder.

- The development of a hydrometallurgical cleaning process for MCP synthesized Ti-Mg is still evolutionary; with equimolar cysteine/ascorbic acid tests being a pointer towards a direction in which to start looking further. It is
thus recommended to generate speciation behaviour data for both Ti and Mg in future proposed media of leaching; where both residue and solution analysis is conducted to close the mass balance of various species.
REFERENCES

Bachman M; Cleaning procedures for glass substrates, UCI Integrated Nanosystems Research Facility, 1999.


References


Olanipekun E; A kinetic study of the leaching of a Nigerian ilmenite ore by hydrochloric acid, Hydrometallurgy Volume 53, pp 1-10, 1999.


References


APPENDICES

Appendix A1: Milled sample calculations

Relative Molecular Masses (RMM)

<table>
<thead>
<tr>
<th>Substance</th>
<th>RMM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>47.9</td>
</tr>
<tr>
<td>Mg</td>
<td>24.3</td>
</tr>
<tr>
<td>TiO2</td>
<td>79.9</td>
</tr>
<tr>
<td>MgO</td>
<td>40.3</td>
</tr>
</tbody>
</table>

Stoichiometric reaction of TiO$_2$ with Mg:

$$TiO_2 + 2Mg \rightarrow Ti + 2MgO$$

$$(79.9g) + (48.61g) = (80.6g) + (47.9g)$$

Thus for stoichiometric quantities, 47.9g Ti is synthesized (assuming 100% conversion)

To this amount of Ti 15wt.% Mg (excess) was added:

$$(15/100) \times 47.9 = 7.19g$$

Total Mg to be added = stoichiometric amount + excess amount

$$= 48.61g + 7.19g$$

$$= 55.8g$$

Therefore total amount of powder blend milled = mass of TiO$_2$ + total Mg

$$= 79.9 + 55.8$$

$$= 135.7g$$

Appendix A2: Calculation of proportion of Ti-Mg synthesized

$$TiO_2 + 2Mg \rightarrow Ti + 2MgO$$

$$(79.9g) + (48.61g) = (80.6g) + (47.9g)$$
From Equation 5.1 (Lai et al, 2002) TiO$_2$ conversion was 90.4%

Mass of TiO$_2$ in the milled blend = 79.9g

Mass of TiO$_2$ converted = (90.4/100) x 79.9

= 72.2g

Mass of unreacted TiO$_2$ = 79.9 – 72.2

= 7.7g

Masses of products formed

MgO = (72.2/79.9) x 80.6

= 72.9g

Ti = (72.2/79.9) x 47.9

= 43.3g

Amount of Mg that reacted to form MgO

= ((72.9/79.9) x 48.6

= 44.3g

Amount of free Mg = 55.8 – 44.3

= 11.5g

This free Mg is assumed to all go into solution in Ti

Thus mass of Ti-Mg alloy formed

= 43.3 + 11.5

= 54.8g

Therefore mass of MgO formed

= (44.3/48.61) x 80.6

= 73.5g
Therefore phases in the milled product, and their % proportions

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass (g)</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ (unreacted)</td>
<td>7.7</td>
<td>5.7</td>
</tr>
<tr>
<td>MgO</td>
<td>73.5</td>
<td>53.6</td>
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<tr>
<td>Ti-Mg</td>
<td>54.8</td>
<td>40.7</td>
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</table>

Appendix B1: Raw PSA Data for unmilled TiO₂-Mg powders

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Vol Under %</th>
<th>Size (µm)</th>
<th>Vol Under %</th>
<th>Size (µm)</th>
<th>Vol Under %</th>
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<th>Vol Under %</th>
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<td>0.010</td>
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Figure B1: Graph of Volume (%) vs Particle Size (microns) for unmilled powder
Appendix B2: Raw PSA Data for TiO\textsubscript{2}- Mg powder milled for 2 hours

