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 Wiwatersrand, 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.

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_2SO_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

1. **Mushove, T.,** Chikwanda, H.K., Machio C., Ndlovu S., 2009. Ti-Mg Alloy Powder Synthesis via Mechanochemical Reduction of TiO_2 by Elemental Magnesium, Materials Science Forum (Volumes 618 - 619), pp517 – 520. Published and presented at the 4th Light Metals Technology Conference 2009, Gold Coast, Australia, 29 June – 1 July, 2009.

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.

TABLE OF CONTENTS

DECLARATION i
ABSTRACT ii
PUBLICATIONS AND PRESENTATIONS iii
DEDICATION iv
ACKNOWLEDGEMENTS v
TABLE OF CONTENTS vi
APPENDICES ix
LIST OF FIGURES xi
LIST OF TABLES xiv
LIST OF ABBREVIATIONS xv
MINERAL NAMES xvi
CHAPTER 1 1
1.1 Background and Motivation 1
1.3 Possible applications of Ti-Mg alloys 4
1.3.1 Biomedical applications 4
1.3.2 Aerospace applications 4
1.4 Problem Statement 5
1.5 Objectives of the Study 5
1.6 Hypothesis 5
1.7 Research Questions 6
1.8 Dissertation Layout 6
CHAPTER 2 7
2.0 Literature Survey 7
2.1 The Kroll Process for Ti production 7
2.2 Mechanochemical Processing 9
2.2.1 MCP in the synthesis of Ti-Mg alloys 10
2.3 Hydrometallurgical removal of waste powders. 11
2.3.1 Metal oxide dissolution 11
2.3.1.1 Dissolution of MgO 13

2.3.1.2 Dissolution of TiO_2/TiO 15
2.3.2 Reagents for leaching TiO_2 16
2.3.2.1 Sulphuric acid leaching 17
2.3.2.2 Hydrochloric acid leaching 19
2.3.2.3 Aqua regia leaching 20
2.3.2.4 Organic acid leaching 21
2.3.3 Stability of Titanium and its alloys in aggressive media 21
2.3.3.1 Dissolution of Ti-Mg alloys 22
2.3.4 Influence of mechanical activation on dissolution 23
2.3.5 Benefits of leaching out waste powders 24
CHAPTER 3 25
3.0 Experimental Procedures 25
3.1 Introduction 25
3.2 Test powders 25
3.3 Powder Characterisation 26
3.3.1 X-ray Diffraction (XRD) 26
3.3.2 Particle size analysis 27
3.3.3 Morphological characterisation of MCP powders 28
3.4 Hydrometallurgical experiments for recovery of MCP synthesized Ti-Mg alloy powder 28
CHAPTER 4 31
4.0 Results and discussion 31
4.1 XRD characterisation of powders 31
4.1.1 Proportion of Ti-Mg synthesized 32
4.1.2 Morphological evolution of MCP powders 34
4.1.3 Particle Size Analysis 36
4.2 Hydrometallurgical recovery of MCP synthesized Ti-Mg alloy powder 36
4.2.1 Effect of leaching in dilute sulphuric acid 39
4.2.2 Effect of leaching in concentrated sulphuric acid (with enhancers) 42
4.2.3 Effect of leaching in hydrochloric acid. 46

4.2.3.1 Cyclic leaching with 0.1M HCl 49
4.2.4 Effect of leaching in aqua regia 52
4.2.5 Effect of leaching in oxalic/ascorbic acids 54
4.2.5 Effect of leaching in equimolar cysteine/ascorbic acids 57
4.2.6 Leaching in combined HCl and equimolar cysteine/ascorbic acids 61
4.3 Summary of discussion 64
CHAPTER 5 66
5.0 Conclusions and Recommendations 66
5.1 Conclusions 66
5.1.1 Dilute inorganic acids 67
5.1.2 Concentrated sulphuric acid with enhancers 68
5.1.3 Equimolar organic acids 69
5.1.4 Combined inorganic/organic acids 70
5.2 Summary of conclusions 70
5.3 Recommendations 71
REFERENCES 73

APPENDICES

Appendix A1: Milled sample calculations 80

Appendix A2: Calculation of proportion of Ti-Mg synthesized 80

Appendix B1: Raw PSA Data for unmilled TiO_2- Mg powders 82

Appendix B2: Raw PSA Data for TiO_2- Mg powder milled for 2 hours 83

Appendix B3: Raw PSA Data for TiO_2- Mg powder milled for 4 hours 83

Appendix B4: Raw PSA Data for TiO_2- Mg powder milled for 8 hours 84

Appendix B5: Raw PSA Data for TiO_2- Mg powder milled for 16 hours 85

Appendix B6: Raw PSA Data for TiO_2- Mg powder milled for 24 hours 85

Appendix B7: Raw PSA Data for TiO_2- Mg powder milled for 32 hours 86

Appendix B8: d_{10}, d_{50} and d_{90} particle sizes for all the powders 87

Appendix C1: XRD data for unmilled TiO_2- Mg powders 88

Appendix C2: XRD data for TiO_2- Mg powders milled for 2 hours 89

Appendix C3: XRD data for TiO_2- Mg powders milled for 16 hours 90

Appendix C4: XRD data for TiO_2- Mg powders milled for 24 hours 91

Appendix C5: XRD data for TiO_2- Mg powders milled for 32 hours 92

Appendix C6: XRD data for TiO_2- Mg powder leached in 1.3M HCl 94

Appendix C7: XRD data for TiO_2- Mg powder leached in 0.15M oxalic/ascorbic acids 95

Appendix C8: XRD data for TiO_2- Mg powder leached in 0.15M HCl/cysteine/ascorbic acids 96

Appendix C9: XRD data for TiO_2- Mg powder leached in 0.5M H_2SO_4 97

Appendix C10: XRD data for Ti-20Mg leached in 0.5M H_2SO_4 98

Appendix C11: XRD data for Mg leached in 0.5M cysteine/ascorbic acid 104

Appendix D: Raw data for leaching graphs 110

LIST OF FIGURES

		PAGE
FIGURE 2.1	Flowchart for the Kroll process	8
FIGURE 3.1	Schematic diagram of the laser diffraction measurement	27
FIGURE 3.2	Setup of the Julabo SW23 dissolution apparatus	30
FIGURE 4.1	XRD patterns of the TiO_2-Mg powder mixtures milled for different durations	31
FIGURE 4.2	SEM micrographs of the individual starting powders	35
FIGURE 4.3	SEM micrographs of TiO_2-Mg powders milled for different durations.	35
FIGURE 4.4	Particle size distribution of TiO_2-Mg powder milled for 32 hours	36
FIGURE 4.5	XRD pattern of TiO_2-Mg milled for 32 hours	37
FIGURE 4.6	Effect of H_2SO_4 concentration on the leaching of individual powders	39
FIGURE 4.7	XRD spectra of milled TiO_2-Mg residue leached in 0.5M H_2SO_4.	41
FIGURE 4.8	Effect of leaching in concentrated H_2SO_4 with HF	43
FIGURE 4.9	XRD pattern of milled TiO_2-Mg residue leached in H_2SO_4 (with 0.1M HF)	43
FIGURE 4.10	Effect of leaching individual powders in concentrated H_2SO_4 with $(NH_4)_2SO_4$	44

FIGURE 4.11	XRD pattern of milled TiO_2-Mg residue leached in H_2SO_4 with $(NH_4)_2SO_4$	45
FIGURE 4.12	Effect of HCl concentration on the leaching of individual powders	47
FIGURE 4.13	XRD spectra of milled TiO_2-Mg residue leached in 1.3M HCl acid	48
FIGURE 4.14	Cyclic leaching of the individual powders at 0.1M HCl	51
FIGURE 4.15	Effect of aqua regia concentration on the leaching of the individual powders	52
FIGURE 4.16	XRD pattern of milled TiO_2-Mg residue leached in aqua regia	53
FIGURE 4.17	Effect of oxalic/ascorbic acid concentration on the leaching of the individual powders	54
FIGURE 4.18	XRD spectra of milled TiO_2-Mg residue leached in 0.15M ascorbic/oxalic acids.	56
FIGURE 4.19	Effect of equimolar cysteine/ascorbic acid concentration on the leaching of the individual powders	57
FIGURE 4.20	XRD pattern of milled TiO_2-Mg residue leached in equimolar cysteine ascorbic acids	59
FIGURE 4.21	Graph of combined HCl and equi-molar cysteine/ascorbic acids.	62

FIGURE 4.22 XRD spectra of milled TiO_2-Mg residue leached in combined HCl and equi-molar cysteine/ascorbic acids 63

LIST OF TABLES

		PAGE
TABLE 4.1	Calculated composition of the milled powder at 32 hours of milling.	34
TABLE 4.2	Leaching in 0.1M cysteine/ascorbic at different durations.	61

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

Periclase	:	MgO
Rutile	:	TiO_2
Ilmenite	:	$FeTiO_3$
Magnesium	:	Mg
Sphene	:	$CaTiSiO_5$

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 (between4.43 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 TiO_2 with Mg, using hydrometallurgical means. The Ti-Mg alloy powder was formed through reduction of TiO_2 by 15wt.% excess magnesium via mechanochemical processing (MCP). The other by-products of the MCP process are MgO, unreacted Mg, unreacted TiO_2 and incompletely reduced titanium oxides of the type Ti_xO_y 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 in-growth 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:

$$2Mg(l) + TiCl_4(g) \Rightarrow 2MgCl_2(l) + Ti(s) \qquad \text{(Eq 2.1)}$$

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).

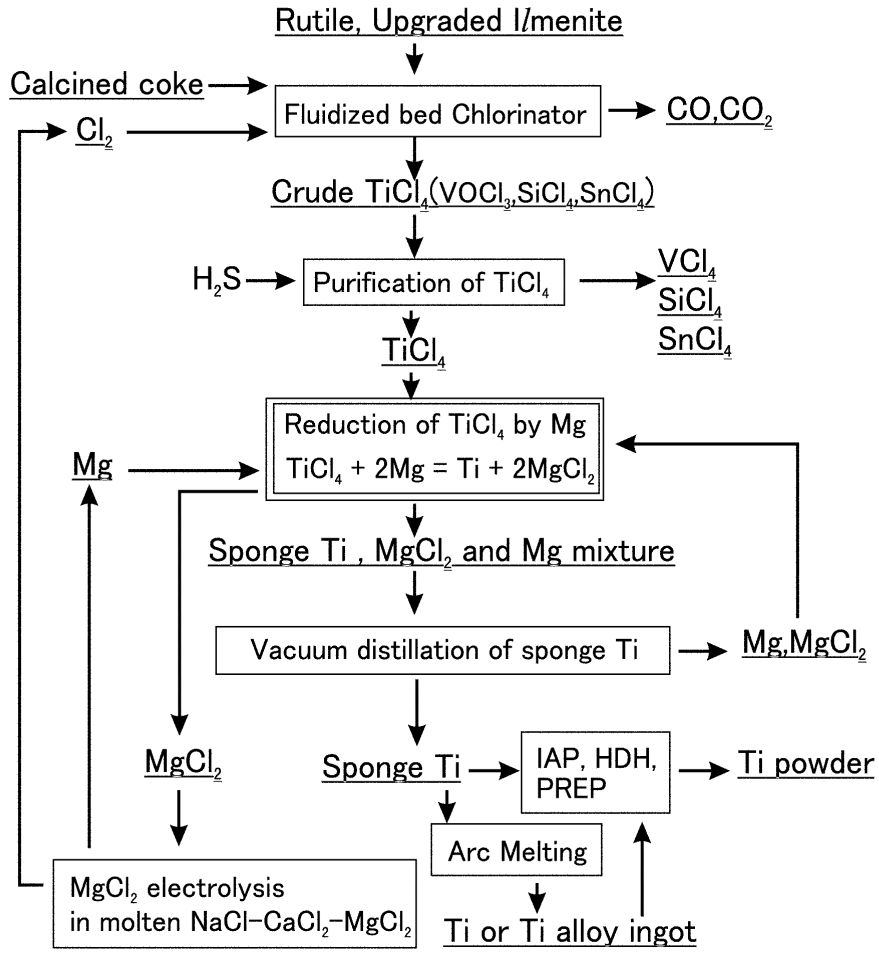


Figure 2.1: Flowchart for the Kroll process (Kroll, 1940)

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.

$$TiO_2 + Mg \Rightarrow TiO + MgO \qquad \text{(Eq 2.2)}$$

$$TiO + Mg \Rightarrow Ti + MgO \qquad \text{(Eq 2.3)}$$

$$Ti + Mg \Rightarrow Ti - Mg \qquad \text{(Eq 2.4)}$$

For synthesis of Ti-Mg alloys, more Mg than the stoichiometric quantity is added to the TiO_2. 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:

$$TiO_2 + 3Mg \Rightarrow Ti - Mg + 2MgO \qquad \text{(Eq 2.5)}$$

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_2O, 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_2SO_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.

$$MgO(s) + 2H^+(aq) \Rightarrow Mg^{2+} + H_2O(l) \qquad \text{(Eq. 2.6)}$$

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:

$$CH_3COOH \Rightarrow H^+ + CH_3COO^- \quad \text{(Eq. 2.7)}$$

$$MgO + 2CH_3COO^- + 2H^+ \Rightarrow Mg^{2+} + 2CH_3COO^- + H_2O \quad \text{(Eq. 2.8)}$$

$$MgO + 2H^+ \Rightarrow Mg^{2+} + H_2O \quad \text{(Eq. 2.9)}$$

$$MgO + H_2O \Rightarrow Mg^{2+} + 2OH^- \quad \text{(Eq. 2.10)}$$

Acetic acid (Eq. 2.7) is a weak organic acid with a small equilibrium constant of about 1.8×10^{-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 (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)

$$TiO_2 + H^+ + H_2O \Rightarrow Ti(OH)_3 \qquad \text{(Eq. 2.11)}$$

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_2O, Ti_3O_2 or Ti_2O_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_2SO_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+}) (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 $TiOSO_4.2H_2O$, 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).

$$TiO^{2+} + SO_4^{2-} \Rightarrow TiOSO_4 \quad \text{(Eq. 2.12)}$$

$$TiOSO_4 + SO_4^{2-} \Rightarrow TiO(SO_4)_2^{2-} \quad \text{(Eq. 2.13)}$$

$$TiO(SO_4)_2^{2-} + 2SO_4^{2-} + 2H^+ \Rightarrow TiO(SO_4)_4^{4-} + H_2O \quad \text{(Eq. 2.14)}$$

Polymerized titanium (IV) species exist in aqueous sulphate media (from H_2SO_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_2SO_4 to dissolve TiO_2. Some of these reagents were concentrated H_2SO_4 mixed with $(NH_4)_2SO_4$, and concentrated H_2SO_4 mixed with HF (Korn et al, 2002). For $H_2SO_4/(NH_4)_2SO_4$, 0.4g of

TiO_2 was dissolved in 16ml of concentrated H_2SO_4 with 0.06M (6.4g) of $(NH_4)_2SO_4$. The mixture was heated for 30 minutes at 250°C to effect complete dissolution of the sample (Korn et al, 2002). With H_2SO_4 in HF, a 4g oxide sample was digested in 10ml of concentrated HF and 16ml of concentrated H_2SO_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 (CH_3OH-H_2O) 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 TiO_2 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^{n+}). The hydrochloric acid provides a ready supply

of chloride ions (Cl^-), which react with the metal cations to produce chlorometal anions, also in solution.

2.3.2.4 Organic acid leaching

TiO_2 dissolves in organic reducing reagents namely ascorbic acid, oxalic acid and l-cysteine. Studies indicate that a maximum of about 45% TiO_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_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_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 ($E°$=−1.63 V/S.H.E. $Ti^{2+}/Ti\downarrow$). 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^{4+} ions, which in acids, exist only as titanyl ions ($Ti(OH)_2^{2+}$) even at pH values below 1**.** Beyond that, they evolve into $Ti(OH)_4$, which precipitates and dehydrates, resulting in the most stable form TiO_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_2SO_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_2SO_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

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 K*c* 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° 2θ, with a step of 0.02° 2θ 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.

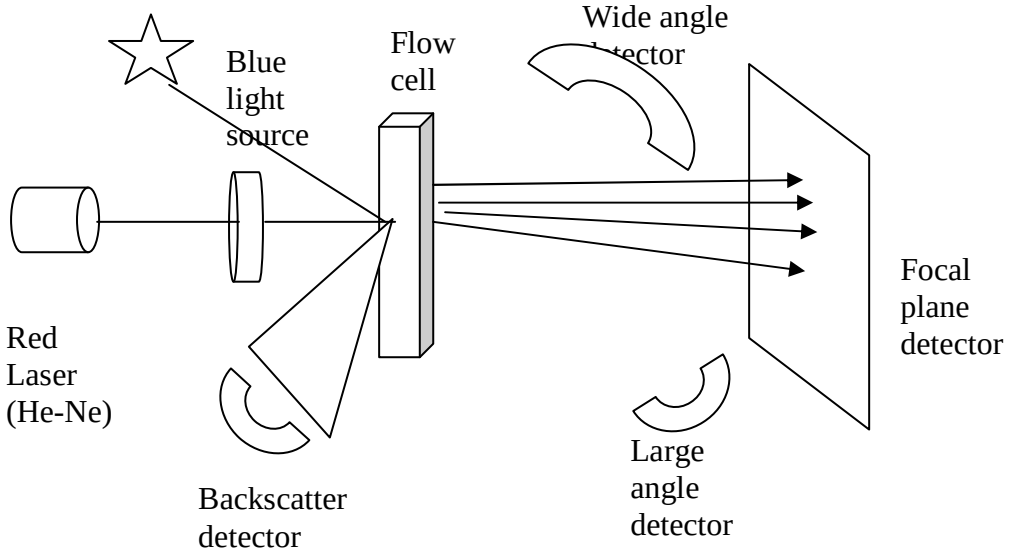


Figure 3.1: Schematic diagram of the laser diffraction measurement

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_2SO_4), hydrochloric acid (HCl), aqua regia, concentrated H_2SO_4 with hydrofluoric acid (HF), and concentrated H_2SO_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_2SO_4), hydrochloric acid (HC*l*), 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_2SO_4 with a morality of 3M, 4M, 5M and 6M mixed with 0.06M ammonium sulphate, and with 0.1M hydrofluoric acid.

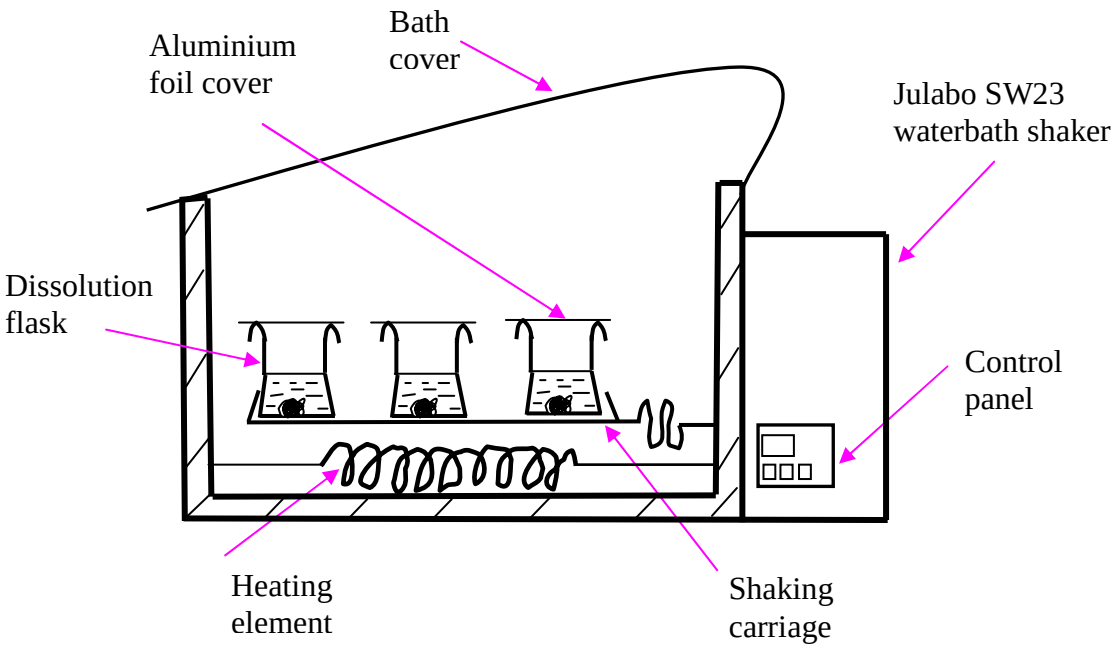


Figure 3.2 Setup of the Julabo SW23 dissolution apparatus

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.

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.

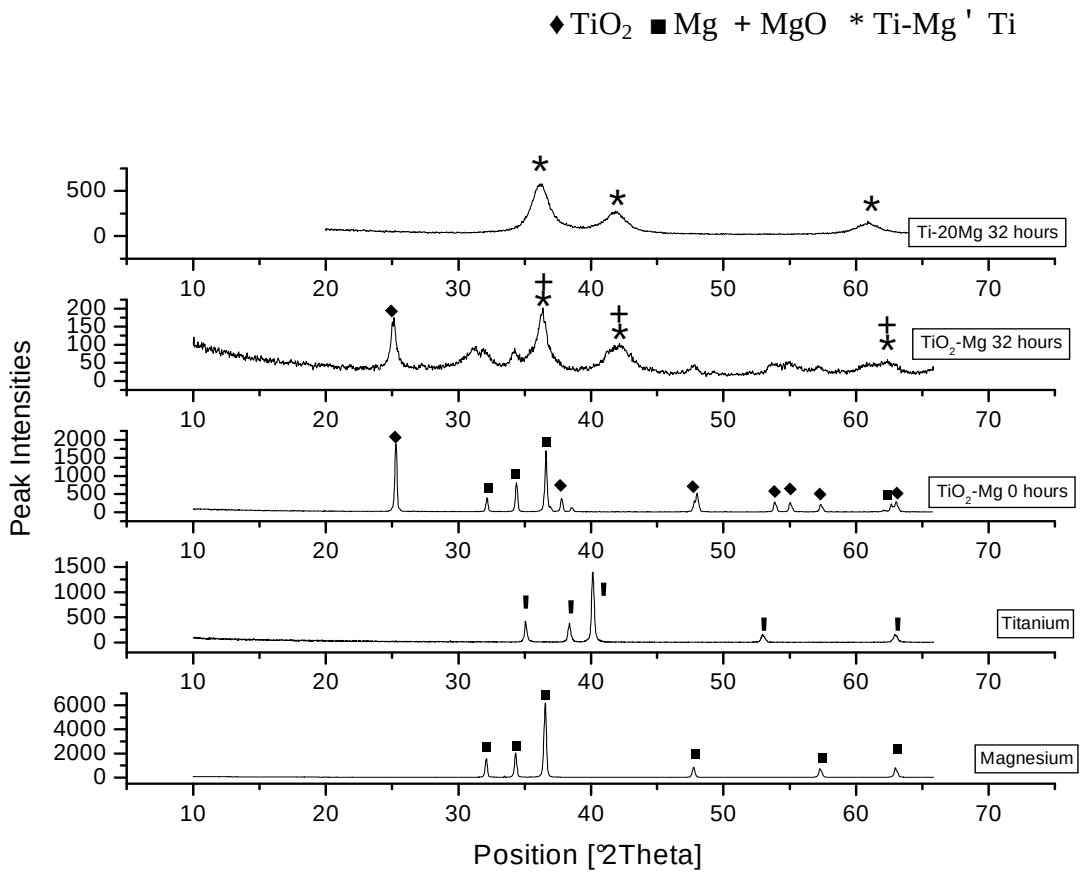


Figure 4.1: X-ray diffraction patterns of the TiO_2-Mg powder mixtures milled for various durations

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

$$TiO_2 + 2Mg \Rightarrow Ti + 2MgO \qquad \text{(Eq. 4.1)}$$

The enthalpy of formation for 2MgO is -1 204kJ 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):

$$\text{D} = \left(\frac{I(TiO_2)}{[I(TiO_2) + I(MgO)}\right) \times 100 \qquad \text{(Eq. 4.2)}$$

where I is the intensity of the diffraction peaks of MgO and TiO_2. The initial TiO_2 peak intensity was 1 625 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_xO_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_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_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_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_2 and Mg (Eq. 4.1) formed the precursor powder blends mechanochemically processed (MCP) for different durations.

$$TiO_2 + 2Mg \Rightarrow Ti + 2MgO \qquad \text{(Eq. 4.1)}$$

$$Ti + 15wt.\%Mg \Rightarrow Ti - Mg \qquad \text{(Eq. 4.3)}$$

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_2 mass was achieved. The remaining TiO_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_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% TiO_2 reduction was calculated to be 43.3g such that the total mass of Ti-Mg alloy synthesized was 55.2g.