Table B2: PSA results for TiO\textsubscript{2}- Mg powder milled for 2 hours

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Figure B2: Volume (%) vs Particle Size (microns), milling duration 2 hours

Appendix B3: Raw PSA Data for TiO\textsubscript{2}- Mg powder milled for 4 hours

Table B3: PSA results for TiO\textsubscript{2}- Mg powder milled for 4 hours

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Appendices
Figure B3: Volume (%) vs Particle Size (microns), milling duration 4 hours

Appendix B4: Raw PSA Data for TiO₂-Mg powder milled for 8 hours

Table B4: PSA results for TiO₂-Mg powder milled for 8 hours

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Figure B4: Volume (%) vs Particle Size (microns), milling duration 8 hours
Appendices

Appendix B5: Raw PSA Data for TiO$_2$-Mg powder milled for 16 hours

Table B5: PSA results for TiO$_2$-Mg powder milled for 16 hours

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Figure B5: Volume (%) vs Particle Size (microns), milling duration 16 hours

Appendix B6: Raw PSA Data for TiO$_2$-Mg powder milled for 24 hours

Table B6: PSA results for TiO$_2$-Mg powder milled for 24 hours

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Figure B6: Volume (%) vs Particle Size (microns), milling duration 16 hours

Appendix B6: Raw PSA Data for TiO$_2$-Mg powder milled for 24 hours

Table B6: PSA results for TiO$_2$-Mg powder milled for 24 hours

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Vol Under %</th>
<th>Size (µm)</th>
<th>Vol Under %</th>
<th>Size (µm)</th>
<th>Vol Under %</th>
<th>Size (µm)</th>
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Figure B6: Volume (%) vs Particle Size (microns), milling duration 24 hours

Appendix B7: Raw PSA Data for TiO$_2$-Mg powder milled for 32 hours

Table B7: PSA results for TiO$_2$-Mg powder milled for 32 hours

<table>
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<th>%Chan % Pass</th>
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<tr>
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## Figure B7: % Passing vs Particle Size (microns), milling duration 32 hours

Appendix B8: d10, d50 and d90 particle sizes for all the powders

### Table B1: Results of Particle Size Analysis

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<thead>
<tr>
<th>Milling hours</th>
<th>d(0.1) um microns</th>
<th>d(0.5) um microns</th>
<th>d(0.9) microns</th>
<th>Specific surface area m²/g</th>
<th>Weighted residual (%)</th>
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Appendices

Appendix C1: XRD data for unmilled TiO$_2$-Mg powders

Figure C1: XRD pattern for unmilled TiO$_2$-15Mg

Table C1: Peak List

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<td>2.60797</td>
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Table C2: Identified Patterns List

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<th>Compound Name</th>
<th>Displacement [°2Th.]</th>
<th>Scale Factor</th>
<th>Chemical Formula</th>
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Appendix C2: XRD data for TiO$_2$- Mg powders milled for 2 hours

![XRD pattern for TiO$_2$-15Mg milled for 2 hours]

**Figure C2: XRD pattern for TiO$_2$-15Mg milled for 2 hours**

Table C3: Peak List

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</tr>
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Table C4: Identified Patterns List

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<th>Scale Factor</th>
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Appendix C3: XRD data for TiO$_2$- Mg powders milled for 16 hours

Figure C3: TiO$_2$-15Mg milled for 16 hours
Table C5: Peak List

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Table C6: Identified Patterns List

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<th>Scale Factor</th>
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Appendix C4: XRD data for TiO₂- Mg powders milled for 24 hours

Figure C4: TiO₂-15Mg milled for 24 hours
Appendices

Table C7: Peak List

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<td>2,58526</td>
<td>80,31</td>
<td>0,0400</td>
<td>34,6700</td>
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<td>0,5760</td>
<td>2,12563</td>
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<td>42,4937</td>
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Table C8: Identified Patterns List