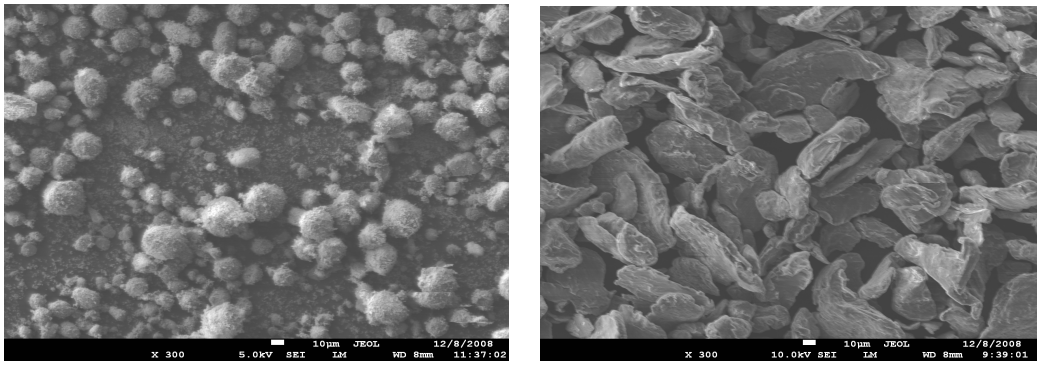
The constituents in the mechanochemically processed product and their respective masses are 7.7g unreduced TiO_2, 72.9g MgO and 55.2g Ti-Mg alloy. This translated to weight percentages of 5.6%, 53.7% and 40.7% respectively. Thus at 32 hours of milling 40.7% Ti-Mg alloy powder is synthesized (Appendix A2). The proportions of the various constituents in the milled powder are shown in Table 4.1.

Table 4.1: Calculated composition of the milled powder at 32 hours of milling

Constituent	**Unreacted TiO_2**	**Ti-Mg alloy**	**MgO**
Weight %	5.7	40.7	53.7
Constituent mass, (g) {from 2g samples}	0.114	0.814	1.07

4.1.2 Morphological evolution of MCP powders

Figure 4.2 gives the morphologies of the MCP TiO_2-Mg powders; the perfectly spherical particles in Figure 4.2(a) are TiO_2 while the irregular platy particles in Figure 4.2(b) are Mg. There was a discernable size difference between the Mg and TiO_2 powders, with the former being coarser.



(a) TiO_2 **(b) Mg**

Figure 4.2: SEM micrographs of the individual starting powders

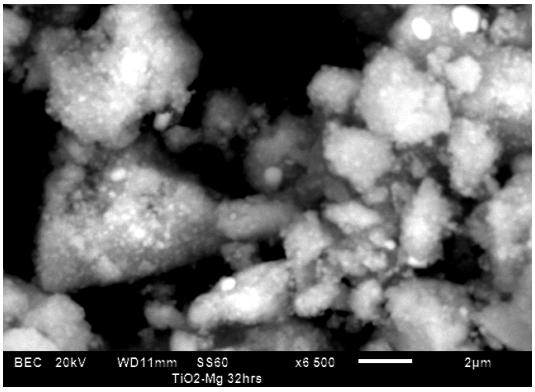


Figure 4.3: SEM micrograph of TiO_2-Mg powders milled for different durations.

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.

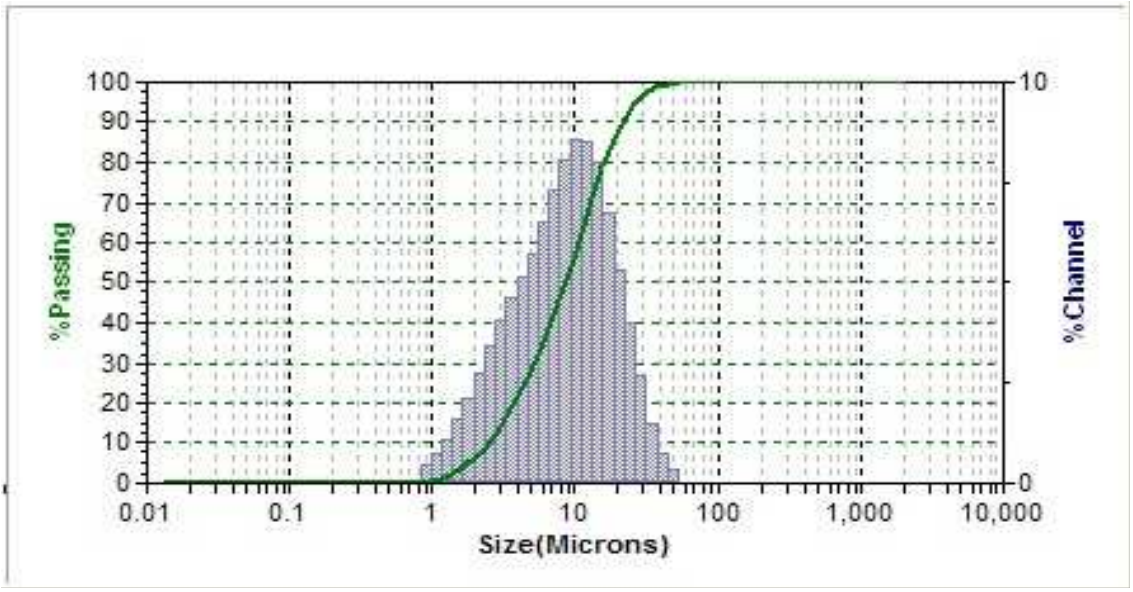


Figure 4.4: Particle size distribution of TiO_2-Mg powder milled for 32 hours

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.

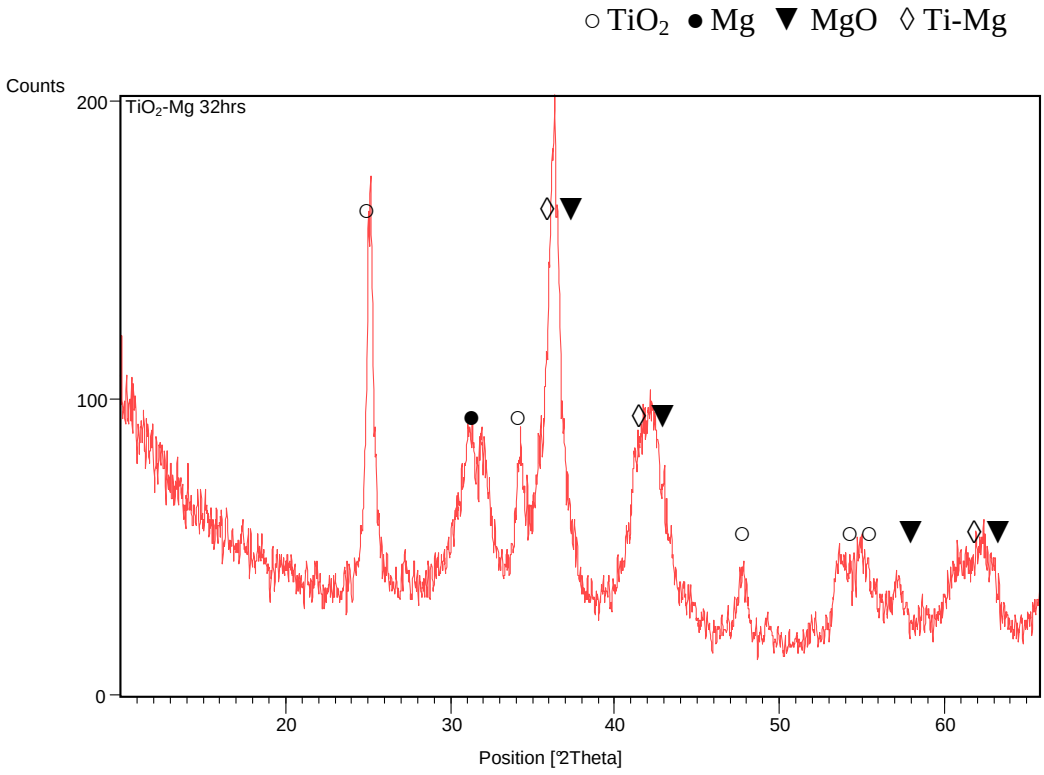


Figure 4.5: XRD spectra of TiO_2-Mg milled for 32 hours

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 2θ values of 36.5, 42,5 and 62°.

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_2SO_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.

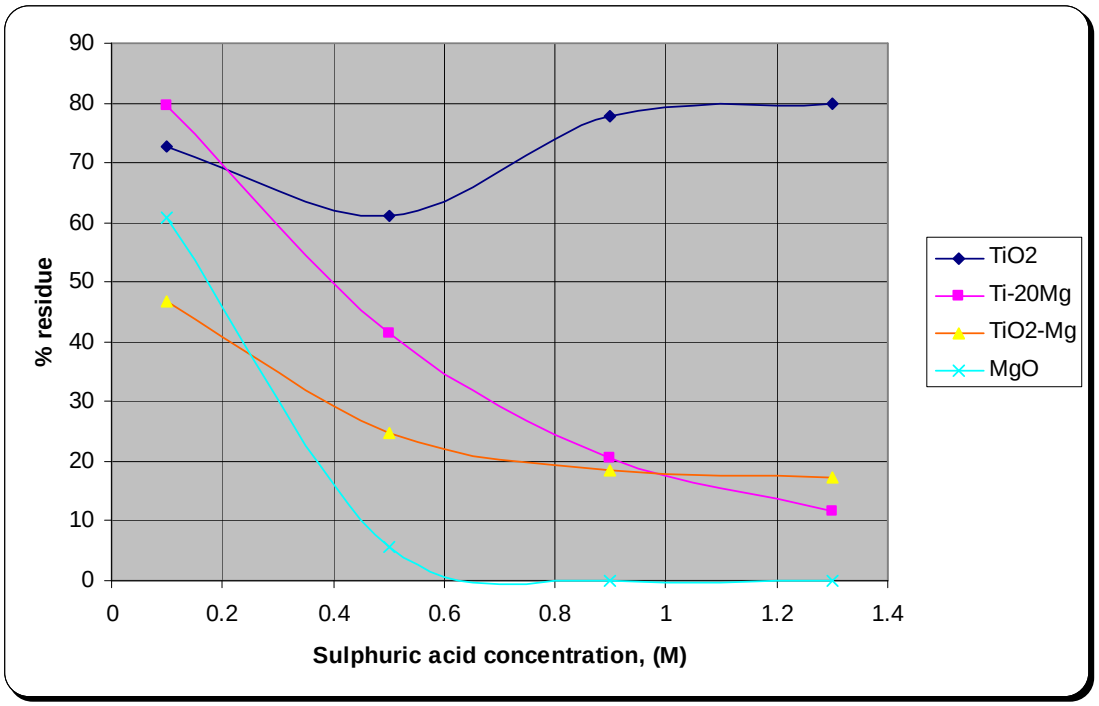


Figure 4.6 Effect of H_2SO_4 concentration on the leaching of the individual powders

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_2SO_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_2SO_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.

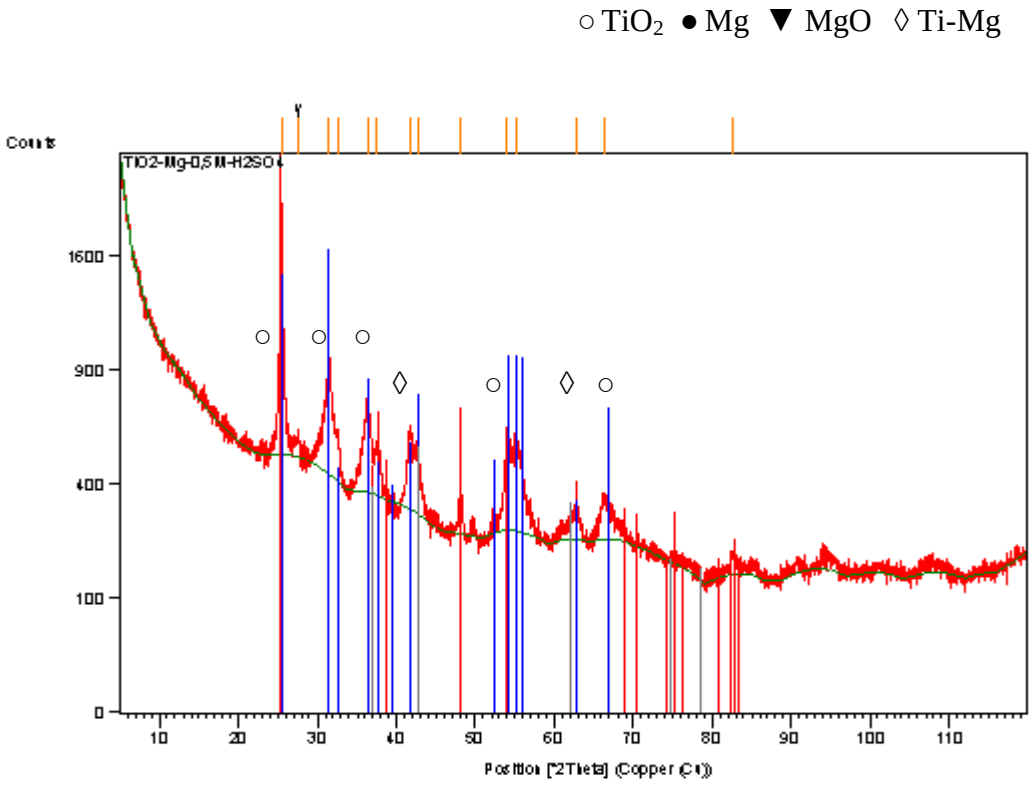


Figure 4.7 XRD pattern of milled TiO_2-Mg residue leached in 0.5M H_2SO_4.

Figure 4.7 shows the XRD pattern of mechanochemically processed TiO_2-Mg residue leached at 0.5M H_2SO_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_2SO_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_2SO_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_2SO_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.

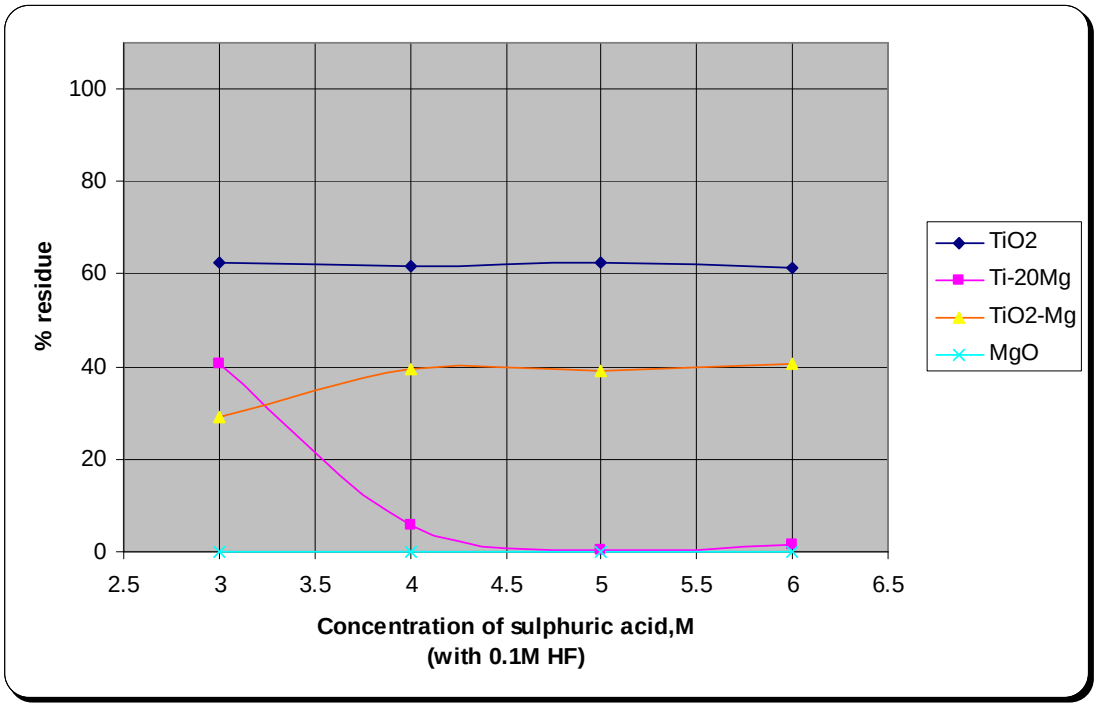


Figure 4.8: Effect of leaching in concentrated H_2SO_4 with HF

Figure 4.9 shows the XRD patterns of TiO_2-Mg powder leached in 0.5M H_2SO_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.

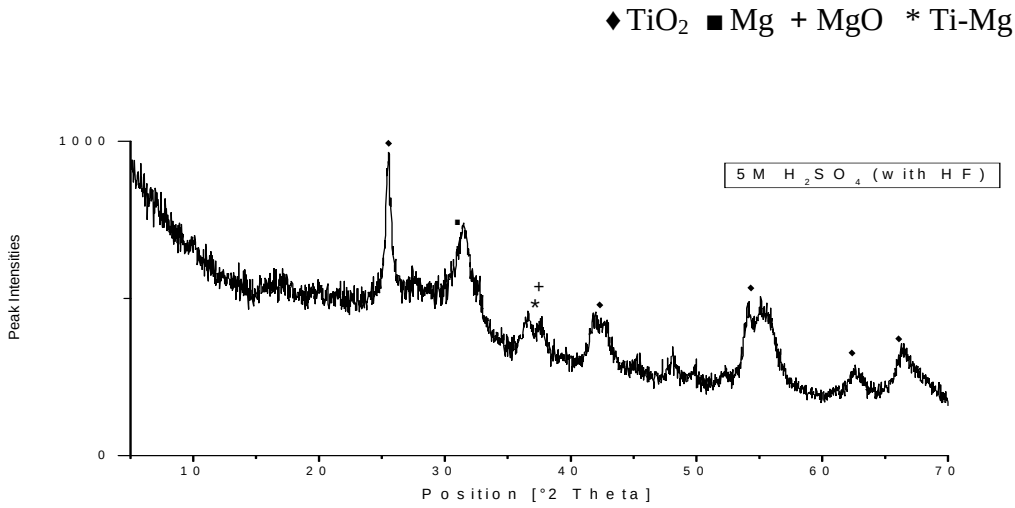


Figure 4.9 XRD pattern of milled TiO_2-Mg residue leached in 0.5M H_2SO_4 (with 0.1M HF)

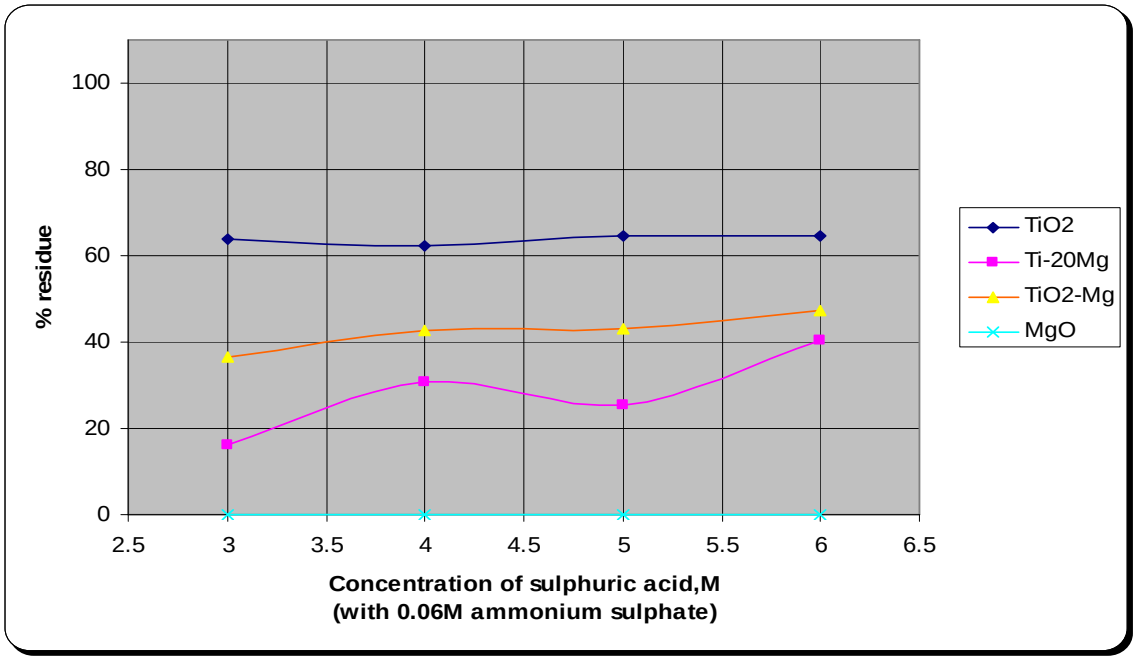


Figure 4.10: Effect of leaching individual powders in concentrated H_2SO_4 with $(NH_4)_2SO_4$

Figure 4.10 shows the extent of dissolution in relation to increase in the concentration of H_2SO_4 (enhanced with 0.06M $(NH_4)_2SO_4$). 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.

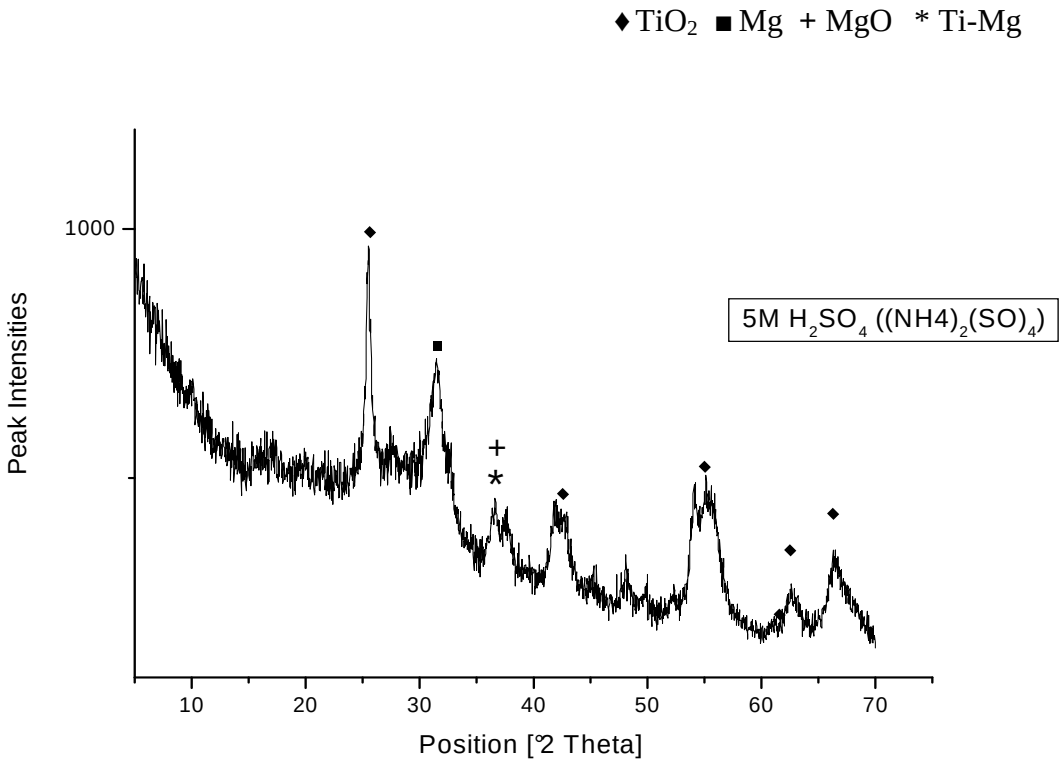


Figure 4.11 XRD pattern of milled TiO_2-Mg residue leached in 0.5M H_2SO_4 (with 0.06M $(NH_4)_2SO_4$

Figure 4.11 shows the XRD pattern of the MCP TiO_2-Mg powder residue leached in 0.5M H_2SO_4 (with 0.06M $(NH_4)_2SO_4$. Just like the patterns of powders leached with H_2SO_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_2SO_4 with 0.1M HF (Figure 4.8), and in concentrated H_2SO_4 with 0.06M $(NH_4)_2SO_4$ (Figure 4.10) showed that TiO_2 was largely undissolved in both leach media. The degree of dissolution of TiO_2 in both H_2SO_4/HF and H_2SO_4/$(NH_4)_2SO_4$ was virtually the same. It follows that the individual

additions of HF and $(NH_4)_2SO_4$ to concentrated H_2SO_4 leach media did not have any effect on the dissolution properties of TiO_2.

Concentrated H_2SO_4 with 0.1M HF cannot be satisfactorily used to isolate Ti-Mg alloy from MCP TiO_2-Mg powders because the oxides of Ti did not show much amenability to dissolution. There was about 60% (Figure 4.8) undissolved polycrystalline TiO_2 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 TiO_2-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 TiO_2-Mg and MgO powders whose residues drastically decreased with increase in HCl concentration. The proportion of TiO_2-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 TiO_2-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.