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<th>Displacement [°2Th.]</th>
<th>Scale Factor</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>00-045-0946</td>
<td>35</td>
<td>Periclase, syn</td>
<td>-0,387</td>
<td>0,734</td>
<td>Mg O</td>
</tr>
</tbody>
</table>

Appendix C5: XRD data for TiO$_2$- Mg powders milled for 32 hours

![XRD data for TiO$_2$- Mg powders milled for 32 hours](image)

Figure C5: TiO$_2$-15Mg milled for 32 hours
### Table C8: Peak List

<table>
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<tr>
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</thead>
<tbody>
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<td>27.17</td>
<td>0.6400</td>
<td>01-089-5003</td>
</tr>
<tr>
<td>34,2031</td>
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<td>2.62164</td>
<td>19.65</td>
<td>0.4800</td>
<td>01-089-5003</td>
</tr>
<tr>
<td>36,4939</td>
<td>173.00</td>
<td>0.4723</td>
<td>2.46217</td>
<td>100.00</td>
<td>0.4800</td>
<td>01-089-5003; 00-045-0946; 01-075-1537</td>
</tr>
<tr>
<td>42,7836</td>
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<td>0.9446</td>
<td>2.11364</td>
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<td>0.9600</td>
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</tr>
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<td>1.89900</td>
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<td>0.5600</td>
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</tr>
<tr>
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<td>1.70717</td>
<td>9.83</td>
<td>0.6400</td>
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<td>1.60609</td>
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### Table C9: Identified Patterns List

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<th>Scale Factor</th>
<th>Chemical Formula</th>
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<td>Magnesium</td>
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<td>0.975</td>
<td>Mg</td>
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<td>Periclase, syn</td>
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<td>0.138</td>
<td>Mg O</td>
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<td>01-075-1537</td>
<td>38</td>
<td>Anatase</td>
<td>-0.676</td>
<td>0.475</td>
<td>Ti O2</td>
</tr>
</tbody>
</table>

* Indicates a peak that is matched by at least three different patterns.
Appendix C6: XRD data for TiO$_2$- Mg powder leached in 1.3M HCl

Figure C6: TiO$_2$-15Mg leached in 1.3M HCl

Table C12: Peak List

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</thead>
<tbody>
<tr>
<td>10,2412</td>
<td>30,49</td>
<td>0,4723</td>
<td>8,63772</td>
<td>16,05</td>
<td>0,4800</td>
<td>01-089-4921</td>
</tr>
<tr>
<td>24,6584</td>
<td>189,98</td>
<td>0,2755</td>
<td>3,61046</td>
<td>100,00</td>
<td>0,2800</td>
<td>01-089-4921</td>
</tr>
<tr>
<td>30,8925</td>
<td>58,09</td>
<td>0,5510</td>
<td>2,89462</td>
<td>30,58</td>
<td>0,5600</td>
<td>01-089-4921</td>
</tr>
<tr>
<td>35,8097</td>
<td>27,08</td>
<td>0,4723</td>
<td>2,50762</td>
<td>14,25</td>
<td>0,4800</td>
<td>01-089-4921</td>
</tr>
<tr>
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<td>25,49</td>
<td>0,4723</td>
<td>2,43173</td>
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<td>0,4800</td>
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<td>41,0099</td>
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<td>0,4723</td>
<td>2,20087</td>
<td>12,56</td>
<td>0,4800</td>
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</tr>
<tr>
<td>47,4267</td>
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<td>0,2755</td>
<td>1,91698</td>
<td>14,86</td>
<td>0,2800</td>
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<tr>
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<td>42,57</td>
<td>0,4723</td>
<td>1,71903</td>
<td>22,41</td>
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<td>1,67440</td>
<td>19,48</td>
<td>0,9600</td>
<td>01-089-4921</td>
</tr>
<tr>
<td>62,1421</td>
<td>15,97</td>
<td>0,9600</td>
<td>1,49254</td>
<td>8,41</td>
<td>0,8000</td>
<td>01-089-4921</td>
</tr>
</tbody>
</table>
Appendices