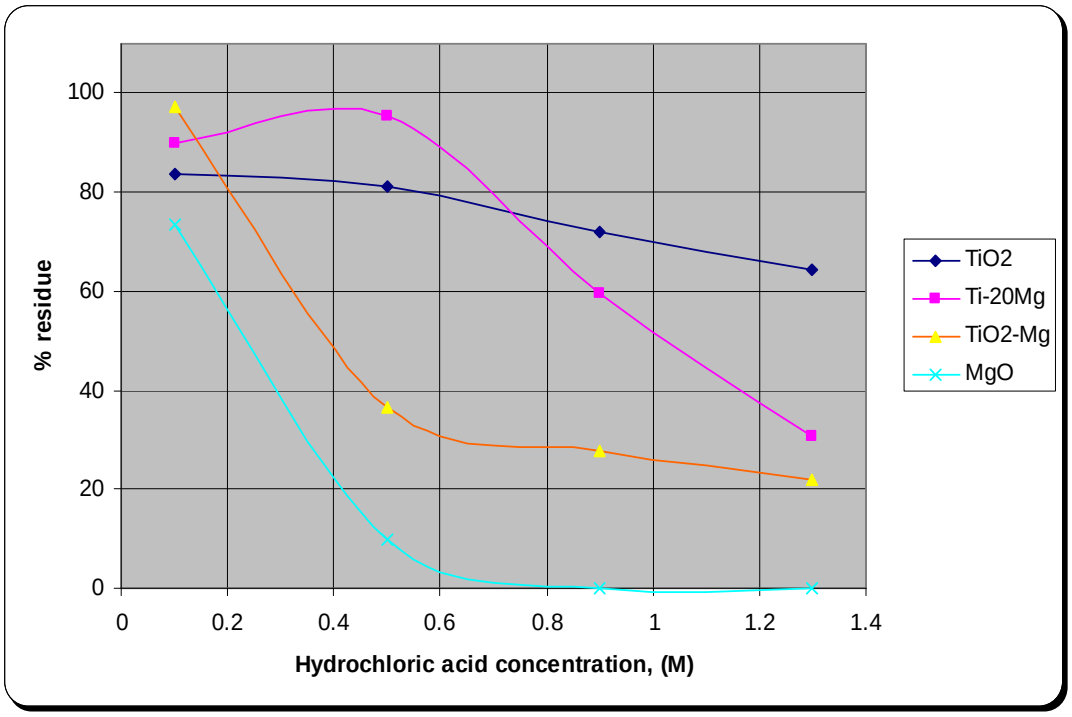


Figure 4.12: Effect of HCl concentration on the leaching of the individual powders.

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):

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

The intermediate then disintegrates to give a TiO_2 precipitate and water (Eq. 4.5).

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

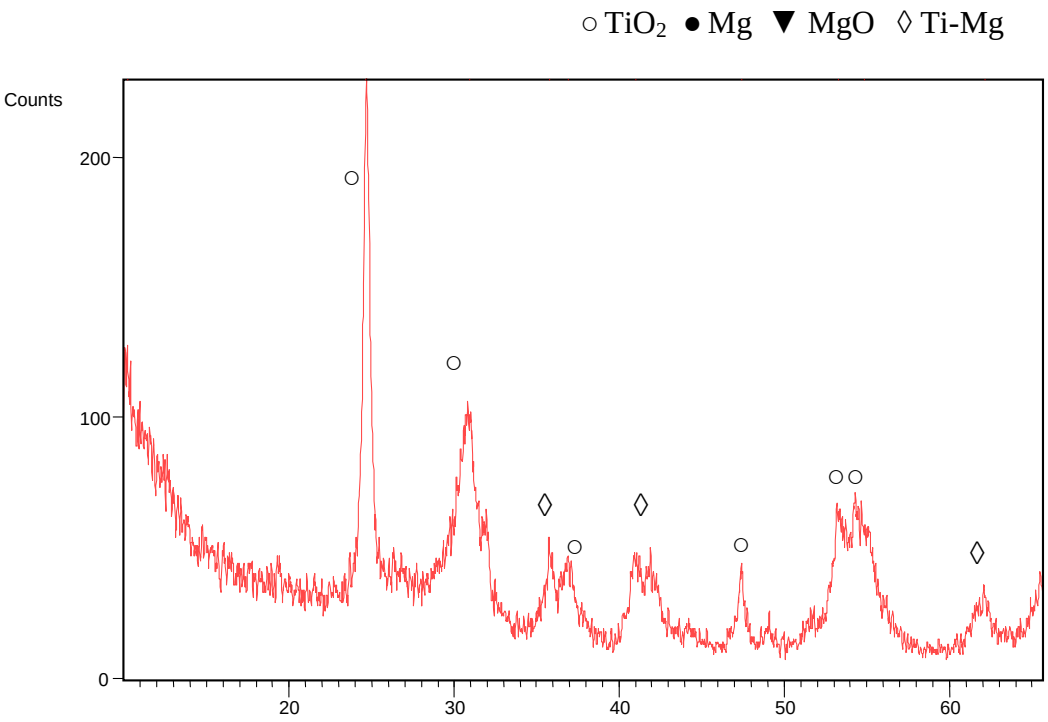


Figure 4.13: XRD pattern of milled TiO_2-Mg residue leached in 1.3M HCl acid

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 2θ 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

(in the milled TiO_2-Mg) to a larger extent. For purposes of comparing the dissolution behaviour 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.

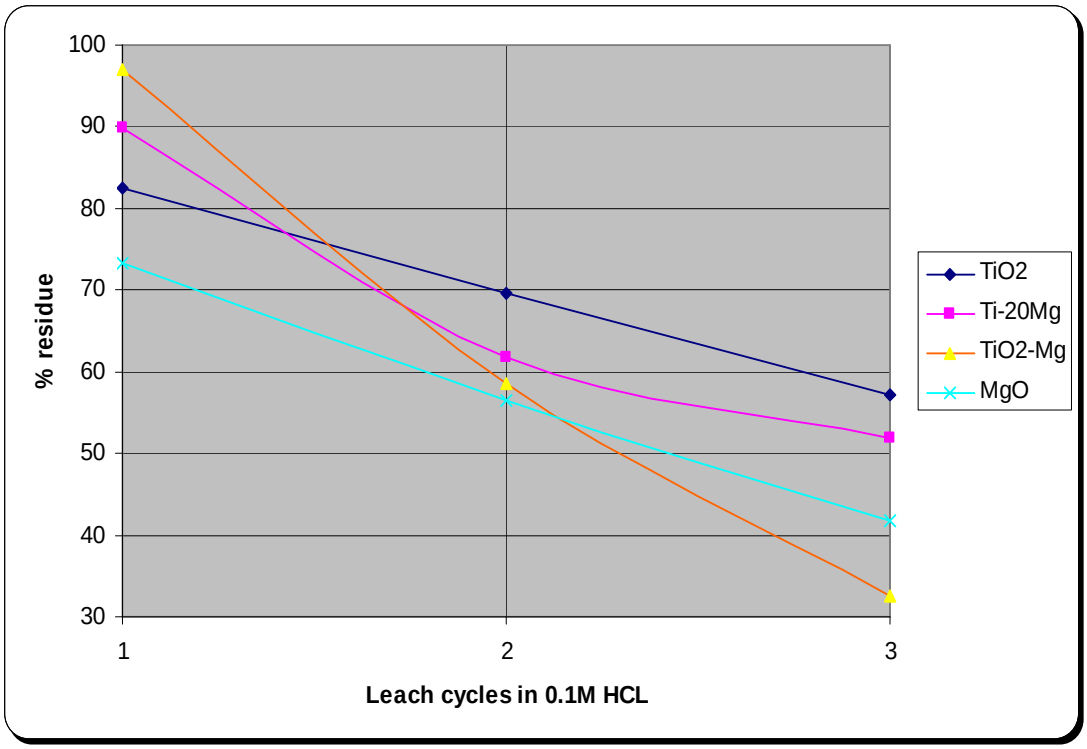


Figure 4.14: Cyclic leaching of the individual powders at 0.1M HCl

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.

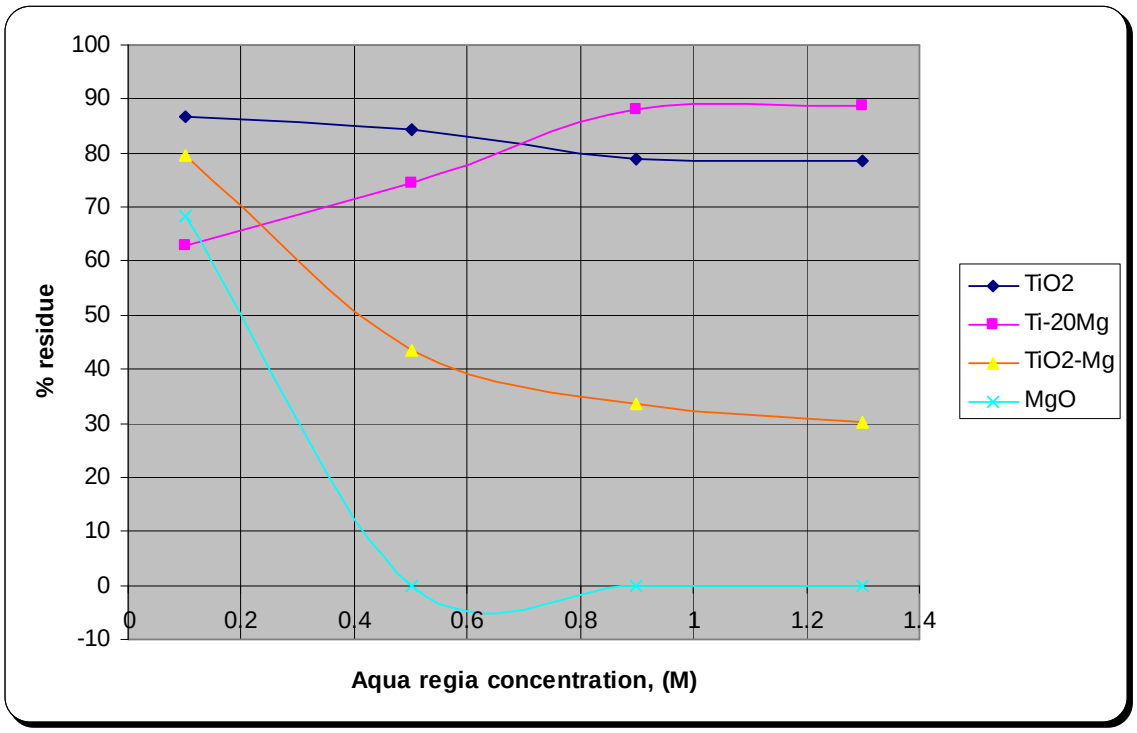


Figure 4.15: Effect of aqua regia concentration on the leaching of the individual powders.

The situation with aqua regia was the same as for H_2SO_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 HNO_3 acid with HCl acid to form nitrosyl chloride (NOC*l*), Cl_2, and water. Both Cl_2 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 TiO_2 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 TiO_2-Mg powder leached in 0.9M aqua regia. The pattern confirmed what the dissolution graph showed (Figure 4.15): TiO_2 was not amenable to much dissolution in the media used, and it thus became the most dominat phase after leaching despite it being only 5.7% initially.

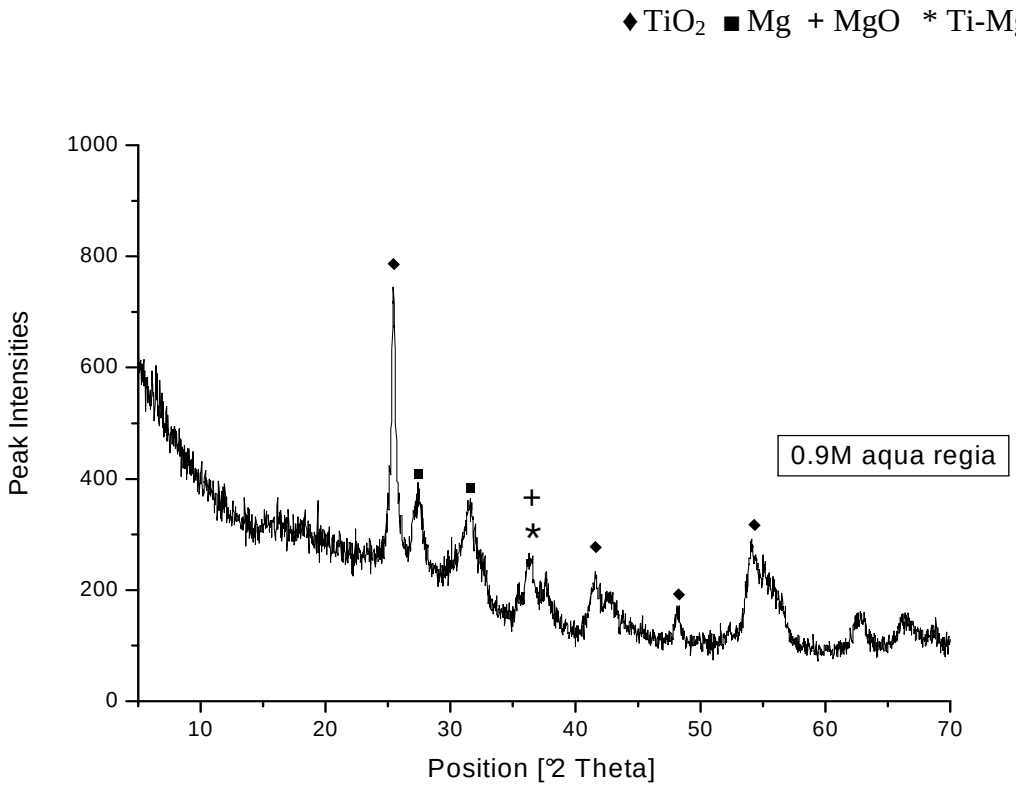


Figure 4.16: XRD pattern of milled TiO_2-Mg residue leached in 0.9M aqua regia

4.2.5 Effect of leaching in oxalic/ascorbic acids

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

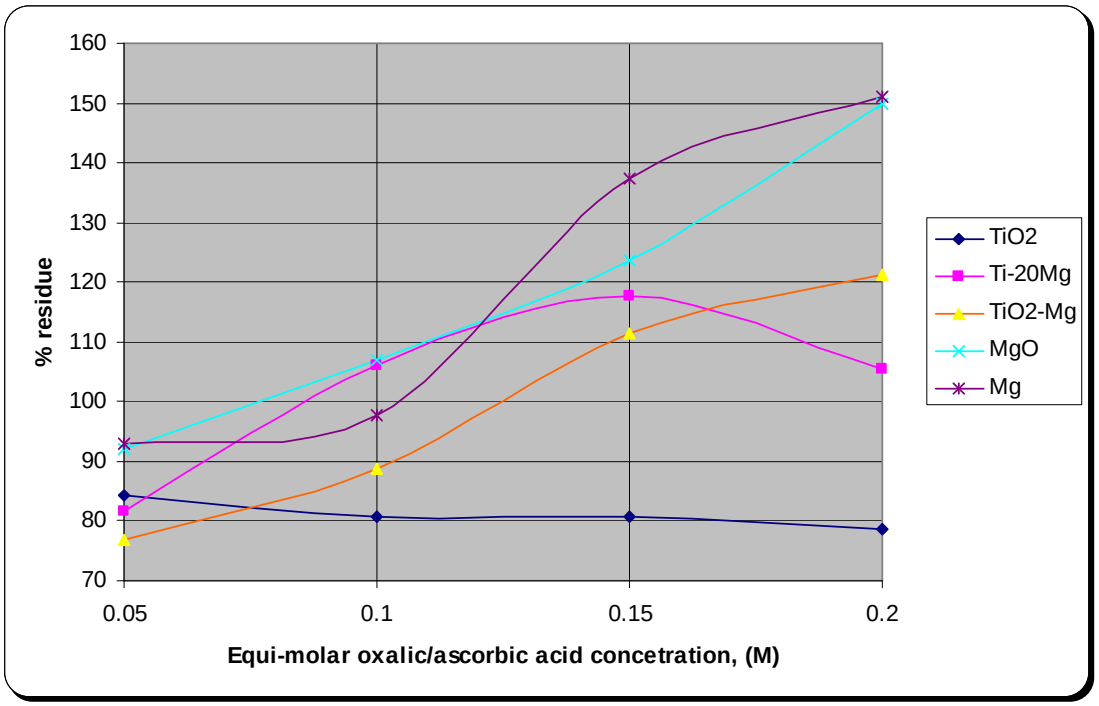


Figure 4.17: Effect of oxalic/ascorbic acid concentration on the leaching of the individual powders

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

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_2-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_2-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_2 in MgO (in both crystalline MgO and milled TiO_2-Mg), and alloyed to Ti (in both MCP TiO_2-Mg, and Ti-20Mg).

Independent polycrystalline TiO_2 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^{2+} ions (from the dissolved Mg bearing phases) in the equimolar oxalic/ascorbic acid mixture were hydrolysing to $Mg(OH)_2$. XRD analysis of the residues (Fig 5.18) showed the presence of $Mg(OH)_2$; the Mg in both the oxide and the Ti alloys probably went into solution as Mg^{2+} cations before being quickly hydrolysed to $Mg(OH)_2$. 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 $Mg(OH)_2$ precipitate. Indeed, XRD analysis of elemental Mg leached in 0.15M concentration (Appendix C11) showed the presence of $Mg(OH)_2$ phases, over and above those of undissolved Mg.

$$MgO(s) + 2H^+(aq) \Rightarrow Mg^{2+} + H_2O(l) \qquad \text{(Eq. 3.5)}$$

$$Mg^{2+} + 2OH^{-} \Rightarrow Mg(OH)_2(s) \qquad \text{(Eq. 3.5)}$$

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_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 $Mg(OH)_2$ as shown by the labelled peaks. No MgO was detected in the XRD analysis; all the oxide had probably hydrolyzed to $Mg(OH)_2$.

○ TiO_2 ● Mg ▼ $Mg(OH)_2$ ◊ Ti-Mg

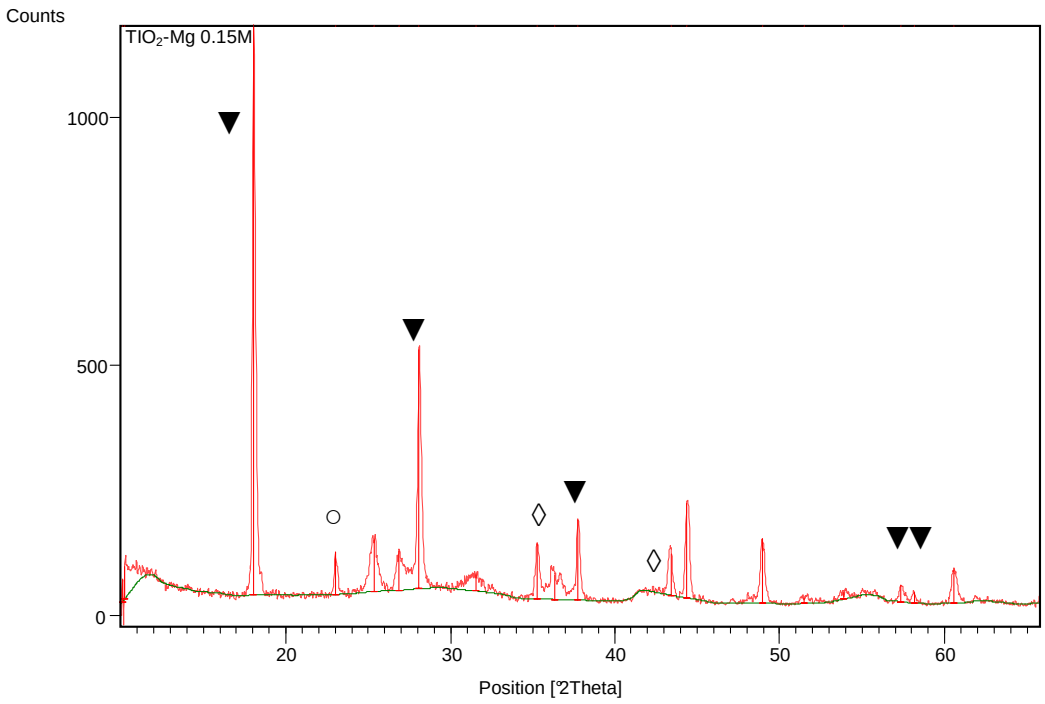


Figure 4.18: XRD spectra of milled TiO_2-Mg residue leached in 0.15M ascorbic/oxalic acids

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.

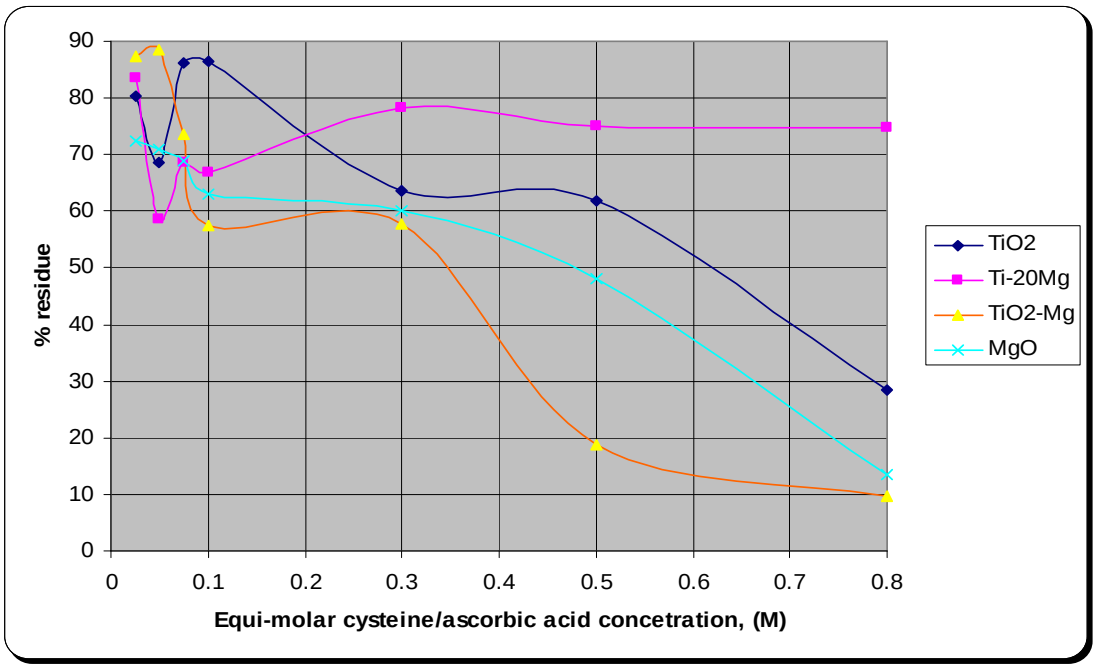


Figure 4.19: Effect of equimolar cysteine/ascorbic acids on the leaching of the individual powders

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.

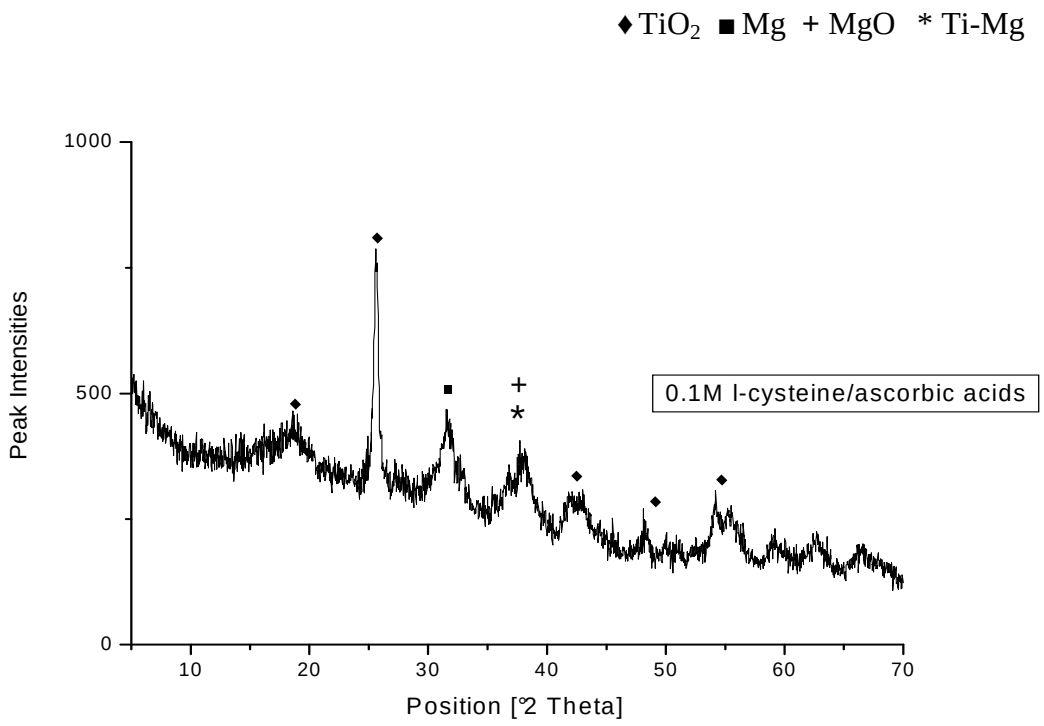


Figure 4.20: XRD pattern of milled TiO_2-Mg residue leached in 0.1M equimolar cysteine/ascorbic acids

Equimolar cysteine/ascorbic acid showed a lot of potential in separation of Ti-Mg from the MCP TiO_2-Mg. At lower acid concentrations, more of the MCP TiO_2-Mg is retained at concentrations 0.025 and 0.05M than any other powder. A lot more independent TiO_2 dissolved at these same concentrations, particularly at 0.05M. It is postulated that the oxides of Ti from the milled TiO_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_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

Powder	% residue at 2.5hrs	% residue at 1hr	% difference
TiO_2	68.3	81.9	13.6
Ti-20Mg	58.3	70.1	11.8
TiO_2-Mg	87.1	66.5	-20.57
MgO	70.8	77.5	6.7

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.

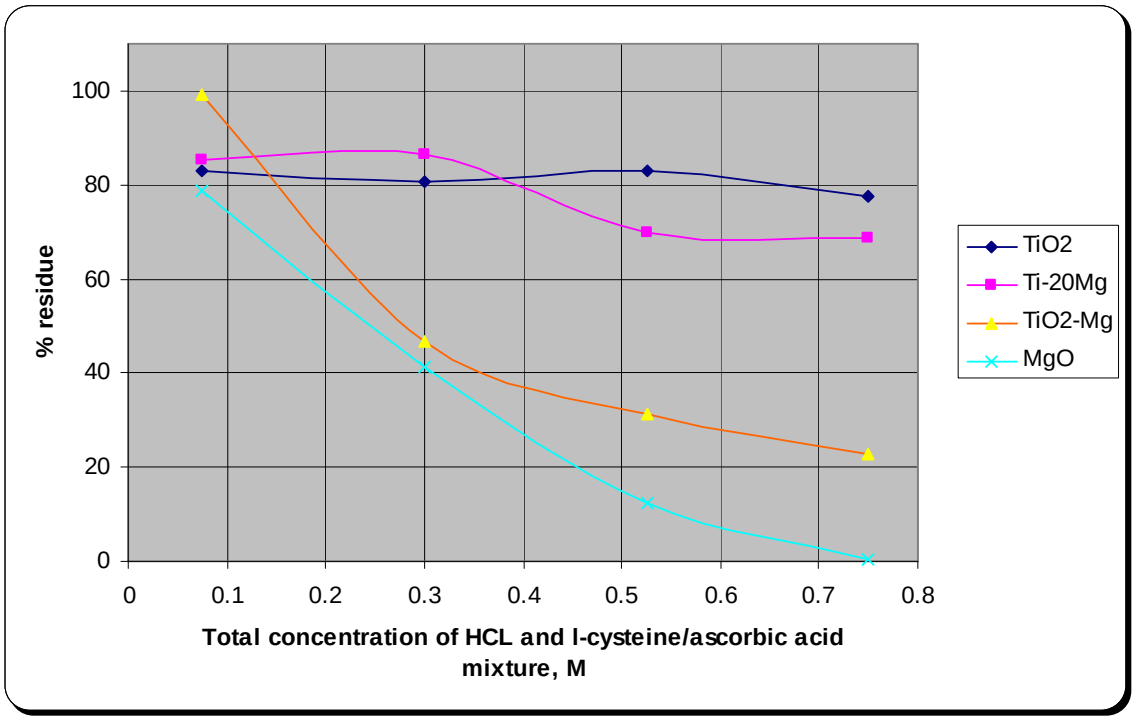


Figure 4.21 Graph of combined HCl and equi-molar cysteine/ascorbic acids

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.

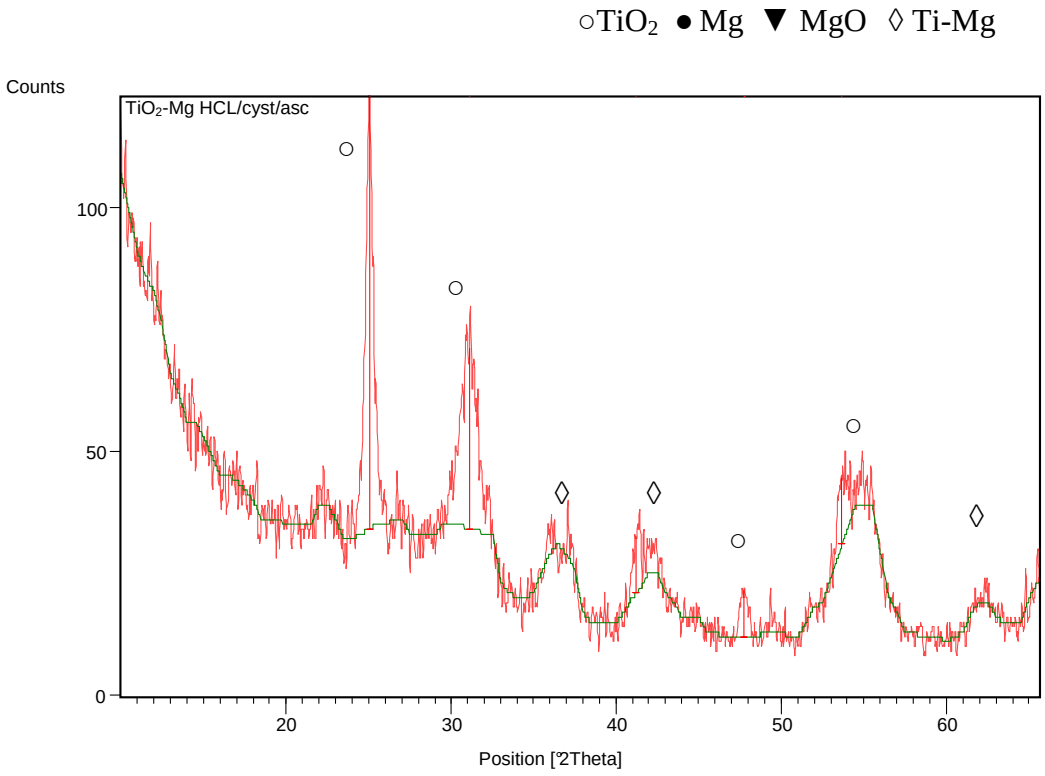


Figure 4.22: XRD spectra of milled TiO_2-Mg residue leached in combined HCl and equi-molar cysteine/ascorbic acids

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 TiO_2 in cysteine/ascorbic acids combination. Most of the TiO_2 was dissolved at higher concentrations. However, milled TiO_2-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 TiO_2.

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_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_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_2SO_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_2SO_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_2SO_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_2SO_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_2SO_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).

- Ti-Mg alloy powder was not recovered using concentrated H_2SO_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_2SO_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.

Banfield J. F and Veblen D. R; Conversion of perovskite to anastase and TiO_2: A TEM study and the use of fundamental building blocks for understanding relationships among TiO_2 minerals, American Mineralogist, volume 77, pp 545-557, 1992.

Chun L, Liang B and Wang H; Preparation of synthetic rutile by hydrochloric acid leaching of mechanically activated Panzhihua ilmenite, ScienceDirect Hydrometallurgy, 121 – 128, 2008.

Chung Kong Chau and Zongjin Li; Accelerated Reactivity Assessment of Light Burnt Magnesium Oxide, Journal of American Ceramic Society, 91 [5] 1640–1645, 2008.

Dias L, Coelho C, Trindade B and Froes F.H; Mg-rich Light Alloys Synthesised by Mechanical Alloying, Key Engineering Materials Vols. 230-232, pp 283-286, 2002.

El-Hazek N, Lasheen T. A, El-Sheikh R and Zaki S. A; Hydrometallurgical criteria for TiO_2 leaching from Rosetta ilmenite by hydrochloric acid, Journal of Hydrometallurgy 87, pp 45 – 50, 2007.

Fedorockova A. and Raschman P., Effects of pH and acid anions on the dissolution kinetics of MgO, Chemical Engineering Journal 143, pp 265 – 272, 2008.

Frantsevich I. N., Karpinos D.N, Yagupol'skaya L.N., Tuchinskii L.I., Sapozhnikova A.B. and Dzeganovskii V.P; Corrosion Resistance Of Titanium-Magnesium Pseudoalloys, Powder Metallurgy and Metal Ceramics, Volume 20, Number 11, pp 814-816, 1981.

Froes F.H. and Trindade B., The mechanochemical processing of aerospace metals, Journal Of Materials Science **39**, Mechanochemistry And Mechanical Alloying, pp 5019 – 5022, 2004.

Froes FH, D. Eylon. Powder metallurgy of titanium alloys- A review. Powder Metallurgy International 17(4), pp163-167, 1993.

Gerdemann Steven J, Albany Research Center Albany, Oregon; Titanium Process Technologies, Advanced Materials & Processes, 2001.

Gutman E.M.; Mechanochemistry of materials, Cambridge International Science Publishing, pp 82 – 83, 1998.

Imahashi M and Takamatsu N., Bulletin of the Chemical Society of Japan, Vol. 49 (6), pp 1549 - 1553, 1976.

Jones C.F., Segall R.L., Smart R. and Turner P.S; Initial dissolution Kinetics of Ionic Oxides, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, Vol. 374, No. 1756, pp 141 - 153, 1981.

Kiejna A, Pabisiak T and S W Gao: The energetics and structure of rutile TiO2(110), Institute Of Physics Publishing Journal Of Physics: Condensed Matter 18, pp 4207–4217, 2006.

Kim A. G; CCB leaching summary: Survey of methods and results, National Energy Technology laboratory, US Department of Energy Pittsburgh, Pennsylvania, 2004.

Koch C.C., Top-down synthesis of nanostructured materials: Mechanical and Thermal Processing Methods, Rev. Adv. Sci. 5, pp 91 – 99, 2003.

Koch., The synthesis and structure of nanocrystalline materials produced by mechanical attrition, Nanostructured Materials Volume 2, pp 109–129, 1993.

Korn MA, Ferreira A.C, Costa A.S.S, Nobrega J.A, Silva C.R; Comparison of decomposition procedures for analysis of titanium dioxide using inductively coupled plasma optical emission spectrometry, Microchemical Journal 71, pp 41-48, 2002.

Kroll W.; The production of ductile titanium, Tr. Electrochem. Soc, 78, pp 35 - 47, 1940.

Lai M.O, Lu L and Chung B.Y; Formation of Mg-Al-Ti/MgO composite via reduction of TiO_2, Composite Structures 57, pp 183 - 187, 2002.

Leyens C and Peters M., Titanium and Titanium Alloys Fundamentals and Applications, Wiley-Vch Verlag GmbH & Co.KgaA, Weinheim, ISBN:3-527-30534-3, 2003.

McCormick P.G and Froes F.H, The fundamentals of Mechanochemical Processing JOM 50, pp 61, 1998.

Mukherjee A, Raichur A. M, Modak J. M; Dissolution studies on TiO_2 with organics, ScienceDirect Hydrometallurgy, pp 585 – 588, 2005.

Nicula R, Lüthen F, Stir M, Nebe B, Burkel E; Spark plasma sintering synthesis of porous nanocrystalline titanium alloys for biomedical applications, Biomol Eng, 24(5), pp 564 – 567, 2007.

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

Raschman P and Fedoročková A; Dissolution of periclase in excess of hydrochloric acid: Study of inhibiting effect of acid concentration on the dissolution rate, Chemical Engineering Journal Volume 117, Issue 3, pp 205-211, 2006.

Reyes-Coronado D, Rodriguez-Gattorno G, Espinosa-Pesqueira M. E, Cab C, de Cross R and Oskam G; Phase-pure TiO2 nanoparticles: anastase, brookite and rutile, IOP Publishing, Nanotechnology 19, 145605 (10pp), 2008.

Sangwal K; Mechanism of dissolution of MgO crystals in acids, Journal Of Materials Science 15, pp 237 – 246, 1980.

Sasikumar C., Rao D.S., Srikanth S., Mukhopadhyay N.K. and Mehrotra S.P; Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H_2SO_4, Scince Direct, Hydrometallurgy 88, pp 154 – 169, 2007.

Shankar V., Lu L., and Lai M.O; Mechanochemical activation of solid state reaction between Mg and TiO_2, JSME International Journal, Series A, Vol. 46, No.3, pp 251 – 254, 2003.

Sheibani S, Ataie A and Heshmati-Manesh S; Kinetics analysis of mechano-chemically and thermally synthesized Cu by Johnson–Mehl–Avrami model, Journal of Alloys and Compounds Volume 455, Issues 1 – 2, pp 447, 2008.

Sibum H; Titanium and titanium alloys – From raw materials to semi-finished products, Advanced Engineering Materials, 2003.

Sole K.C; Recovery of titanium from leach liquors of titaniferous magnetites by solvent extraction, ScienceDirect Hydrometallurgy Vol 1, pp 239 – 253, 1999.

Sun F and Froes F.H; Synthesis and characterization of mechanical-alloyed Ti-*x*Mg alloys, Journal of Alloys and Compounds 340, pp 220 – 225, 2002.

Suryanarayana C, Ivanov E and Boldyrev V. V; The science and technology of mechanical alloying, Materials Science and Engineering A Volumes 304-306, pp 151 - 158, 2001.

Takeda O and Okabe T.H.; Fundamental Study on Magnesiothermic Reduction of Titanium Dichloride, Journal of Metallurgical and Materials Transactions B (Chemistry and Materials Science), Volume 37, pp 823 - 830, 2006.

Valeeva A. A., Rempel A. A. and Gusev A.I; Electrokinetic and Magnetic Properties of Cubic Titanium Monoxide with a Double-Defect Structure, Doklady Physics, Vol. 47, No. 1, pp 39 – 43, 2002. Translated from Doklady Akademii Nauk, Vol. 382, No. 3, pp 320 – 324, 2002.

Vanhumbeeck J, In situ monitoring of the internal stress evolution during titanium thin film anodising, Google books, pp 71, 2009.

Ward-Close C.M, Patridge P. G, Holdway P and Bowen A. W; Titanium ’92 Science and Technology, edited by Froes F. H and Caplan I. R (TMS Warrendale, PA, pp 659, 1993.

Welham N. J, Williams J. S, Carbothermic Reduction of Ilmenite (FeTiO3) and Rutile (TiO2), Metallurgical And Materials Transactions B, 1076-1081—Volume 30b, 1999.

Welham N. J; Mechanically induced reduction of ilmenite (FeTiO3) and rutile (TiO_2) by magnesium, Journal of Alloys and Compounds 274, pp 260 - 265, 1998.

Wendt S., Schaub R., Matthiesen J., Vestergaard E.K., Wahlstro¨m E., Rasmussen M.D., Thostrup P., Molina L.M., Lægsgaard E., Stensgaard I., Hammer B. and Besenbacher F.; Oxygen vacancies on TiO_2(110) and their interaction with H_2O and O_2: A combined high-resolution STM and DFT study, Science Direct, Surface Science 598, pp 226 – 245, 2005.

Wilkes D. M. J, Goodwin P. S, Ward-Close C.M, Bagnall K and Steeds J; Solid solution of Mg in Ti by mechanical alloying, Material Letters 27, pp 47-52, 1996.

Wilson J. A and Steeds J. W; Reaction of magnesium boride particles in mechanically alloyed Ti-4wt%MgB_2, Journal of Material Science, 36, pp 67-75, 2001.

Zhou E., Suryanarayana C and Froes F.H., Effect of premilling elemental powders on solid solubility extension of magnesium in titanium by mechanical alloying, ELSEVIER Materials Letters 23, pp 27 – 31, 1995.

APPENDICES

Appendix A1: Milled sample calculations

Relative Molecular Masses (RMM)

Substance	RMM
Ti	47.9
Mg	24.3
TiO2	79.9
MgO	40.3

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) x 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

Product	Mass (g)	Proportion (%)
TiO_2 (unreacted)	7.7	5.7
MgO	73.5	53.6
Ti-Mg	54.8	40.7

Appendix B1: Raw PSA Data for unmilled TiO_2- Mg powders

Table B1: PSA results for unmilled TiO_2-Mg powder mixture

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.00	0.634	8.07	5.053	19.67	40.244	53.79	320.535	100.00
0.011	0.00	0.090	0.00	0.717	9.42	5.709	20.06	45.469	59.71	362.148	100.00
0.013	0.00	0.102	0.00	0.810	10.76	6.450	20.50	51.371	65.87	409.163	100.00
0.014	0.00	0.115	0.00	0.915	12.04	7.287	21.00	58.041	72.05	462.281	100.00
0.016	0.00	0.130	0.00	1.034	13.24	8.233	21.56	65.575	78.01	522.296	100.00
0.018	0.00	0.147	0.00	1.168	14.31	9.302	22.20	74.089	83.52	590.102	100.00
0.021	0.00	0.166	0.00	1.320	15.26	10.510	22.94	83.707	88.38	666.711	100.00
0.024	0.00	0.187	0.03	1.491	16.05	11.874	23.81	94.574	92.45	753.265	100.00
0.027	0.00	0.211	0.16	1.684	16.71	13.416	24.85	106.852	95.64	851.056	100.00
0.030	0.00	0.239	0.46	1.903	17.24	15.157	26.14	120.724	97.95	961.542	100.00
0.034	0.00	0.270	0.89	2.150	17.66	17.125	27.74	136.397	99.43	1086.372	100.00
0.038	0.00	0.305	1.50	2.429	18.00	19.348	29.75	154.104	100.00	1227.408	100.00
0.043	0.00	0.345	2.27	2.745	18.28	21.860	32.24	174.110	100.00	1386.753	100.00
0.049	0.00	0.389	3.20	3.101	18.53	24.698	35.30	196.714	100.00	1566.785	100.00
0.055	0.00	0.440	4.27	3.503	18.77	27.904	38.99	222.251	100.00	1770.189	100.00
0.062	0.00	0.497	5.45	3.958	19.04	31.527	43.32	251.105	100.00	2000.000	100.00
0.070	0.00	0.561	6.73	4.472	19.33	35.620	48.28	283.704	100.00		

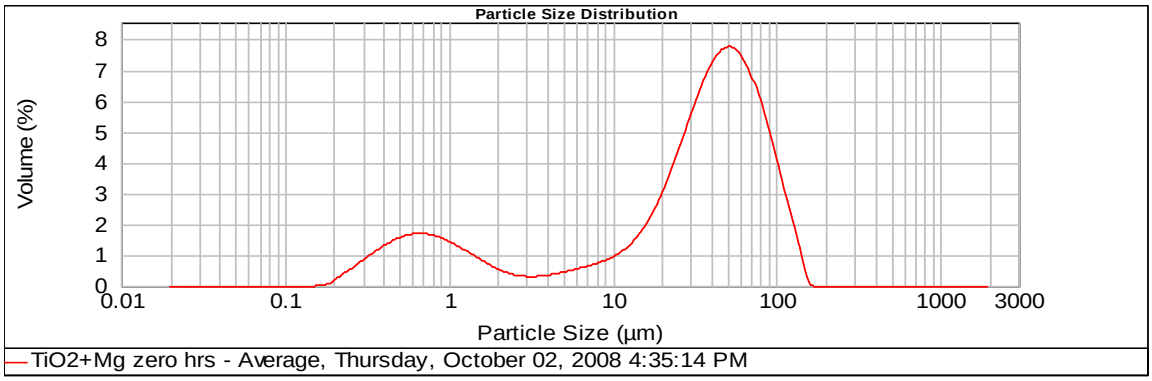


Figure B1: Graph of Volume (%) vs Particle Size (microns) for unmilled powder

Appendix B2: Raw PSA Data for TiO_2- Mg powder milled for 2 hours
Table B2: PSA results for TiO_2- Mg powder milled for 2 hours

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.00	0.634	0.00	5.053	2.00	40.244	50.49	320.535	99.93
0.011	0.00	0.090	0.00	0.717	0.00	5.709	2.34	45.469	58.75	362.148	99.99
0.013	0.00	0.102	0.00	0.810	0.00	6.450	2.68	51.371	66.81	409.163	100.00
0.014	0.00	0.115	0.00	0.915	0.00	7.287	3.02	58.041	74.31	462.281	100.00
0.016	0.00	0.130	0.00	1.034	0.00	8.233	3.38	65.575	80.98	522.296	100.00
0.018	0.00	0.147	0.00	1.168	0.00	9.302	3.78	74.089	86.62	590.102	100.00
0.021	0.00	0.166	0.00	1.320	0.01	10.510	4.31	83.707	91.11	666.711	100.00
0.024	0.00	0.187	0.00	1.491	0.05	11.874	5.04	94.574	94.48	753.265	100.00
0.027	0.00	0.211	0.00	1.684	0.12	13.416	6.12	106.852	96.83	851.056	100.00
0.030	0.00	0.239	0.00	1.903	0.20	15.157	7.68	120.724	98.26	961.542	100.00
0.034	0.00	0.270	0.00	2.150	0.31	17.125	9.89	136.397	98.97	1086.372	100.00
0.038	0.00	0.305	0.00	2.429	0.45	19.348	12.91	154.104	99.24	1227.408	100.00
0.043	0.00	0.345	0.00	2.745	0.62	21.860	16.87	174.110	99.38	1386.753	100.00
0.049	0.00	0.389	0.00	3.101	0.83	24.698	21.84	196.714	99.45	1566.785	100.00
0.055	0.00	0.440	0.00	3.503	1.08	27.904	27.83	222.251	99.54	1770.189	100.00
0.062	0.00	0.497	0.00	3.958	1.36	31.527	34.73	251.105	99.65	2000.000	100.00
0.070	0.00	0.561	0.00	4.472	1.67	35.620	42.38	283.704	99.80		

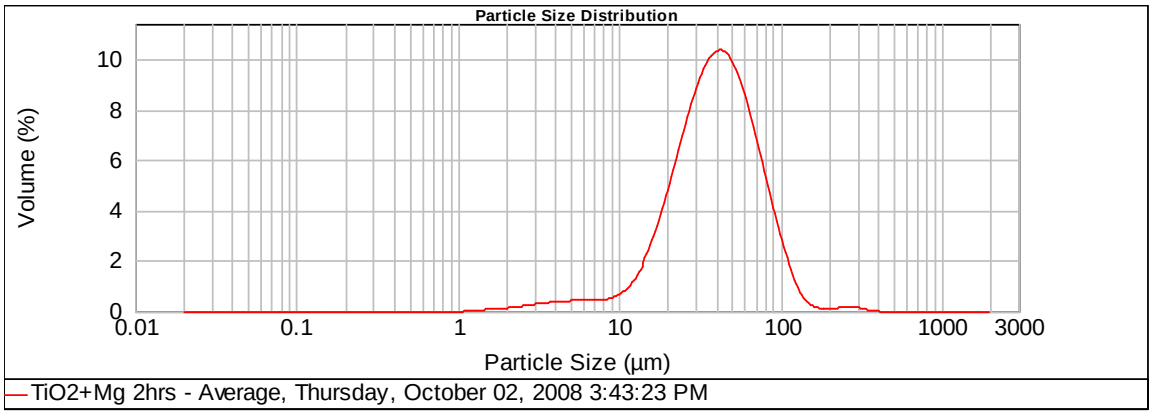


Figure B2: Volume (%) vs Particle Size (microns), milling duration 2 hours

Appendix B3: Raw PSA Data for TiO_2- Mg powder milled for 4 hours
Table B3: PSA results for TiO_2- Mg powder milled for 4 hours

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.00	0.634	1.23	5.053	22.98	40.244	87.15	320.535	99.81
0.011	0.00	0.090	0.00	0.717	1.52	5.709	25.69	45.469	89.47	362.148	99.91
0.013	0.00	0.102	0.00	0.810	1.88	6.450	28.65	51.371	91.50	409.163	99.98
0.014	0.00	0.115	0.00	0.915	2.34	7.287	31.88	58.041	93.27	462.281	100.00
0.016	0.00	0.130	0.00	1.034	2.90	8.233	35.39	65.575	94.80	522.296	100.00
0.018	0.00	0.147	0.00	1.168	3.58	9.302	39.20	74.089	96.10	590.102	100.00
0.021	0.00	0.166	0.00	1.320	4.39	10.510	43.29	83.707	97.17	666.711	100.00
0.024	0.00	0.187	0.00	1.491	5.34	11.874	47.63	94.574	98.00	753.265	100.00
0.027	0.00	0.211	0.04	1.684	6.43	13.416	52.16	106.852	98.60	851.056	100.00
0.030	0.00	0.239	0.12	1.903	7.66	15.157	56.78	120.724	98.97	961.542	100.00
0.034	0.00	0.270	0.21	2.150	9.04	17.125	61.42	136.397	99.15	1086.372	100.00
0.038	0.00	0.305	0.30	2.429	10.57	19.348	65.96	154.104	99.22	1227.408	100.00
0.043	0.00	0.345	0.41	2.745	12.24	21.860	70.31	174.110	99.28	1386.753	100.00
0.049	0.00	0.389	0.52	3.101	14.06	24.698	74.39	196.714	99.35	1566.785	100.00
0.055	0.00	0.440	0.65	3.503	16.04	27.904	78.13	222.251	99.45	1770.189	100.00
0.062	0.00	0.497	0.81	3.958	18.17	31.527	81.50	251.105	99.56	2000.000	100.00
0.070	0.00	0.561	1.00	4.472	20.48	35.620	84.50	283.704	99.69		