Table C13: Identified Patterns List

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<th>Score</th>
<th>Compound Name</th>
<th>Displacement [°2Th.]</th>
<th>Scale Factor</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>01-089-4921</td>
<td>77</td>
<td>Anatase, syn</td>
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<td>Ti O2</td>
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<td>01-087-0651</td>
<td>13</td>
<td>Periclase</td>
<td>-1.142</td>
<td>0.097</td>
<td>Mg O</td>
</tr>
</tbody>
</table>

Appendix C7: XRD data for TiO$_2$- Mg powder leached in 0.15M oxalic/ascorbic acids

Figure C7: TiO$_2$-15Mg leached in 0.15M oxalic/ascorbic acids

Table C14: Peak List

<table>
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<tr>
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<th></th>
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</tr>
</thead>
<tbody>
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<tr>
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<td>114,969</td>
<td>0.1968</td>
<td>4.91421</td>
<td>100.00</td>
<td>0.2000</td>
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<td>84,20</td>
<td>0.2362</td>
<td>3.86621</td>
<td>7.32</td>
<td>0.2400</td>
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<tr>
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<td>105,07</td>
<td>0.3936</td>
<td>3.51004</td>
<td>9.14</td>
<td>0.4000</td>
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<tr>
<td>26,8927</td>
<td>79,18</td>
<td>0.2755</td>
<td>3.31536</td>
<td>6.89</td>
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</tr>
<tr>
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<td>0.1574</td>
<td>3.17820</td>
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<td>0.1600</td>
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</tr>
<tr>
<td>31,5507</td>
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<td>0.6298</td>
<td>2.83572</td>
<td>2.87</td>
<td>0.6400</td>
<td></td>
</tr>
<tr>
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<td>110,82</td>
<td>0.2362</td>
<td>2.54187</td>
<td>9.64</td>
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</tr>
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<td>0.2400</td>
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</tr>
<tr>
<td>43,4535</td>
<td>82,96</td>
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<td>2.08260</td>
<td>7.22</td>
<td>0.2800</td>
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Table C15: Identified Patterns List

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<th>Scale Factor</th>
<th>Chemical Formula</th>
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</thead>
<tbody>
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<td>Brucite</td>
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<td>0.128</td>
<td>Mg (OH)2</td>
</tr>
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</table>

Appendix C8: XRD data for TiO$_2$ - Mg powder leached in 0.15M HCl/cysteine/ascorbic acids

Figure C8: TiO$_2$-15Mg leached in 0.15M HCl/cysteine/ascorbic acids

Table C16: Peak List

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</thead>
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<td>0.4800</td>
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</tr>
<tr>
<td>30.7417</td>
<td>29.82</td>
<td>0.7872</td>
<td>2.90848</td>
<td>41.70</td>
<td>0.8000</td>
<td>00-021-1236</td>
</tr>
<tr>
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<td>38.86</td>
<td>0.7872</td>
<td>2.49707</td>
<td>54.34</td>
<td>0.8000</td>
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</tr>
<tr>
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<td>0.9446</td>
<td>2.15974</td>
<td>41.78</td>
<td>0.9600</td>
<td>00-045-0946; 00-021-1236</td>
</tr>
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<td>1.72095</td>
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Table C17: Identified Patterns List

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<th>Chemical Formula</th>
</tr>
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<tr>
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<td>25</td>
<td>Titanium Oxide</td>
<td>-0.401</td>
<td>0.274</td>
<td>Ti O2</td>
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</table>

Appendix C9: XRD data for TiO\(_2\)-Mg powder leached in 0.5M H\(_2\)SO\(_4\)

Figure C9: TiO\(_2\)-15Mg leached in 0.5M H\(_2\)SO\(_4\)