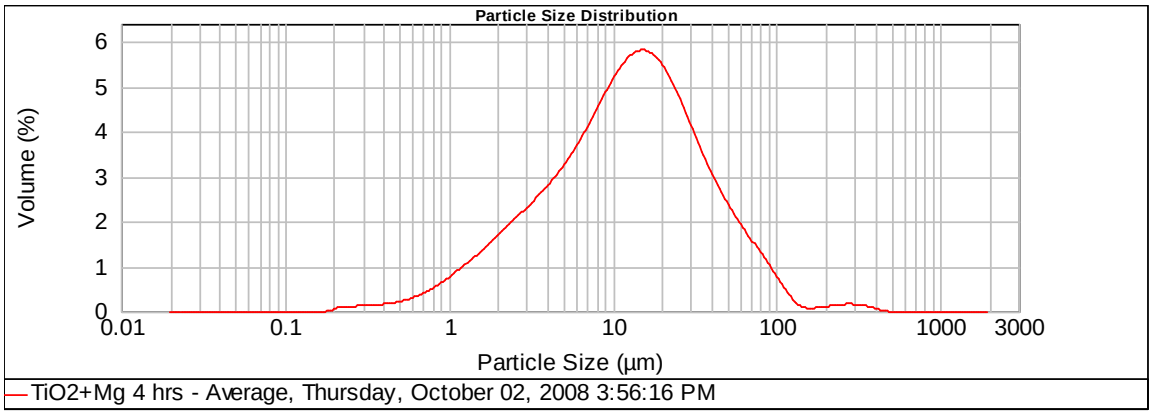


Figure B3: Volume (%) vs Particle Size (microns), milling duration 4 hours

Appendix B4: Raw PSA Data for TiO_2- Mg powder milled for 8 hours

Table B4: PSA results for TiO_2- Mg powder milled for 8 hours

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.00	0.634	0.99	5.053	20.28	40.244	81.99	320.535	94.85
0.011	0.00	0.090	0.00	0.717	1.18	5.709	23.54	45.469	84.06	362.148	95.20
0.013	0.00	0.102	0.00	0.810	1.42	6.450	27.17	51.371	86.01	409.163	95.76
0.014	0.00	0.115	0.00	0.915	1.73	7.287	31.13	58.041	87.84	462.281	96.59
0.016	0.00	0.130	0.00	1.034	2.10	8.233	35.39	65.575	89.51	522.296	97.63
0.018	0.00	0.147	0.00	1.168	2.56	9.302	39.86	74.089	90.99	590.102	98.78
0.021	0.00	0.166	0.00	1.320	3.11	10.510	44.46	83.707	92.25	666.711	99.87
0.024	0.00	0.187	0.00	1.491	3.77	11.874	49.07	94.574	93.24	753.265	100.00
0.027	0.00	0.211	0.04	1.684	4.54	13.416	53.59	106.852	93.96	851.056	100.00
0.030	0.00	0.239	0.11	1.903	5.44	15.157	57.92	120.724	94.41	961.542	100.00
0.034	0.00	0.270	0.20	2.150	6.49	17.125	61.98	136.397	94.58	1086.372	100.00
0.038	0.00	0.305	0.29	2.429	7.70	19.348	65.71	154.104	94.59	1227.408	100.00
0.043	0.00	0.345	0.38	2.745	9.12	21.860	69.10	174.110	94.59	1386.753	100.00
0.049	0.00	0.389	0.48	3.101	10.76	24.698	72.17	196.714	94.59	1566.785	100.00
0.055	0.00	0.440	0.58	3.503	12.66	27.904	74.94	222.251	94.59	1770.189	100.00
0.062	0.00	0.497	0.70	3.958	14.86	31.527	77.47	251.105	94.60	2000.000	100.00
0.070	0.00	0.561	0.83	4.472	17.39	35.620	79.80	283.704	94.67		

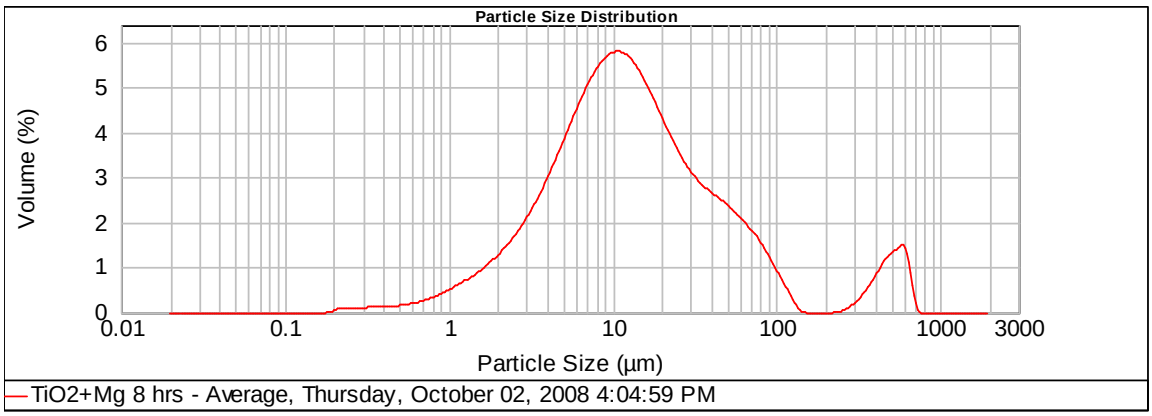
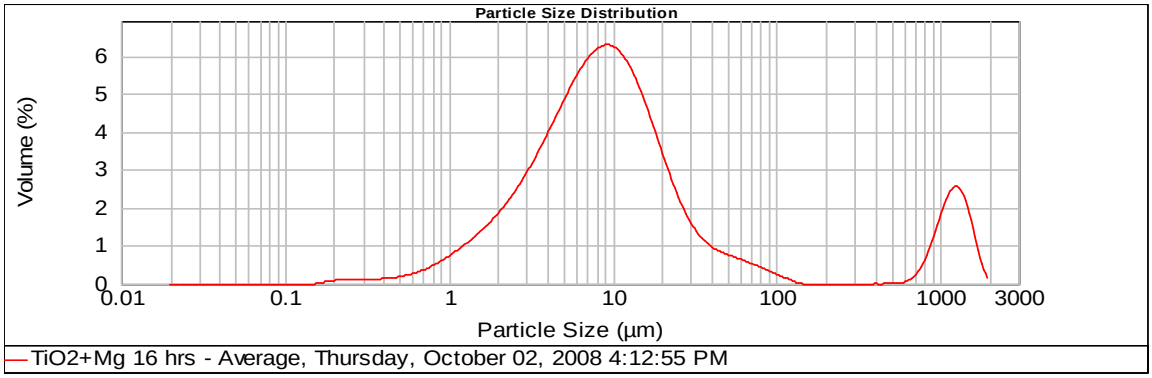


Figure B4: Volume (%) vs Particle Size (microns), milling duration 8 hours

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

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.00	0.634	1.13	5.053	27.69	40.244	86.20	320.535	90.05
0.011	0.00	0.090	0.00	0.717	1.39	5.709	31.75	45.469	86.92	362.148	90.05
0.013	0.00	0.102	0.00	0.810	1.73	6.450	36.15	51.371	87.56	409.163	90.05
0.014	0.00	0.115	0.00	0.915	2.16	7.287	40.83	58.041	88.13	462.281	90.05
0.016	0.00	0.130	0.00	1.034	2.70	8.233	45.73	65.575	88.64	522.296	90.05
0.018	0.00	0.147	0.00	1.168	3.36	9.302	50.75	74.089	89.08	590.102	90.06
0.021	0.00	0.166	0.00	1.320	4.16	10.510	55.75	83.707	89.44	666.711	90.12
0.024	0.00	0.187	0.04	1.491	5.12	11.874	60.63	94.574	89.71	753.265	90.31
0.027	0.00	0.211	0.11	1.684	6.25	13.416	65.23	106.852	89.89	851.056	90.79
0.030	0.00	0.239	0.18	1.903	7.56	15.157	69.46	120.724	90.01	961.542	91.73
0.034	0.00	0.270	0.27	2.150	9.08	17.125	73.20	136.397	90.05	1086.372	93.25
0.038	0.00	0.305	0.35	2.429	10.83	19.348	76.42	154.104	90.05	1227.408	95.21
0.043	0.00	0.345	0.45	2.745	12.83	21.860	79.10	174.110	90.05	1386.753	97.24
0.049	0.00	0.389	0.54	3.101	15.12	24.698	81.26	196.714	90.05	1566.785	98.87
0.055	0.00	0.440	0.65	3.503	17.73	27.904	82.96	222.251	90.05	1770.189	99.76
0.062	0.00	0.497	0.77	3.958	20.69	31.527	84.29	251.105	90.05	2000.000	100.00
0.070	0.00	0.561	0.93	4.472	24.00	35.620	85.34	283.704	90.05		



FigureB5: 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

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.010	0.00	0.080	0.84	0.634	6.40	5.053	43.12	40.244	94.23	320.535	100.00
0.011	0.00	0.090	1.10	0.717	7.17	5.709	46.69	45.469	95.26	362.148	100.00
0.013	0.00	0.102	1.38	0.810	8.13	6.450	50.42	51.371	96.19	409.163	100.00
0.014	0.00	0.115	1.69	0.915	9.29	7.287	54.30	58.041	97.06	462.281	100.00
0.016	0.00	0.130	2.00	1.034	10.66	8.233	58.29	65.575	97.85	522.296	100.00
0.018	0.00	0.147	2.32	1.168	12.24	9.302	62.33	74.089	98.55	590.102	100.00
0.021	0.00	0.166	2.65	1.320	14.02	10.510	66.37	83.707	99.13	666.711	100.00
0.024	0.00	0.187	2.97	1.491	15.98	11.874	70.31	94.574	99.57	753.265	100.00
0.027	0.00	0.211	3.28	1.684	18.09	13.416	74.09	106.852	99.87	851.056	100.00
0.030	0.01	0.239	3.57	1.903	20.35	15.157	77.62	120.724	99.97	961.542	100.00
0.034	0.03	0.270	3.85	2.150	22.73	17.125	80.85	136.397	100.00	1086.372	100.00
0.038	0.07	0.305	4.10	2.429	25.23	19.348	83.73	154.104	100.00	1227.408	100.00
0.043	0.12	0.345	4.35	2.745	27.85	21.860	86.24	174.110	100.00	1386.753	100.00
0.049	0.20	0.389	4.61	3.101	30.60	24.698	88.39	196.714	100.00	1566.785	100.00
0.055	0.31	0.440	4.92	3.503	33.48	27.904	90.22	222.251	100.00	1770.189	100.00
0.062	0.44	0.497	5.30	3.958	36.53	31.527	91.76	251.105	100.00	2000.000	100.00
0.070	0.62	0.561	5.78	4.472	39.73	35.620	93.08	283.704	100.00		

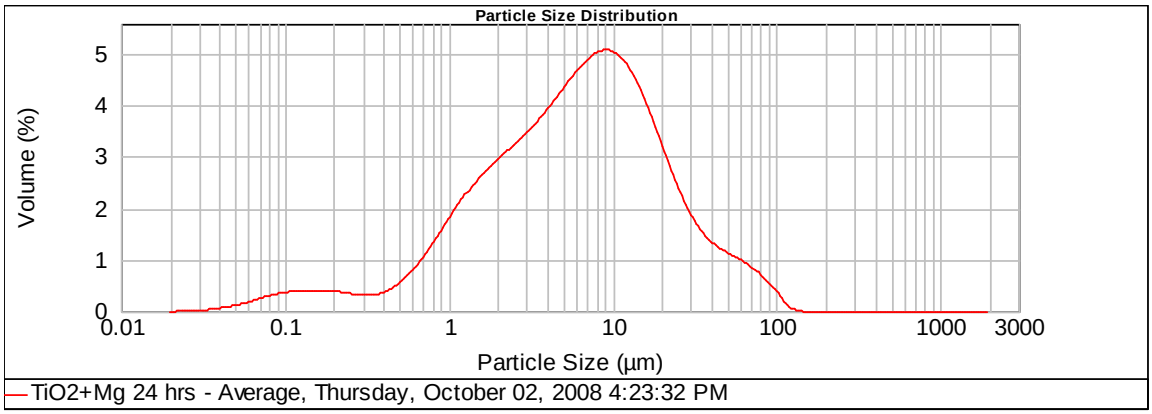


Figure B6: Volume (%) vs Particle Size (microns), milling duration 24 hours

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

Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
2000	0.00	100.00	5.50	5.74	31.75
1674	0.00	100.00	4.62	5.16	26.01
1408	0.00	100.00	3.89	4.62	20.85
1184	0.00	100.00	3.27	4.05	16.23
995.5	0.00	100.00	2.750	3.41	12.18
837.1	0.00	100.00	2.312	2.75	8.77
703.9	0.00	100.00	1.944	2.13	6.02
591.9	0.00	100.00	1.635	1.58	3.89
497.8	0.00	100.00	1.375	1.11	2.31
418.6	0.00	100.00	1.156	0.74	1.20
352.0	0.00	100.00	0.972	0.46	0.46
296.0	0.00	100.00	0.817	0.00	0.00
248.9	0.00	100.00	0.687	0.00	0.00
209.3	0.00	100.00	0.578	0.00	0.00
176.0	0.00	100.00	0.486	0.00	0.00
148.0	0.00	100.00	0.409	0.00	0.00
124.4	0.00	100.00	0.344	0.00	0.00
104.6	0.00	100.00	0.2890	0.00	0.00
87.99	0.00	100.00	0.2430	0.00	0.00
73.99	0.00	100.00	0.2040	0.00	0.00
62.22	0.00	100.00	0.1720	0.00	0.00
52.32	0.35	100.00	0.1450	0.00	0.00
44.00	0.72	99.65	0.1220	0.00	0.00
37.00	1.51	98.93	0.1020	0.00	0.00
31.11	2.68	97.42	0.0860	0.00	0.00
26.16	3.98	94.74	0.0720	0.00	0.00
22.00	5.33	90.76	0.0610	0.00	0.00
18.50	6.76	85.43	0.0510	0.00	0.00
15.55	8.00	78.67	0.0430	0.00	0.00
13.08	8.52	70.67	0.0360	0.00	0.00
11.00	8.56	62.15	0.0300	0.00	0.00
9.25	8.03	53.59	0.02550	0.00	0.00

7.78 7.30 45.56 0.02150 0.00 0.00
6.54 6.51 38.26 0.01810 0.00 0.00

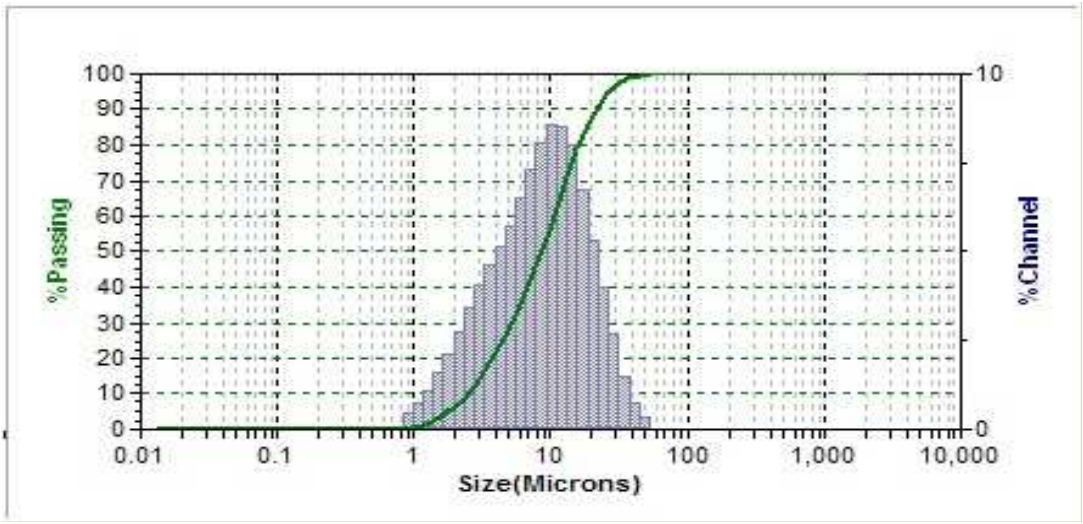


Figure B7: % Passing vs Particle Size (microns), milling duration 32 hours

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

Table B1: Results of Particle Size Analysis

Milling hours	d(0.1) um microns	d(0.5) um microns	d(0.9) microns	Specific surface area m^2/g	Weighted residual (%)
0	0.755	37.050	87.607	2.010	0.967
2	17.210	39.952	80.959	0.221	1.012
4	2.324	12.663	46.868	1.130	0.609
8	2.937	12.172	68.146	0.997	0.859
16	2.298	9.135	119.722	1.230	0.704
24	0.977	6.364	27.467	4.100	0.720
32	2.471	8.580	21.41	-	-

Appendix C1: XRD data for unmilled TiO_2- Mg powders

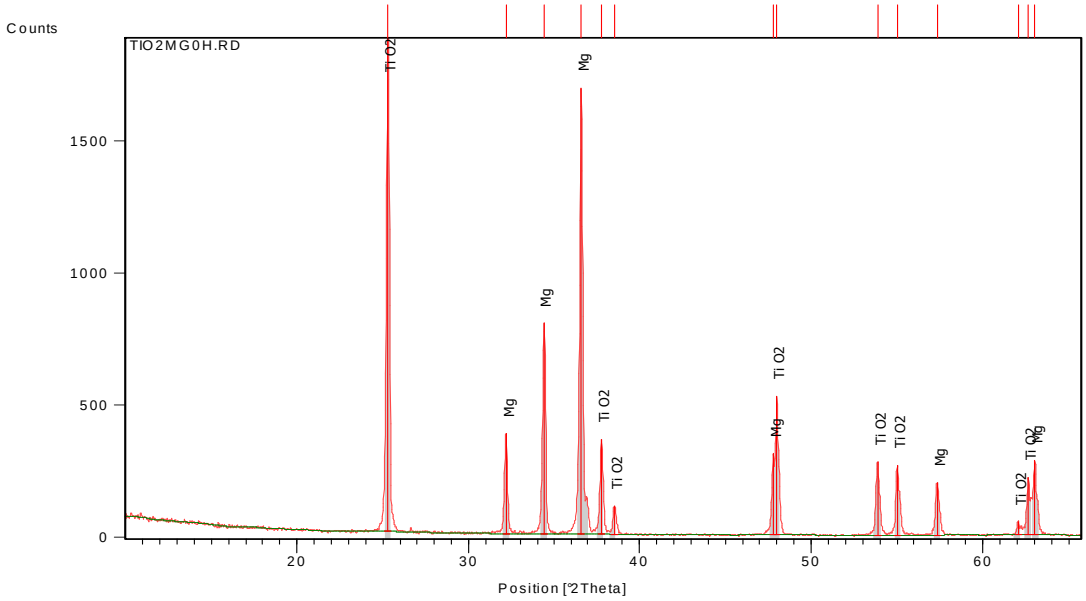


Figure C1: XRD pattern for unmilled TiO_2-15Mg

Table C1: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
25,2983	1881,21	0,1771	3,52057	100,00	0,1800	00-004-0477
32,1687	378,26	0,1574	2,78264	20,11	0,1600	00-035-0821
34,3880	794,42	0,1968	2,60797	42,23	0,2000	00-035-0821
36,6062	1685,11	0,1378	2,45487	89,58	0,1400	00-035-0821
37,7901	357,32	0,1968	2,38064	18,99	0,2000	00-004-0477
38,5569	105,63	0,1968	2,33505	5,62	0,2000	00-004-0477
47,7999	307,43	0,0720	1,90131	16,34	0,0600	00-035-0821
48,0044	523,22	0,0984	1,89526	27,81	0,1000	00-004-0477
53,8631	275,65	0,1574	1,70213	14,65	0,1600	00-004-0477
55,0215	263,46	0,1181	1,66900	14,00	0,1200	00-004-0477
57,3307	196,50	0,1378	1,60715	10,45	0,1400	00-035-0821
62,0550	51,25	0,1181	1,49566	2,72	0,1200	00-004-0477
62,6538	215,02	0,1574	1,48280	11,43	0,1600	00-004-0477
63,0253	280,06	0,1440	1,47373	14,89	0,1200	00-035-0821

Table C2: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-035-0821	64	Magnesium	-0,038	0,957	Mg
*	00-004-0477	64	Anatase, syn	-0,092	0,881	Ti O2

Appendix C2: XRD data for TiO_2- Mg powders milled for 2 hours

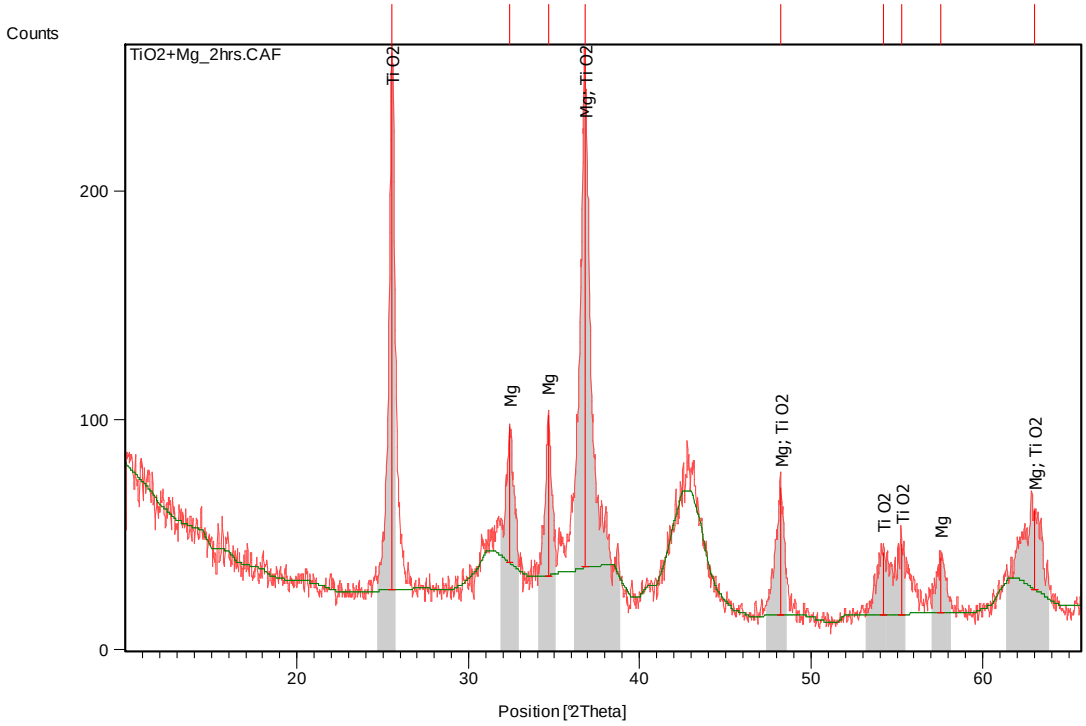


Figure C2: XRD pattern for TiO_2-15Mg milled for 2 hours

Table C3: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
25,5447	234,14	0,2755	3,48717	100,00	0,2800	00-004-0477
32,3911	58,95	0,4723	2,76404	25,18	0,4800	00-035-0821
34,6454	69,52	0,2362	2,58919	29,69	0,2400	00-035-0821
36,8184	225,93	0,2362	2,44121	96,49	0,2400	00-035-0821; 00-004-0477
48,2383	55,29	0,4723	1,88661	23,61	0,4800	00-035-0821; 00-004-0477

54,2230	27,20	0,6298	1,69168	11,62	0,6400	00-004-0477
55,2814	30,45	0,4723	1,66177	13,00	0,4800	00-004-0477
57,5741	23,82	0,4723	1,60093	10,17	0,4800	00-035-0821
63,0361	34,40	1,1520	1,47350	14,69	0,9600	00-035-0821; 00-004-0477

Table C4: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-035-0821	77	Magnesium	0,170	0,920	Mg
*	00-004-0477	39	Anatase, syn	-0,143	0,336	Ti O2

Appendix C3: XRD data for TiO_2- Mg powders milled for 16 hours

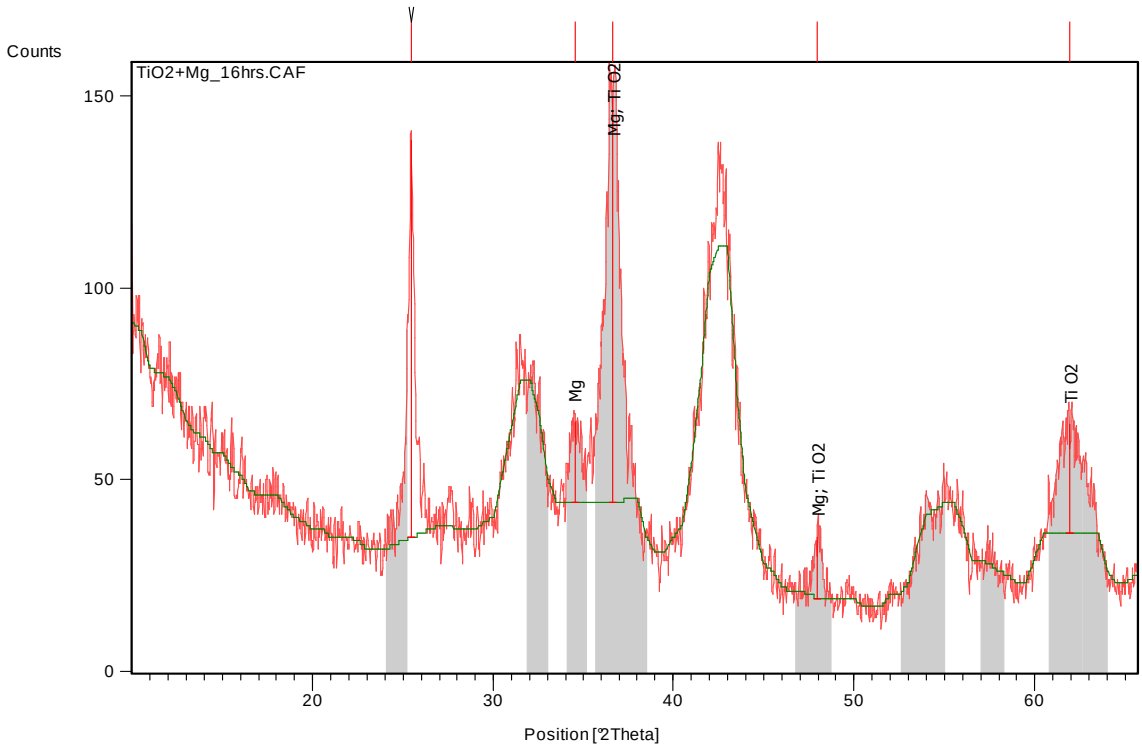


Figure C3: TiO_2-15Mg milled for 16 hours

Table C5: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
25,4432	103,45	0,1574	3,50086	97,80	0,1600	
34,5264	20,81	0,4723	2,59783	19,67	0,4800	00-035-0821
36,6594	105,78	0,5510	2,45143	100,00	0,5600	00-035-0821; 00-021-1272
47,9851	15,83	0,4723	1,89598	14,97	0,4800	00-035-0821; 00-021-1272
61,9214	28,27	1,1520	1,49733	26,72	0,9600	00-021-1272