Table C18: Peak List

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<th>FWHM [^{2\text{Th.}}]</th>
<th>d-spacing [Å]</th>
<th>Rel. Int. [%]</th>
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<td></td>
<td></td>
</tr>
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<td>27.5063</td>
<td>83.73</td>
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</tr>
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<td>2.74152</td>
<td>12.74</td>
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<td></td>
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<td>0.8187</td>
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<td>22.53</td>
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<td></td>
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<td>2.16437</td>
<td>19.70</td>
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<td>0.6140 00-019-1370</td>
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Table C19: Pattern List

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<td>Fac.</td>
<td>Chem. Formula</td>
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<td></td>
</tr>
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<td>54</td>
<td>Anatase, syn</td>
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<tr>
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<td>0.101</td>
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</table>

Appendix C10: XRD data for Ti-20Mg leached in 0.5M H$_2$SO$_4$

* Ti-Mg

Figure C10: Ti-20Mg leached in 0.5M H$_2$SO$_4$
### Table C20 Intensities

|          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 1518     | 1444     | 1387     | 1444     | 1479     | 1411     | 1376     | 1385     | 1417     | 1429     | 1415     | 1427     | 1413     | 1377     | 1353     | 1369     | 1378     | 1347     | 1391     | 1329     | 1342     | 1306     | 1330     | 1391     | 1353     | 1278     | 1336     | 1347     | 1247     | 1289     |
| 1204     | 1225     | 1272     | 1247     | 1243     | 1290     | 1247     | 1230     | 1193     | 1208     | 1257     | 1204     | 1200     | 1188     | 1243     | 1204     | 1186     | 1177     | 1164     | 1184     | 1212     | 1145     | 1148     | 1174     | 1198     | 1107     | 1179     | 1094     | 1098     | 1155     |
| 1198     | 1126     | 1086     | 1153     | 1092     | 1124     | 1089     | 1107     | 1064     | 1123     | 1135     | 1064     | 1148     | 1066     | 1117     | 1092     | 1118     | 1083     | 1113     | 1092     | 1085     | 1121     | 1116     | 1097     | 1148     | 1107     | 1110     | 1221     | 1050     | 1043     | 1050     |
| 1074     | 1052     | 997      | 1059     | 1024     | 1046     | 1035     | 1043     | 1028     | 1023     | 984      | 1080     | 981      | 1020     | 1062     | 1000     | 1033     | 1013     | 1083     | 1029     | 962      | 1045     | 997      | 984      | 983      | 1012     | 1003     | 1017     | 1030     | 963      | 969      | 971      |

Appendices
Appendix C11: XRD data for Mg leached in 0.5M cysteine/ascorbic acid.

![Graph showing XRD data for Mg leached in 0.5M cysteine/ascorbic acid.](image)

Figure C11: Mg leached in 0.5M cysteine/ascorbic acid.
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Appendices
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Appendices
Appendices
Appendix D: Raw data for leaching graphs

On the leaching experiments, the residue is the powder left undissolved after subjecting a given powder species to specific leaching reagent at a specific concentration.

Thus \( \% \text{ Residue} = \left( \frac{\text{final}}{\text{initial}} \right) \times 100 \)

where final = dry residue mass after leaching (g)

initial = initial powder mass before leaching (g)

Table D1: Effect of H\(_2\)SO\(_4\) concentration on the leaching of Ti-Mg alloy

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Table D2: Effect of HCl concentration on the leaching of Ti-Mg alloy

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Table D3: Effect of Aqua regia concentration on the leaching of Ti-Mg alloy

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Table D4: Effect of equi-molar oxalic/ascorbic acid concentration on the leaching of Ti-Mg alloy

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Table D5: Effect of equi-molar cysteine/ascorbic acid concentration on the leaching of Ti-Mg alloy

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### Table D6: Effect of HCl with equi-molar cysteine/ascorbic acid concentration on the leaching of Ti-Mg alloy

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