Table C6: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-035-0821	38	Magnesium	0,240	0,622	Mg
*	00-021-1272	7	Anatase, syn	-0,609	0,250	Ti O2

Appendix C4: XRD data for TiO_2- Mg powders milled for 24 hours

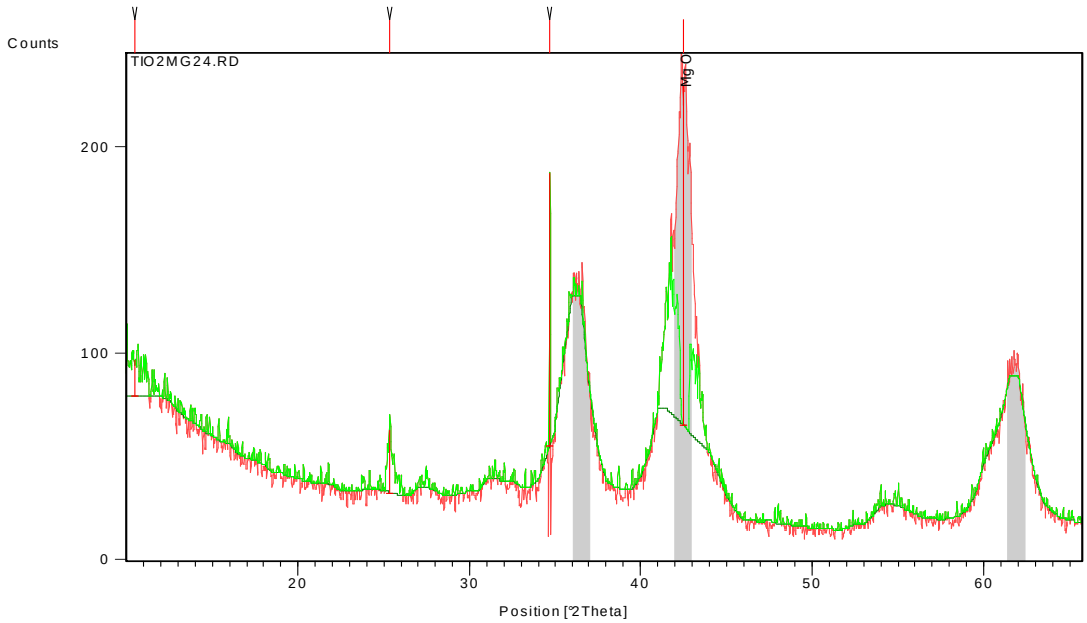


Figure C4: TiO_2-15Mg milled for 24 hours

Table C7: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
10,4986	17,44	0,9446	8,42655	10,57	0,9600	
25,3465	30,40	0,2362	3,51400	18,42	0,2400	
34,6700	132,53	0,0480	2,58526	80,31	0,0400	
42,4937	165,02	0,5760	2,12563	100,00	0,4800	00-045-0946

Table C8: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-045-0946	35	Periclase, syn	-0,387	0,734	Mg O

Appendix C5: XRD data for TiO_2- Mg powders milled for 32 hours

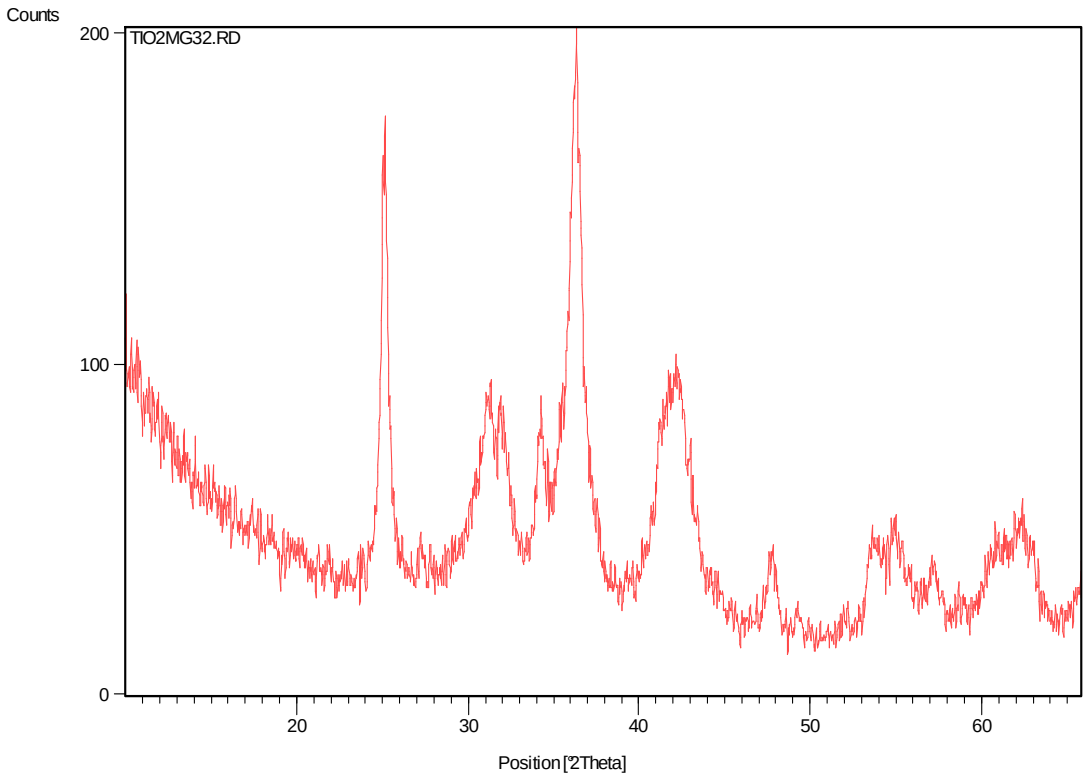


Figure C5: TiO_2-15Mg milled for 32 hours

Table C8:Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
25,2110	150,00	0,4330	3,53257	86,71	0,4400	01-075-1537
32,1400	47,00	0,6298	2,78506	27,17	0,6400	01-089-5003
34,2031	34,00	0,4723	2,62164	19,65	0,4800	01-089-5003
36,4939	173,00	0,4723	2,46217	100,00	0,4800	01-089-5003; 00-045-0946; 01-075-1537
42,7836	21,00	0,9446	2,11364	12,14	0,9600	00-045-0946
47,9038	32,00	0,5510	1,89900	18,50	0,5600	01-089-5003; 01-075-1537
53,6911	17,00	0,6298	1,70717	9,83	0,6400	01-075-1537
57,3199	17,49	0,5760	1,60609	10,11	0,4800	01-089-5003

Table C9: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-089-5003	75	Magnesium	-0,123	0,975	Mg
	00-045-0946	33	Periclase, syn	-0,168	0,138	Mg O
*	01-075-1537	38	Anatase	-0,676	0,475	Ti O2

Appendix C6: XRD data for TiO_2- Mg powder leached in 1.3M HCl

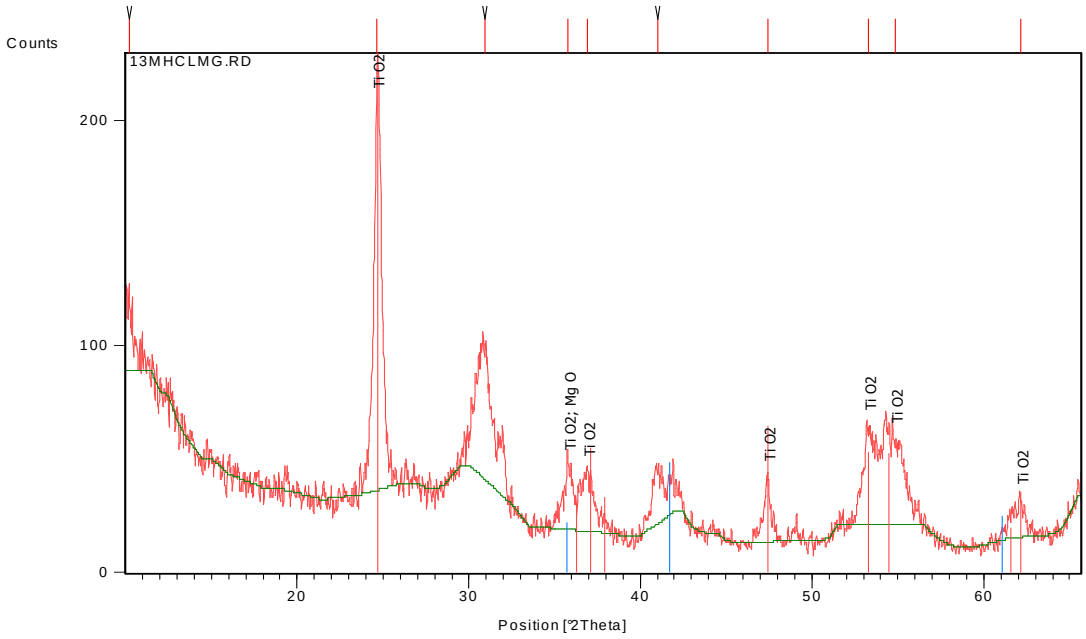


Figure C6: TiO_2-15Mg leached in 1.3M HCl

Table C12: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
10,2412	30,49	0,4723	8,63772	16,05	0,4800	
24,6584	189,98	0,2755	3,61046	100,00	0,2800	01-089-4921
30,8925	58,09	0,5510	2,89462	30,58	0,5600	
35,8097	27,08	0,4723	2,50762	14,25	0,4800	01-089-4921; 01-087-0651
36,9671	25,49	0,4723	2,43173	13,42	0,4800	01-089-4921
41,0099	23,87	0,4723	2,20087	12,56	0,4800	
47,4267	28,24	0,2755	1,91698	14,86	0,2800	01-089-4921
53,2914	42,57	0,4723	1,71903	22,41	0,4800	01-089-4921
54,8293	37,00	0,9446	1,67440	19,48	0,9600	01-089-4921
62,1421	15,97	0,9600	1,49254	8,41	0,8000	01-089-4921

Table C13: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-089-4921	77	Anatase, syn	-0,688	0,962	Ti O2
*	01-087-0651	13	Periclase	-1,142	0,097	Mg O

Appendix C7: XRD data for TiO_2- Mg powder leached in 0.15M oxalic/ascorbic acids

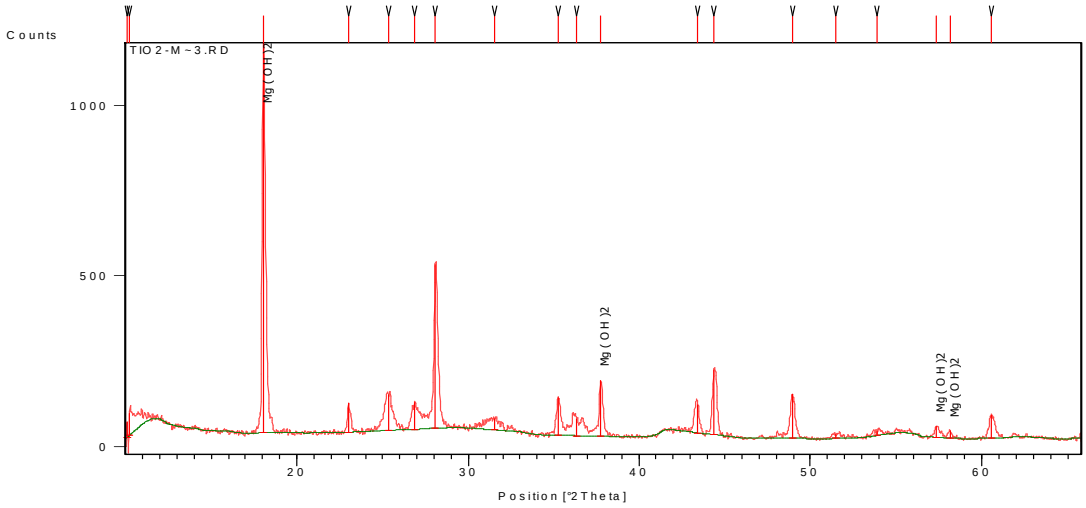


Figure C7: TiO_2-15Mg leached in 0.15M oxalic/ascorbic acids

Table C14: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
10,1027	45,80	0,0590	8,75581	3,98	0,0600	
10,2448	63,59	0,0787	8,63469	5,53	0,0800	
18,0516	1149,69	0,1968	4,91421	100,00	0,2000	01-074-2220
23,0042	84,20	0,2362	3,86621	7,32	0,2400	
25,3755	105,07	0,3936	3,51004	9,14	0,4000	
26,8927	79,18	0,2755	3,31536	6,89	0,2800	
28,0766	479,59	0,1574	3,17820	41,72	0,1600	
31,5507	33,04	0,6298	2,83572	2,87	0,6400	
35,3113	110,82	0,2362	2,54187	9,64	0,2400	
36,3856	48,28	0,6298	2,46925	4,20	0,6400	
37,7771	163,37	0,2362	2,38143	14,21	0,2400	01-074-2220
43,4535	82,96	0,2755	2,08260	7,22	0,2800	
44,3788	190,43	0,1771	2,04130	16,56	0,1800	
48,9657	130,17	0,1574	1,86027	11,32	0,1600	
51,5065	13,83	0,4723	1,77432	1,20	0,4800	
53,8791	13,06	0,6298	1,70166	1,14	0,6400	

57,3666	32,59	0,3149	1,60623	2,83	0,3200	01-074-2220
58,1339	20,99	0,2362	1,58684	1,83	0,2400	01-074-2220
60,5707	65,65	0,3840	1,52744	5,71	0,3200	

Table C15: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
	01-074-2220	22	Brucite	-0,250	0,128	Mg (O H)2

Appendix C8: XRD data for TiO_2- Mg powder leached in 0.15M HCl/cysteine/ascorbic acids

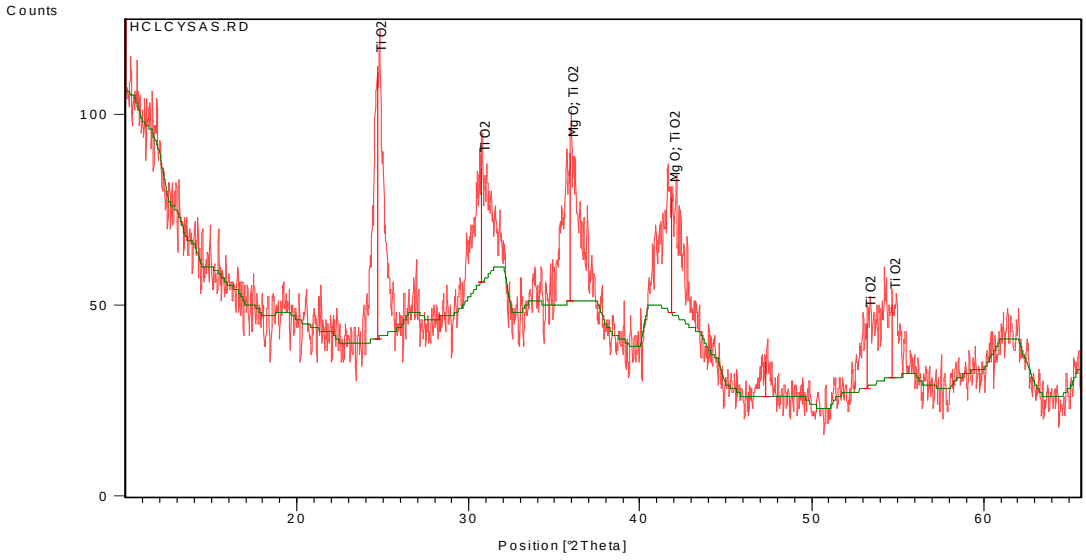


Figure C8: TiO_2-15Mg leached in 0.15M HCl/cysteine/ascorbic acids

Table C16: Peak List

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip width [°2Th.]	Matched by
24,7194	71,51	0,4723	3,60170	100,00	0,4800	00-021-1236
30,7417	29,82	0,7872	2,90848	41,70	0,8000	00-021-1236
35,9662	38,86	0,7872	2,49707	54,34	0,8000	00-045-0946; 00-021-1236
41,8269	29,88	0,9446	2,15974	41,78	0,9600	00-045-0946; 00-021-1236
47,3051	8,99	0,9446	1,92163	12,57	0,9600	
53,2273	17,06	0,9446	1,72095	23,86	0,9600	00-021-1236

54,6801	18,84	1,1520	1,67722	26,34	0,9600	00-021-1236

Table C17: Identified Patterns List

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
	00-045-0946	36	Periclase, syn	-1,041	0,248	Mg O
*	00-021-1236	25	Titanium Oxide	-0,401	0,274	Ti O2

Appendix C9: XRD data for TiO_2- Mg powder leached in 0.5M H_2SO_4

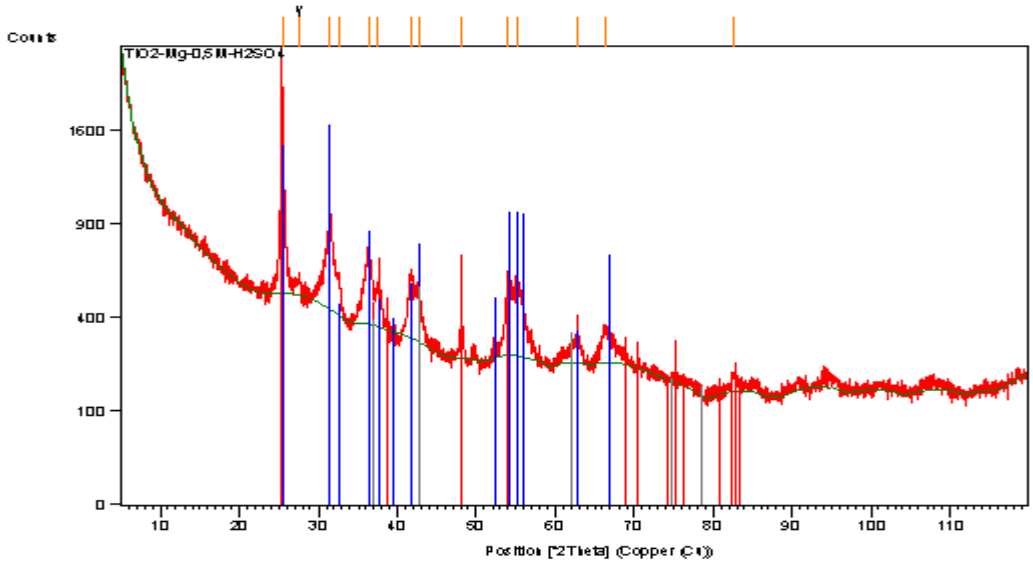


Figure C9: TiO_2-15Mg leached in 0.5M H_2SO_4

Table C18: Peak List

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]	Tipwidth[°2Th.]	Matched by
25.4071	1450.65	0.2303	3.50575	100.00	0.2763	01-089-4921;00..
27.5063	83.73	0.6140	3.24278	5.77	0.7368	
31.4792	467.38	0.5117	2.84200	32.22	0.6140	00-019-1370
32.6647	184.87	0.3070	2.74152	12.74	0.3684	00-019-1370
36.5211	326.90	0.8187	2.46040	22.53	0.9824	00-019-1370;01..
37.5766	198.53	0.6140	2.39367	13.69	0.7368	01-089-4921;00..
41.7334	285.80	0.5117	2.16437	19.70	0.6140	00-019-1370

```
    42.7270       206.67       0.5117       2.11631        14.25
0.6140  00-019-1370;01..
    48.0994       165.97       0.2047       1.89174        11.44
0.2456  01-089-4921
    53.9724       352.90       0.2047       1.69894        24.33
0.2456  01-089-4921;00..
    55.1613       329.68       0.3070       1.66510        22.73
0.3684  01-089-4921;00..
    62.7222       126.78       0.4093       1.48135         8.74
0.4912  01-089-4921;00..
    66.3457       129.19       0.8187       1.40896         8.91
0.9824  00-019-1370
    82.7042        49.93       0.7488       1.16591         3.44
0.8986  01-089-4921
```

Table C19: Pattern List

Visible	Ref.Code	Score	Compound Name	Displ.[°2Th]	Scale Fac.	Chem. Formula
*	01-089-4921	54	Anatase, syn	0.000	0.887	Ti O2
*	00-019-1370	42	Titanium Oxide	0.000	0.505	Ti O2
*	01-079-0612	21	Magnesium Oxide	0.000	0.101	Mg O

Appendix C10: XRD data for Ti-20Mg leached in 0.5M H_2SO_4

* Ti-Mg

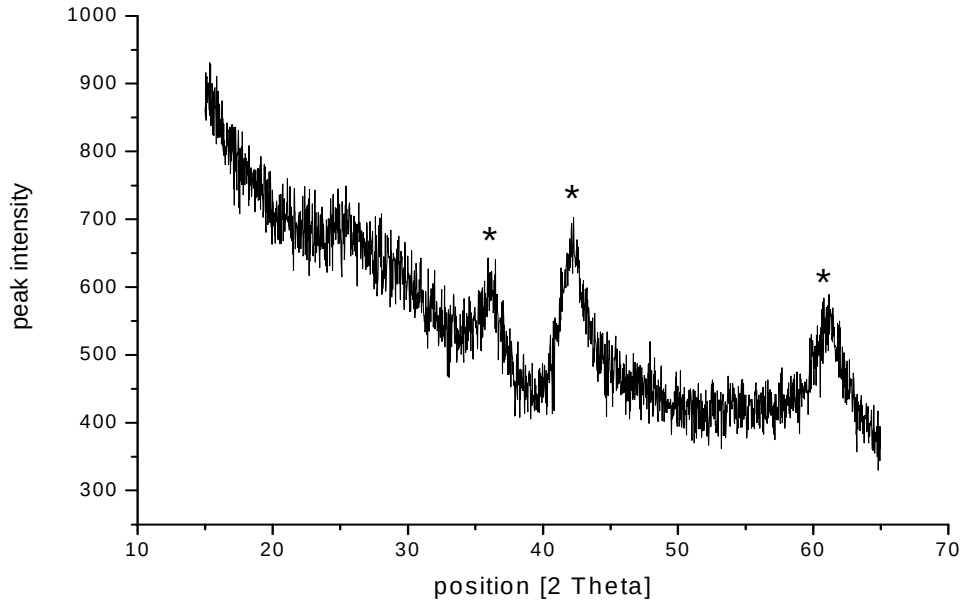


Figure C10: Ti-20Mg leached in 0.5M H_2SO_4

Table C20 Intensities

1518 1444 1387 1444 1446 1479 1411 1376 1385 1417 1429 1415
1427 1346 1413 1377 1353 1369 1378 1347 1391 1329 1322 1342
1306 1311 1330 1391 1353 1278 1336 1347 1247 1289 1341 1319
1304 1259 1208 1243 1261 1142 1291 1225 1272 1247 1243 1203
1244 1251 1290 1247 1230 1193 1208 1257 1204 1200 1188 1243
1204 1186 1177 1164 1184 1212 1145 1148 1174 1198 1107 1179
1060 1173 1138 1094 1098 1155 1122 1050 1173 1110 1221 1116
1198 1126 1086 1153 1092 1124 1089 1107 1064 1123 1135 1064
1097 1148 1066 1117 1092 1118 1083 1113 1092 1085 1121 1113
1035 1054 1070 1024 1050 1043 1050 1057 1055 1040 1066 1015
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 1016 1051 985 993 991 975 967 982 986
955 990 1032 979 990 926 929 1000 973 933 882 974 1000 946 914
932 935 887 972 928 929 932 910 983 887 968 906 977 894 894 901
853 937 960 907 871 905 964 865 970 883 901 886 855 868 892 916
933 865 852 916 846 907 910 872 882 895 901 898 861 931 853 884
929 838 873 862 857 900 882 825 869 888 823 893 894 864 866 849
811 911 839 859 885 820 889 834 841 870 866 821 846 847 845 811
875 809 849 805 800 841 794 817 794 792 780 807 795 804 842 808
826 832 810 780 793 836 800 809 767 788 836 786 805 840 801 799
794 745 836 721 801 811 771 836 812 784 743 797 798 795 831 794
717 787 708 805 781 775 756 779 807 751 829 798 767 736 748 790
751 797 795 780 790 757 753 770 785 778 765 782 720 809 729 764
753 750 776 769 733 755 760 758 769 746 767 773 758 717 711 772
744 732 756 749 734 756 775 728 731 763 774 729 780 715 793 736
738 752 730 737 703 712 712 774 781 759 778 728 701 681 758 710
759 692 738 735 703 770 735 701 695 771 730 694 688 714 663 743
728 723 691 710 677 687 665 716 696 699 727 720 703 689 679 670
720 677 736 664 705 697 737 664 699 699 736 752 752 668 709 696
730 682 706 697 700 708 700 725 711 760 714 696 704 692 684 711
748 673 680 718 687 668 694 705 649 673 625 684 736 746 712 711
657 678 695 690 686 658 686 690 705 651 710 675 657 691 712 657
694 675 699 689 734 646 647 679 685 748 686 648 680 714 686 717
640 721 669 715 730 730 617 744 638 683 651 691 679 697 694 723
687 646 662 662 668 706 743 637 687 710 679 651 681 664 689 661
710 710 680 629 672 707 655 674 660 680 718 676 701 657 693 691
663 665 640 665 657 631 667 699 622 667 689 665 701 687 700 684
631 676 693 730 691 670 659 706 625 698 737 663 690 681 696 685
717 670 685 688 716 686 681 745 664 718 679 665 722 681 685 671
667 637 615 726 691 682 682 664 708 641 652 701 721 710 749 674
711 715 685 698 678 684 716 724 709 700 673 646 706 688 677 656
662 648 665 681 663 705 669 653 696 677 646 693 655 601 693 688
689 681 724 667 670 696 680 642 675 679 683 670 646 627 647 681
659 672 646 667 664 626 626 633 695 681 630 636 631 646 668 634
631 638 697 619 663 648 665 672 682 620 639 618 638 597 649 652
626 704 642 605 676 646 587 607 612 647 691 664 645 702 685 637
630 630 708 589 594 624 598 614 645 612 638 637 612 679 594 604
620 637 676 651 673 652 647 643 645 619 571 600 684 619 653 585

614 641 596 635 650 645 639 643 611 575 641 607 617 656 604 649
669 644 634 675 606 608 638 601 581 653 636 645 617 604 609 623
628 583 567 610 666 650 607 609 582 598 603 612 646 624 612 620
585 564 615 617 564 610 612 654 590 587 582 603 609 568 614 624
555 562 593 599 635 616 568 590 576 592 570 574 611 577 585 636
603 643 587 563 596 588 579 577 595 566 549 558 534 538 593 572
545 530 560 570 510 558 627 576 544 535 565 580 587 549 598 571
569 597 568 605 541 585 568 601 625 538 562 563 550 579 575 536
537 539 558 513 517 551 553 570 526 534 546 596 520 565 523 543
544 539 528 534 602 512 570 539 538 561 562 469 517 523 567 562
467 559 529 489 573 558 555 540 512 545 559 549 560 590 587 531
528 517 571 549 557 550 489 498 539 531 507 536 510 529 522 528
560 514 543 501 527 517 518 565 521 500 489 583 534 532 540 504
514 516 561 532 508 524 556 521 534 586 543 535 579 506 562 533
554 539 534 520 494 552 557 551 561 570 570 554 540 551 531 541
509 542 567 595 575 545 593 578 573 574 591 506 593 564 599 526
571 542 557 584 609 537 591 557 579 569 569 584 556 614 643 586
618 574 565 589 622 595 615 580 623 611 587 591 595 562 572 610
590 618 539 641 559 533 570 568 590 566 561 559 493 547 551 552
555 551 520 533 527 577 554 472 527 580 565 552 489 544 493 505
499 527 535 503 528 471 497 487 513 471 507 486 539 474 506 453
520 506 500 497 492 471 489 455 462 449 410 423 442 460 453 501
447 434 519 466 466 456 475 468 408 479 435 453 478 478 451 463
447 498 501 462 446 413 438 434 485 438 469 443 459 434 435 416
453 472 476 455 472 449 406 437 425 447 425 488 434 440 431 440
431 417 465 435 440 455 419 443 437 437 416 441 420 439 478 415
480 439 473 439 461 468 430 451 487 445 467 438 449 485 483 460
452 429 477 412 471 424 471 472 464 502 483 459 459 512 516 529
477 486 456 413 524 439 550 466 418 475 512 555 525 538 526 523
547 536 520 544 526 513 542 577 584 535 561 551 628 568 589 564
622 600 592 591 595 599 602 618 626 605 599 630 638 650 633 602
646 641 649 625 671 655 629 660 646 684 694 644 654 620 653 679
703 649 646 642 630 640 643 654 632 670 643 621 639 659 629 639
637 577 613 581 586 592 570 569 592 604 556 610 550 569 566 576
574 597 591 531 591 599 562 581 556 512 570 555 545 541 522 549
517 548 516 549 544 555 483 510 509 489 515 561 530 521 520 516
500 485 477 533 461 524 477 499 472 484 514 534 473 531 479 507
494 500 532 498 487 500 441 516 458 437 479 490 409 494 534 482
478 440 493 496 521 518 477 476 459 469 459 514 461 424 476 444
463 473 496 492 494 507 528 480 447 497 509 451 454 466 480 458
472 505 496 465 486 441 459 460 443 477 480 444 487 471 456 486
445 452 467 412 500 432 457 471 455 432 453 443 477 406 461 417
424 475 450 459 453 447 468 434 502 438 476 434 489 452 478 457
441 444 443 487 440 458 459 482 468 428 420 485 449 442 404 481
448 466 441 458 448 427 460 470 461 464 437 465 463 454 420 452
442 473 474 487 399 460 450 520 430 433 467 477 434 446 430 409
445 418 471 453 496 451 476 426 430 455 446 419 414 402 463 447
447 453 417 445 432 443 472 484 436 403 420 447 442 450 402 420
444 422 453 456 415 432 417 415 429 435 422 421 429 430 421 426
423 435 427 383 423 425 406 430 429 410 414 446 428 420 440 467

439 475 400 441 395 441 454 426 437 395 444 405 477 404 436 395
393 401 440 422 442 421 415 392 452 432 412 418 417 382 432 424
435 428 435 412 426 448 405 419 431 450 446 431 390 374 413 433
413 449 387 370 389 447 411 413 385 438 377 425 422 436 434 458
391 424 433 409 391 416 393 443 378 393 432 388 418 421 388 393
417 418 427 405 448 401 422 407 380 432 415 404 367 399 410 433
418 426 394 443 457 429 441 463 410 415 459 423 406 412 444 396
402 385 397 386 447 429 423 380 428 434 433 424 417 432 445 425
362 431 427 434 432 442 381 408 417 381 413 431 378 400 425 415
426 436 444 469 435 428 449 429 447 395 458 420 432 420 439 458
452 432 437 451 404 399 442 431 427 412 406 436 424 384 404 392
454 407 415 443 435 443 393 439 455 463 393 420 464 420 458 405
427 441 416 411 425 441 399 377 384 399 423 424 390 435 441 425
434 432 433 434 433 392 435 418 426 394 403 421 401 391 446 441
455 459 412 448 400 416 407 434 432 407 441 396 422 392 430 434
444 413 420 419 386 452 390 383 431 413 416 439 406 461 405 409
402 399 423 463 421 407 445 430 416 449 414 438 411 445 431 423
423 393 413 426 383 430 419 375 442 407 442 404 413 420 423 404
404 459 448 458 449 431 399 473 410 408 420 481 400 406 442 417
418 441 392 401 435 433 408 431 435 441 435 425 450 438 459 430
414 437 407 442 469 421 450 453 444 459 418 464 443 431 471 452
423 422 415 438 416 475 433 421 400 448 449 438 384 428 472 443
465 448 424 458 445 455 453 438 443 449 435 449 460 451 454 444
464 448 443 447 412 445 448 466 473 525 445 454 492 450 530 504
498 503 521 492 456 504 494 513 480 507 503 455 529 484 483 543
497 520 506 505 500 529 504 438 540 492 539 567 531 578 487 523
507 584 532 536 554 538 504 558 570 563 515 562 535 573 506 589
531 535 551 567 561 556 560 522 532 519 569 531 558 528 541 512
512 514 504 490 511 512 491 547 492 534 543 467 503 550 506 540
466 479 467 474 464 512 495 436 483 503 453 493 460 430 463 480
466 427 486 491 434 447 447 448 435 493 443 458 465 465 455 464
437 416 417 425 473 461 435 442 401 430 432 438 383 390 357 442
417 390 431 417 423 425 388 413 433 401 440 415 410 426 384 384
408 384 410 370 397 411 409 406 428 387 390 389 414 424 387 370
398 399 380 395 398 402 396 419 383 361 361 389 359 426 393 386
355 380 386 372 375 376 394 350 380 417 330 387 388 395 382 344
394 363 354 381 397 365 345 341 405 359 379 377 352 339 371 386
374 346 341 371 401 416 362 338 370 334 381 417 373 364 350 384
377 339 359 385 353 343 350 354 364 335 358 354 322 322 367 323
346 354 347 369 303 340 379 345 311 379 365 344 332 321 376 342
352 324 368 360 344 336 360 329 329 302 318 334 301 323 349 315
321 332 365 345 337 321 372 336 370 334 343 336 327 337 314 339
325 329 303 311 320 366 361 325 300 329 330 344 303 336 336 311
302 340 333 332 332 370 338 352 328 335 345 350 303 359 344 333
361 312 312 327 343 320 322 331 339 317 355 308 352 341 320 324
330 348 315 312 343 309 295 350 316 325 290 316 295 344 333 317
323 301 327 291 318 285 303 312 302 298 335 327 327 335 309 343
330 292 331 293 333 303 325 353 372 313 306 317 358 305 328 328
306 290 273 348 309 345 316 298 328 322 334 308 339 333 339 280
319 328 306 328 339 309 307 334 304 311 297 301 312 366 329 296

304 357 287 324 302 308 332 290 293 315 314 308 306 330 342 329
326 325 330 302 316 314 293 329 305 306 349 282 325 303 293 326
263 292 325 301 315 345 299 322 305 335 306 313 320 287 298 310
320 335 322 336 300 320 313 331 315 337 302 350 290 321 342 321
293 330 322 332 319 309 364 360 330 325 315 299 346 285 293 327
323 344 314 319 321 328 326 324 306 338 294 322 316 295 336 294
346 346 338 333 357 307 311 341 331 352 319 338 351 326 346 290
328 307 321 324 330 325 331 287 324 327 324 339 338 296 306 348
316 296 299 298 298 323 309 272 302 322 285 304 280 282 299 343
315 302 288 303 305 306 272 303 312 291 278 283 307 297 292 314
305 310 299 328 294 289 330 298 332 297 281 293 313 262 277 279
261 300 277 272 296 270 287 292 284 315 279 314 311 272 265 295
278 258 313 299 274 297 313 288 291 303 290 312 328 315 293 317
282 340 304 296 305 306 305 283 277 239 258 305 336 280 293 302
320 307 308 288 261 285 298 276 298 279 301 299 278 294 291 294
304 312 291 280 286 296 302 290 285 281 297 319 291 289 270 314
299 286 302 295 266 272 263 313 308 313 262 272 262 256 309 274
295 259 289 261 267 255 288 249 300 285 287 292 270 260 295 282
298 278 279 298 268 273 239 274 301 262 261 281 266 291 242 254
277 273 247 251 266 280 249 275 299 256 273 257 266 217 270 266
277 261 244 280 241 236 259 254 265 267 234 256 217 270 254 237
257 232 262 278 249 245 277 249 244 248 233 247 268 237 244 243
241 233 227 259 262 241 252 254 260 229 230 228 234 242 257 280
259 272 254 209 246 266 241 242 264 258 282 229 246 243 255 271
256 248 247 220 236 239 256 247 239 257 254 272 237 247 226 267
280 218 243 240 234 261 250 226 241 258 251 248 220 222 240 251
237 238 240 242 246 236 269 232 243 231 247 255 274 245 228 230
241 229 214 212 268 256 237 260 244 217 231 244 223 256 241 240
258 260 233 235 256 211 257 239 243 202 253 218 221 229 260 244
239 240 219 238 253 228 233 240 246 247 270 238 242 231 236 261
250 228 246 221 251 253 252 212 228 227 224 227 231 229 246 214
230 229 214 229 238 211 245 220 220 231 253 227 239 219 233 237
239 235 201 214 224 234 222 231 203 245 228 195 252 217 247 219
226 190 246 225 229 246 208 232 248 233 226 236 230 225 220 244
227 247 246 210 265 185 197 233 220 272 210 214 228 221 220 217
212 226 212 210 223 211 202 225 209 205 206 242 207 215 222 218
203 218 222 201 230 220 242 219 235 230 221 213 209 220 260 232
223 230 213 218 243 225 232 223 213 217 221 225 200 206 221 196
218 235 197 233 226 190 246 216 199 190 247 230 236 224 197 239
210 221 225 208 221 215 222 205 208 219 214 233 214 228 208 225
229 206 214 219 202 218 198 225 216 245 219 195 215 229 227 215
213 208 228 219 210 218 233 230 234 224 222 211 226 213 208 228
197 203 227 212 192 229 219 217 229 222 210 197 194 231 247 240
209 225 233 203 216 194 219 218 237 213 207 218 226 240 255 221
223 241 217 227 206 228 191 229 219 220 216 211 231 205 214 224
230 212 210 225 205 168 220 232 223 216 213 198 232 228 196 222
196 208 213 231 217 200 209 210 223 203 220 205 213 208 225 220
217 261 248 231 212 211 243 215 262 220 226 230 214 206 219 204
211 232 229 216 240 271 226 239 228 225 238 233 237 231 247 258
229 239 213 221 249 216 247 234 225 268 218 214 233 231 246 249

227 213 246 243 223 219 240 217 216 227 231 236 223 208 243 231
227 233 196 225 220 229 217 227 232 254 223 211 257 218 231 212
223 224 235 199 229 209 239 220 231 221 209 237 240 225 213 248
215 214 234 214 238 234 210 204 216 271 224 225 232 220 227 244
228 219 244 209 204 218 240 240 250 206 222 235 246 220 218 204
228 235 228 187 220 218 201 235 256 235 239 239 247 235 214 239
194 198 232 241 211 233 247 235 219 202 205 223 221 215 224 217
231 243 226 226 247 237 244 224 214 223 230 246 232 245 252 215
211 227 240 216 223 205 258 202 196 232 226 229 223 202 215 235
241 230 235 212 232 214 209 222 225 239 206 223 253 225 213 226
228 217 233 243 208 260 223 230 213 229 241 236 228 212 219 206
189 231 225 222 209 223 214 251 239 226 253 213 240 226 240 225
243 187 228 222 221 242 255 215 239 251 240 257 233 206 209 219
259 237 239 262 223 241 243 226 250 219 222 219 224 236 258 213
219 208 226 208 241 218 244 229 249 224 233 220 218 233 261 234
228 248 250 206 245 244 238 226 222 223 224 184 236 227 243 251
225 238 205 236 237 225 227 228 252 289 217 236 217 236 199 200
229 249 226 256 246 234 257 251 222 232 227 250 200 230 238 242
236 247 237 215 247 260 238 242 238 248 228 218 208 219 199 220
242 227 241 241 227 242 241 238 248 209 227 254 236 245 237 235
222 238 227 234 277 230 216 225 260 224 254 250 223 259 245 234
248 232 243 206 208 228 215 263 246 264 240 218 240 237 267 251
228 230 244 216 265 256 266 245 268 212 207 215 261 285 232 226
241 254 226 273 281 222 229 251 241 233 250 228 237 246 235 240
265 242 247 230 248 256 260 217 253 256 256 228 230 234 249 272
258 231 234 241 244 239 245 223 243 235 207 249 236 280 261 244
252 236 226 228 252 244 262 227 249 231 261 242 226 233 247 221
244 262 212 264 230 245 249 243 270 240 262 276 235 231 241 235
259 235 239 230 270 242 261 249 236 271 261 227 272 250 260 262
275 233 263 247 230 249 246 238 255 231 261 228 227 216 239 232
259 228 249 229 260 228 260 266 237 246 241 227 277 239 213 228
230 239 287 232 250 250 235 266 223 272 262 223 229 240 283 251
250 247 252 253 274 226 242 253 262 258 243 237 234 243 261 256
249 239 240 244 225 250 257 268 266 233 245 264 278 254 230 282
282 265 260 283 273 282 236 261 268 255 271 239 241 243 306 250
280 271 284 281 258 235 257 257 251 285 238 266 242 253 266 256
245 273 249 285 239 280 281 258 276 275 253 244 275 241 246 256
227 263 255 285 281 234 261 258 245 254 237 260 242 266 228 246
223 247 233 239 232 237 258 253 263 246 261 221 255 245 225 248
259 235 244 244 237 225 253 229 257 237 244 251 264 254 226 234
240 232 253 254 248 222 238 249 242 249 233 233 249 243 222 240
231 241 248 219 238 246 234 245 250 262 237 231 266 238 218 257
238 257 251 246 233 224 263 213 252 245 238 233 240 251 240 246
212 234 245 263 214 244 252 222 240 234 255 247 218 212 263 236
240 264 202 221 205 252 248 233 228 216 260 233 229 211 209 245
267 237 226 252 238 257 214 228 259 237 217 201 242 198 259 238
219 233 245 236 240 205 223 228 248 274 275 252 230 222 228 219
232 234 210 232 224 254 256 226 212 246 239 241 243 212 252 247
236 231 251 243 247 235 242 243 227 252 273 239 240 223 227 223
242 240 228 232 219 233 225 252 244 260 236 242 249 238 216 237

235 251 250 217 239 267 240 199 255 269 216 239 244 232 256 250
209 249 211 265 256 226 239 265 242 250 253 265 251 241 224 241
263 269 235 250 249 294 258 237 252 278 234 253 242 241 240 252
249 242 265 248 247 243 230 271 252 240 249 238 212 263 248 228
229 259 240 268 254 217 236 241 268 277 261 259 254 257 218 245
274 252 277 254 247 280 231 246 293 222 272 231 273 266 264 233
261 275 236 253 265 259 239 244 230 231 242 214 246 259 248 259
236 254 227 255 278 244 279 243 265 261 255 267 244 244 261 229
221 236 229 261 274 256 269 271 244 320 260 240 269 267 233 242
242 221 262 238 254 264 252 295 264 224 285 238 245 254 260 284
222 253 271 253 261 265 291 274 267 213 253 271 251 286 251 270
260 252 238 253 239 256 253 299 286 238 243 272 282 268 229 258
254 258 257 249 241 264 230 246 232 281 226 235 260 258 283 249
261 233 244 248 252 262 258 217 250 233 237 265 249 260 285 246
275 271 258 231 237 225 238 267 258 244 243 243 234 251 273 262
240 257 294 246 249 255 256 259 224 290 250 274 294 276 241 295
267 267 280 289 299 258 246 290 280 294 279 276 236 330 258 293

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

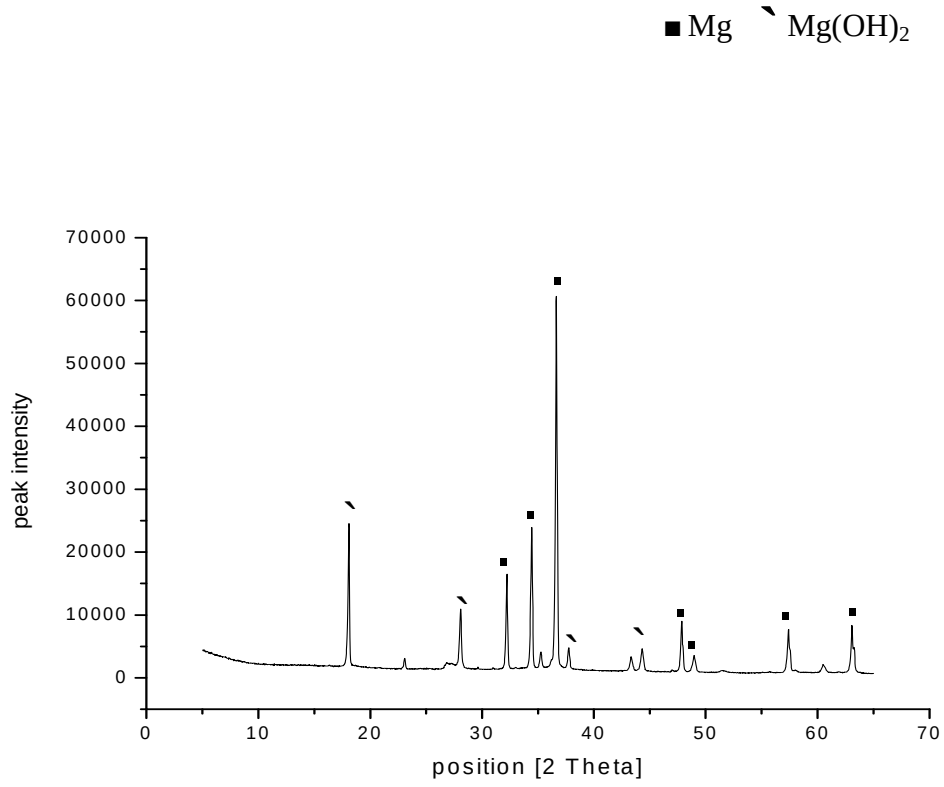


Figure C11: Mg leached in 0.5M cysteine/ascorbic acid.

Table 21 Intensities

69518 64442 60295 56314 52246 48433 44801 40986 38039 34652 31399 28086
24853 22526 19885 16922 14347 12135 10432 9231 8018 7312 6825 6640 6483
6390 6348 6190 5889 5927 5800 5885 5781 5722 5496 5389 5342 5120 5120 5090
5020 4998 4873 4909 4838 4708 4717 4819 4650 4723 4675 4661 4738 4563 4464
4535 4416 4496 4481 4466 4358 4441 4346 4269 4307 4459 4271 4360 4208 4217
4137 4256 4158 4195 4140 4205 4193 4177 4142 4081 3935 4059 4029 3932 4081
3946 3837 3931 3978 4047 3929 4083 3866 3857 3807 3832 3720 3718 3752 3726
3752 3735 3587 3676 3615 3598 3712 3583 3624 3713 3611 3565 3534 3474 3472
3529 3508 3515 3500 3456 3386 3510 3498 3450 3439 3402 3385 3361 3238 3299
3334 3352 3339 3296 3298 3276 3284 3235 3344 3288 3215 3266 3184 3125 3075
3129 3102 3044 3057 2952 3204 3049 3052 3102 3063 2993 2913 2950 2965 2980
2930 2847 2958 2896 2938 2915 2687 2807 2898 2917 2732 2770 2753 2708 2808
2765 2738 2665 2744 2733 2813 2803 2677 2759 2684 2714 2709 2666 2709 2670
2656 2725 2584 2503 2538 2503 2533 2503 2608 2567 2568 2540 2498 2578 2517
2503 2508 2448 2438 2441 2380 2467 2452 2423 2439 2388 2403 2389 2373 2325
2323 2385 2354 2321 2393 2355 2337 2356 2347 2290 2365 2272 2326 2389 2330
2350 2390 2190 2212 2310 2220 2284 2292 2306 2147 2176 2217 2186 2202 2264
2326 2221 2173 2220 2211 2180 2215 2136 2183 2164 2169 2188 2197 2145 2181
2182 2081 2129 2154 2266 2112 2192 2033 2118 2183 2144 2219 2230 2129 2128
2070 2082 2131 2164 2165 2148 2157 2107 2179 2106 2104 2039 2117 2156 2106
2097 2034 2177 2096 2047 2200 2036 1952 2050 2243 1999 2162 2093 2138 2088
2115 2100 2090 1991 2031 2062 2105 2041 2024 2071 2134 2021 2008 2094 1983
2117 2045 2071 2040 2004 2104 2081 2072 2104 2051 1942 2048 1978 2034 2053
2069 2059 2176 1982 2165 2024 2033 2112 2070 1992 1945 2001 2039 1998 2003
2033 1974 2005 2051 2028 2058 2097 2000 2099 2028 2010 2092 2044 2049 2027
2007 2047 2145 2106 2178 2079 1970 2050 2045 2041 1954 2039 2028 2006 2027
2030 2112 2062 2038 2027 1957 1964 2011 2104 2015 1973 2073 2020 2015 1995
2023 2011 2036 1943 2025 1989 2093 2034 2000 2002 2072 1972 1953 2041 1984
2000 2045 1974 1950 2017 1994 1985 1972 2090 2104 1978 1996 2017 1961 2010
1935 1969 2033 1959 1997 2017 1944 1868 1965 2000 1953 2056 1900 2012 1957
1926 1964 2018 1889 1951 1961 1958 1817 1889 1957 1829 1964 1950 1840 1923
1944 1931 1905 1906 1940 1950 1864 1906 1938 1930 1840 1981 1895 1888 1967
1913 1976 1913 1873 1927 1857 1919 1899 1882 1897 1873 1925 1920 1985 1961
2005 2022 1968 2036 1945 1917 1867 1821 1894 1914 1895 1931 1878 1822 1857
1856 1758 1873 1819 1847 1783 1871 1931 1871 1889 1819 1865 1814 1845 1781
1857 1862 1855 1888 1754 1877 1975 1814 1807 1925 1869 1894 1847 1918 1911
1966 1936 1935 1965 1955 2034 2038 2175 2171 2378 2353 2717 2961 3298 3873
4468 5330 6471 7963 10182 13212 17124 21397 24572 23796 18374 11500 6400
3900 2871 2437 2329 2244 2237 1972 2117 2003 1993 2040 1992 2009 1930 1936
1917 1977 2020 1973 1974 1896 1935 1823 1906 1901 1868 1769 1867 1873 1818
1766 1784 1774 1762 1792 1762 1747 1736 1814 1709 1739 1758 1728 1777 1721
1778 1686 1706 1728 1721 1723 1769 1776 1687 1761 1667 1641 1646 1629 1581
1633 1617 1578 1613 1729 1676 1695 1639 1667 1560 1568 1586 1636 1609 1597
1618 1563 1585 1651 1615 1633 1570 1569 1707 1488 1487 1595 1562 1565 1538
1549 1511 1551 1571 1569 1636 1623 1615 1625 1568 1648 1666 1587 1618 1599
1547 1508 1560 1479 1536 1493 1519 1528 1501 1501 1490 1526 1532 1520 1529
1484 1466 1520 1459 1526 1433 1480 1536 1519 1493 1501 1471 1476 1498 1535
1476 1466 1390 1468 1509 1482 1458 1481 1479 1461 1466 1481 1482 1478 1543
1545 1412 1468 1487 1431 1332 1467 1524 1416 1451 1447 1413 1478 1506 1535

1449 1497 1519 1446 1445 1484 1423 1510 1410 1501 1528 1603 1610 1719 1725
1823 2132 2338 2664 2918 3070 2990 2621 2163 1793 1632 1524 1539 1440 1487
1400 1405 1419 1424 1463 1487 1481 1390 1425 1490 1364 1379 1445 1370 1455
1490 1426 1485 1399 1418 1396 1465 1421 1490 1400 1446 1498 1423 1454 1450
1418 1464 1455 1414 1392 1475 1473 1453 1467 1479 1426 1476 1511 1483 1518
1451 1470 1498 1449 1444 1488 1428 1459 1425 1535 1416 1476 1422 1519 1512
1421 1476 1440 1447 1572 1515 1410 1544 1523 1433 1406 1431 1542 1473 1471
1494 1485 1504 1489 1485 1451 1412 1434 1422 1481 1406 1419 1438 1403 1324
1437 1372 1295 1325 1489 1444 1470 1456 1483 1446 1441 1387 1433 1374 1462
1479 1396 1352 1421 1452 1450 1447 1445 1380 1404 1408 1452 1546 1475 1540
1521 1526 1609 1590 1733 1931 2013 1959 2037 2179 2213 2339 2430 2465 2327
2266 2351 2321 2291 2188 2199 2287 2157 2304 2323 2202 2267 2218 2242 2299
2342 2254 2238 2262 2220 2252 2107 2088 2103 2057 2087 2054 1959 2022 2025
2010 2096 2078 2148 2395 2504 2791 3219 3574 4242 5221 6140 7453 9011 10164
10957 10335 8876 7254 5540 4079 3135 2626 2381 2255 1987 1897 1815 1675 1613
1616 1603 1562 1549 1573 1545 1558 1589 1517 1480 1463 1533 1541 1557 1467
1525 1436 1474 1506 1522 1456 1410 1459 1407 1499 1436 1514 1472 1432 1456
1395 1486 1398 1450 1395 1418 1447 1503 1408 1454 1431 1473 1423 1577 1733
1625 1543 1485 1424 1405 1400 1410 1342 1365 1446 1364 1378 1366 1410 1345
1320 1338 1359 1352 1371 1399 1352 1325 1384 1349 1396 1336 1393 1378 1320
1357 1324 1403 1319 1363 1338 1378 1298 1386 1393 1335 1389 1341 1375 1441
1385 1391 1384 1392 1515 1541 1667 1514 1506 1512 1420 1467 1353 1373 1412
1373 1446 1445 1443 1392 1350 1363 1392 1415 1424 1447 1390 1440 1411 1459
1476 1510 1436 1435 1518 1453 1512 1556 1522 1609 1618 1854 1998 2113 2458
2951 3590 4419 5844 7845 10424 12937 15184 16480 14228 10664 8773 6447 3993
2698 2040 1962 1785 1618 1651 1540 1512 1506 1580 1471 1509 1429 1472 1514
1469 1476 1524 1458 1534 1574 1580 1586 1628 1601 1708 1570 1562 1525 1485
1485 1506 1499 1535 1531 1480 1461 1489 1555 1514 1564 1581 1505 1593 1651
1488 1565 1506 1643 1579 1574 1577 1598 1587 1542 1553 1568 1654 1583 1631
1679 1558 1599 1729 1830 1839 1974 2204 2458 2747 3228 4099 5276 6853 9140
12634 16735 20980 23943 21956 15799 13174 11149 7123 3761 2754 2314 1951
1932 1782 1667 1728 1666 1683 1644 1596 1628 1697 1693 1669 1758 1801 1844
2154 2261 2508 2868 3283 3742 4077 4119 3804 3557 3201 2760 2460 2074 1888
1909 1791 1694 1736 1698 1745 1690 1674 1758 1759 1658 1678 1714 1778 1717
1723 1775 1788 1814 1822 1981 1973 2096 2217 2336 2527 2642 2847 2912 2843
2940 3057 3304 3675 4234 5148 6704 8866 11807 16145 21994 29888 39859 50377
59888 60677 49005 37089 32098 24938 14860 8164 5164 3884 3120 2760 2389
2158 2066 2011 1975 1790 1885 1841 1776 1719 1687 1726 1723 1568 1680 1654
1632 1623 1635 1683 1665 1791 1915 2002 2225 2440 2808 3277 3695 4256 4662
4764 4399 3549 3271 2896 2489 1913 1755 1633 1574 1527 1511 1485 1486 1389
1426 1446 1547 1399 1345 1387 1372 1426 1393 1336 1354 1354 1390 1389 1345
1401 1355 1349 1300 1299 1264 1270 1322 1345 1269 1273 1342 1398 1328 1268
1269 1214 1300 1199 1265 1277 1265 1308 1254 1278 1184 1244 1232 1231 1261
1227 1286 1218 1239 1241 1207 1205 1241 1188 1242 1240 1245 1196 1221 1223
1223 1210 1242 1192 1309 1260 1147 1248 1208 1229 1186 1288 1202 1142 1209
1225 1189 1206 1192 1198 1156 1162 1203 1161 1199 1156 1179 1168 1132 1069
1105 1118 1136 1133 1141 1151 1125 1127 1077 1081 1153 1108 1069 1081 1152
1115 1109 1106 1134 1104 1099 1094 1108 1081 1132 1123 1096 1183 1095 1084
1113 1087 1070 1102 1124 1051 1123 1133 1109 1132 1112 1030 1102 1114 1137
1134 1097 1126 1060 1092 1141 1105 1070 1158 1124 1084 1065 1072 1045 1135

1125 1051 1053 1124 1009 1158 1128 1159 1085 1095 1174 1098 1216 1069 1171
1187 1103 1030 1181 1151 1160 1103 1149 1148 1145 1230 1164 1184 1156 1208
1179 1201 1204 1237 1242 1293 1321 1393 1466 1542 1641 1834 2104 2349 2600
2949 3193 3332 3327 3137 2814 2607 2397 2124 1811 1679 1524 1373 1295 1278
1193 1267 1178 1156 1147 1175 1230 1221 1269 1303 1354 1360 1419 1447 1592
1696 1837 2158 2412 2626 3068 3542 3884 4398 4621 4659 4378 4085 3578 3206
2813 2466 2029 1684 1555 1318 1359 1277 1233 1186 1125 1123 1055 1165 1087
1080 1141 1081 1067 1067 1056 1044 1072 1096 1001 1022 1062 1080 1012 990
974 985 989 1012 1006 1011 1073 967 973 959 935 1018 1007 1000 975 956 1069
1061 988 1003 1057 970 1008 1012 977 994 956 958 1028 1038 988 951 1031 1018
1012 959 979 1004 975 949 970 1047 1017 973 1006 972 921 974 981 963 974 969
922 997 1019 1019 961 932 952 993 953 943 1068 1038 1128 1215 1275 1294 1226
1154 1073 1160 1203 1155 1004 1035 987 1086 1052 1115 1059 1054 1016 1024
1149 1148 1266 1269 1424 1622 1771 2029 2439 2943 3678 4634 5800 7160 8427
9016 8066 6206 5275 5204 4776 3882 2544 1827 1482 1298 1256 1198 1129 1139
1047 1030 1034 967 1010 988 1000 1040 1035 1010 1070 1121 1059 1093 1187
1169 1285 1364 1520 1650 1818 2092 2414 2644 2936 3278 3402 3529 3500 3128
2896 2727 2464 2131 1885 1643 1365 1265 1205 1112 1075 1075 970 982 900 992
964 926 930 955 924 907 938 963 973 932 906 900 913 901 927 936 873 923 868
827 892 841 864 903 934 854 873 915 823 833 871 841 919 876 918 807 870 892
837 914 964 837 845 817 892 853 892 926 825 901 857 813 877 814 938 869 889
826 878 850 937 909 901 945 977 974 895 988 1011 990 1023 1070 1097 1086 1113
1135 1151 1130 1109 1114 1165 1070 1086 1069 1089 1113 1068 1035 1063 1084
1068 1052 974 983 929 903 902 947 976 930 932 920 853 919 852 839 847 849 867
849 808 847 856 876 816 812 811 808 845 823 829 834 850 796 826 758 808 801
803 856 862 784 785 783 794 774 819 816 872 738 778 794 817 792 750 748 807
846 836 771 844 777 769 811 786 813 769 745 780 784 776 785 792 781 775 813
828 742 795 748 791 824 765 779 764 837 765 796 778 753 760 791 812 807 775
752 796 788 739 770 804 768 795 830 792 797 834 830 793 784 749 823 774 839
798 779 828 751 803 811 804 816 810 875 848 837 914 845 845 850 796 805 836
841 861 844 831 871 851 842 881 851 868 857 889 870 911 904 1042 982 912 982
864 924 943 922 902 862 866 866 808 826 842 795 848 812 807 843 852 790 792
795 821 882 832 815 833 845 795 833 845 842 803 833 848 809 863 855 846 854
863 852 852 922 924 940 999 1059 1097 1173 1284 1347 1602 1731 1981 2280 2767
3123 3805 4731 5564 6667 7612 7669 7074 5733 4854 4654 4455 4374 3653 2600
1959 1604 1424 1218 1216 1127 1136 1128 1111 1160 1165 1169 1122 1264 1188
1246 1140 1163 1045 1044 1062 1036 1074 923 981 924 903 903 916 929 907 867
839 824 852 877 859 841 854 882 866 912 879 836 809 908 874 860 880 882 856
873 900 829 862 900 861 853 846 842 803 876 867 836 801 830 879 903 827 808
772 835 832 819 846 852 828 788 838 840 842 850 880 846 835 842 862 867 814
843 885 866 915 869 943 990 933 1066 1014 1175 1190 1237 1281 1444 1530 1622
1757 1905 2032 2103 2035 1944 1844 1793 1704 1610 1525 1419 1319 1234 1174
1111 1065 1052 982 879 871 913 859 869 922 877 855 852 887 862 889 818 862 828
802 858 798 847 848 813 819 817 795 841 799 849 839 823 865 884 820 910 951
903 986 900 978 982 941 880 870 905 883 872 858 840 834 882 769 866 839 824
833 852 879 852 885 877 909 932 888 930 879 957 963 1080 1125 1110 1206 1260
1428 1540 1781 1997 2289 2686 3266 4137 5037 6314 7441 8341 8242 6956 5298
4630 4544 4837 4702 4267 3172 2268 1737 1525 1275 1197 1111 1105 996 986 935
954 944 862 833 939 854 834 900 893 866 844 777 747 796 825 769 798 747 751
686 800 720 738 751 719 731 761 742 732 722 759 736 715 663 686 753 740 706

725 717 746 743 695 681 723 663 687 710 700 713 681 703 718 713 680 669 733
734 732 684 728 708 718 691 660 687 722 674 699 705 685 715 621 717 691 720
698 661 756 682 674 702 733 653 692 681 694 667 692 593 700 686 672 667 707
684 760 728 725 708 714 678 741 658 711 701 733 713 710 690 720 676 688 646
722 673 642 712 680 683 689 692 739 688 692 727 702 745 764 748 797 778 800
811 883 855 919 921 1084 1163 1244 1395 1500 1570 1426 1241 1151 1038 1071
1186 1075 1039 933 871 811 748 728 771 731 722 726 784 722 752 744 806 762 782
744 790 820 813 802 841 869 872 951 997 1026 1127 1168 1303 1445 1624 1743
2088 2558 2894 3616 4222 5277 6083 6835 6852 5982 4646 3886 3675 3803 4002
3929 3477 2694 1993 1561 1281 1135 1001 935 1002 893 869 883 796 846 771 818
749 774 820 815 805 835 836 837 876 906 949 960 1110 1092 1279 1291 1347 1400
1427 1488 1722 1903 2165 2522 2900 3400 3976 4463 4725 4293 3518 2853 2600
2679 2631 2728 2686 2256 1732 1377 1167 942 869 904 834 837 790 756 744 690
722 684 693 698 659 711 673 655 658 705 727 708 631 640 663 656 688 644 668
645 640 661 647 630 663 684 601 615 615 661 594 626 646 607 636 648 631 627
657 664 641 629 618 652 608 691 672 675 649 671 601 643 610 666 659 656 668
671 650 679 669 718 727 796 781 786 908 960 1113 1218 1383 1499 1682 1736
1685 1366 1228 1156 1224 1284 1300 1308 1184 1047 868 804 833 745 730 688 665
686 611 630 623 618 579 616 649 624 608 616 597 613 567 616 612 605 665 696
644 665 673 727 784 772 752 828 734 762 742 737 695 728 690 687 638 682 625
643 689 597 591 618 564 624 642 618 667 662 608 640 636 603 655 649 657 676
636 677 618 666 608 626 639 639 559 602 676 651 613 648 569 642 645 594 565
583 603 608 624 644 648 642 655 664 689 636 791 714 746 695 758 713 677 735
696 683 622 748 654 659 686 610 696 639 676 648 651 629 696 646 621 639 622
578 575 639 648 585 643 620 674 655 663 716 753 692 740 741 713 674 723 661
667 701 640 694 702 697 715 693 730 691 662 715 619 632 680 615 615 602 675
591 656 597 645 603 633 621 621 594 621 634 608 661 661 614 608 643 593 665
673 695 662 676 677 709 777 824 897 962 971 1159 1294 1293 1313 1283 1118
1016 929 927 904 936 982 966 853 840 671 671 620 606 598 570 544 538 561 512
562 502 554 543 573 593 554 528 561 512 537 581 552 522 569 495 566 558 601
579 571 596 600 597 587 606 652 630 602 639 649 702 653 646 634 588 606 625
611 567 623 587 550 558 514 535 550 558 569 545 504 549 576 453 542 486 494
490 486 527 476 470 469 518 506 526 490 488 499 492 532 530 506 519 543 533
525 569 543 561 535 554 544 562 614 579 547 499 458 532 557 547 556 545 499
502 540 546 517 488 535 519 599 605 624 573 591 623 617 636 669 733 759 831
951 936 1062 1198 1245 1235 1213 1035 936 855 828 790 817 883 986 846 791 730
594 558 583 509 549 503 514 538 480 546 518 527 527 514 475 452 521 466 496
449 464 464 493 452 499 471 461 465 467 474 483 475 512 470 455 486 478 496
487 487 522 502 456 478 474 480 493 439 478 433 470 476 463 474 463 473 484
460 467 451 446 441 439 455 502 458 472 483 428 497 448 461 421 476 447 465
459 443 475 421 470 469 446 440 437 503 482 449 467 470 479 449 413 429 446
450 434 472 454 470 538 448 473 465 502 458 444 472 475 509 501 543 539 552
530 535 533 562 512 545 506 483 522 525 490 481 475 482 470 520 482 508 457
524 470 451 439 498 468 439 451 454 464 481 445 443 438 444 476 406 476 491
451 431 506 490 453 476 477 528 523 501 519 552 503 532 604 588 640 642 598
645 656 599 637 601 574 560 593 538 563 574 557 517 528 536 529 515 508 483
486 492 500 465 470 486 466 497 475 448 479 453 479 506 514 492 490 514 513
481 488 484 482 476 471 463 464 483 473 460 483 500 453 519 439 494 481 462
502 459 476 485 509 453 473 422 502 473 501 456 532 443 455 455 525 467 445
495 500 492 465 495 495 527 545 523 494 526 501 514 476 495 506 490 512 500

515 517 504 482 495 509 510 494 500 470 462 510 504 491 492 471 450 458 455
485 472 451 496 479 491 455 469 480 526 534 502 474 456 524 497 509 524 454
457 503 523 533 592 530 558 627 581 644 669 695 677 728 858 902 1017 1058 1293
1403 1544 1787 1767 1739 1536 1289 1168 1078 999 1019 1053 1091 1147 1199
1071 1022 850 773 715 652 590 531 585 541 551 526 513 503 475 470 486 482 479
481 506 499 474 486 474 529 464 506 498 442 471 484 481 534 525 485 542 503
485 437 442 481 477 507 468 406 462 468 451 470 475 475 465 448 469 448 483
473 509 463 458 472 535 466 464 480 518 499 486 451 472 456 467 508 482 474
475 523 506 508 446 485 531 540 522 517 463 491 507 507 562 496 455 502 539
558 498 541 517 525 504 503 515 497 555 528 521 486 515 512 495 522 470 526
455 498 497 492 496 497 535 493 508 517 565 489 524 565 617 639 644 742 737
788 816 861 814 798 725 745 644 589 622 656 643 603 722 675 673 633 575 603
544 525 539 527 464 514 557 535 572 552 548 550 508 509 516 503 488 510 519
555 527 518 496 519 471 500 520 505 517 530 529 570 542 508 511 471 517 487
538 524 569 534 546 516 490 570 524 529 488 529 590 557 560 549 533 501 553
591 601 550 583 600 648 651 604 733 727 735 845 878 990 1050 1189 1296 1357
1553 1940 2105 2214 2483 2400 2172 1804 1548 1424 1299 1272 1306 1340 1406
1502 1484 1538 1414 1193 964 957 877 743 739 664 630 668 576 623 560 671 585
600 534 553 588 599 561 557 567 602 552 517 586 557 551 532 543 572 497 595
605 554 636 542 541 544 551 551 570 500 561 575 629 543 551 580 605 592 607
571 604 569 582 631 588 625 624 644 665 689 688 753 758 787 906 917 1025 1136
1225 1346 1468 1726 1850 1877 1723 1504 1306 1160 1154 982 1042 1062 1079
1152 1170 1200 1238 1146 996 924 867 747 666 668 636 643 646 603 604 614 611
593 621 575 577 570 563 559 541 549 571 513 522 527 581 583 567 574 548 518
496 528 523 523 565 588 504 553 526 547 538 570 566 565 577 557 540 589 578
572 566 514 587 521 571 557 558 565 526 571 541 608 565 593 561 535 577 509
493 527 557 572 526 558 521 544 566 539 528 532 552 535 502 524 497 557 544
512 503 562 519 520 564 513 551 535 525 546 542 546 551 518 532 484 566 513
551 497 550 546 523 549 515 544 526 532 476 516 523 504 509 549 553 501 521
508 474 540 572 513 534 510 559 536 546 525 549 517 507 533 607 540 553 557
604 558 555 641 557 586 574 565 605 613 600 631 602 584 644 692 669 665 682
706 756 771 773 859 939 1041 1146 1288 1407 1496 1600 1716 1631 1448 1361
1275 1188 1291 1320 1398 1443 1380 1301 1280 1232 1248 1197 1055 1068 953
932 871 925 915 930 846 787 716 680 657 628 661 625 598 616 596 583 566 585
588 555 586 526 574 531 555 555 530 547 582 528 537 558 525 514 555 541 592
599 532 549 543 580 559 539 500 545 558 560 606 550 552 557 572 569 527 557
547 499 502 566 585 577 522 524 521 537 541 508 536 533 513 564 561 544 499
535 546 530 508 552 542 557 477 526 533 539 503 514 537 518 526 490 535 539
527 534 507 512 545 564 528 554 568 570 569 542 551 570 539 516 514 519 566
532 531 570 584 556 557 550 576 591 593 593 593 653 657 655 692 741 723 764
804 827 832 767 667 648 659 657 559 610 577 636 615 623 685 657 736 625 681
625 580 605 576 518 537 534 589 549 571 534 520 555 542 556 565 532 508 550
524 532 538 604 528 496 494 560 534 572 525 507 567 542 523 532 510 526 573
549 544 534 552 524 537 549 577 504 501 507 560 513 492 560 527 507 520 519
536 575 544 521 522 530 543 524 532 519 556 486 504 521 509 512 500 534 473
542 496 503 523 533 541 576 529 529 528 533 596 596 490 514 517 518 544 512
531 529 525 533 547 525 551 484 534 547 559 506 468 583 505 552 530 505 530
566 553 533 539 596 539 629 557 610 607 547 564 565 616 590 610 593 578 620
666 653 718 721 771 784 847 910 867 887 962 909 772 775 685 732 727 664 710
687 675 694 695 701 759 771 706 789 731 720 659 684 642 624 610 624 636 592

590 607 601 602 608 599 603 577 606 591 649 577 600 550 606 581 601 598 609
635 607 593 589 584 576 572 601 587 599 583 581 599 561 596 579 560 607 615
532 586 601 588 529 597 617 593 548 623 608 565 573 591 583 569 607 537 565
532 577 534 566 534 534 538 519 539 600 595 509 555 563 557 544 550 558 536
523 509 622 526 579 580 562 555 584 600 591 577 570 546 574 563 546 541 529
521 549 565 573 538 557 524 568 563 581 559 554 541 520 606 522 508 557 567
543 617 562 585 491 532 554 562 525 529 559 551 587 573 534 534 576 583 545
571 567 610 528 556 568 588 585 591 579 544 567 611 563 582 589 596 654 542
647 619 581 609 598 611 625 726 648 653 639 687 683 708 751 740 871 929 869
930 1060 1139 1194 1312 1462 1554 1719 1772 1771 1710 1458 1244 1172 1131
1037 953 972 1003 956 963 1014 998 1116 1150 1171 1190 1168 1069 1037 957 816
821 777 752 789 730 648 654 643 610 673 599 621 650 642 643 612 618 614 655
587 600 581 565 606 625 551 561 583 601 639 638 592 631 603 571 590 589 662
576 587 589 624 549 577 609 595 623 600 586 577 610 583 620 575

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 **% Residue =** $(\frac{final}{initial})\times 100$

where final = dry residue mass after leaching (g)

initial = initial powder mass before leaching (g)

Table D1: Effect of H_2SO_4 concentration on the leaching of Ti-Mg alloy

	Residue after leaching in different concentrations			
Constituent	**0.1M**	**0.5M**	**0.9M**	**1.3M**
TiO_2	72.6	61.1	77.7	79.8
Ti-20Mg	79.6	41.3	20.6	11.7
TiO_2-Mg	46.7	24.7	18.4	17.2
MgO	60.8	0.0	0.0	0.0

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

	Residue after leaching in different concentrations			
Constituent	**0.1M**	**0.5M**	**0.9M**	**1.3M**
TiO_2	83.9	**81.3**	**71.9**	64.4
Ti-20Mg	89.8	**95.4**	**59.4**	30.5
TiO_2-Mg	97.1	**36.4**	**27.8**	21.9
MgO	73.4	**9.9**	**0.0**	0.0

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

	Residue after leaching in different concentrations			
Constituent	**0.1M**	**0.5M**	**0.9M**	**1.3M**
TiO_2	86.7	84.3	78.8	78.5
Ti-20Mg	62.8	74.5	88.2	88.7
TiO_2-Mg	79.4	43.6	33.8	30.2
MgO	68.2	0.0	0.0	0.0

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

	Residue after leaching in different concentrations			
Constituent	**0.05**	**0.1**	**0.15**	**0.2**
TiO_2	84.2	80.7	80.795	78.6
Ti-20Mg	81.6	106.0	117.615	105.4
TiO_2-Mg	76.7	88.8	111.475	121.2
MgO	92.0	106.9	123.665	149.7

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

	Residue after leaching in different concentrations			
Constituent	**0.05**	**0.1**	**0.15**	**0.2**
TiO_2	80.4	68.5	86.2	86.4
Ti-20Mg	83.5	58.6	68.7	66.8
TiO_2-Mg	87.3	88.6	73.5	57.4
MgO	72.5	71.1	68.9	63.1

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

	Residue after leaching in different concentrations			
Constituent	**0.075**	**0.3**	**0.525**	**0.75**
TiO_2	83.0	80.6	**83.0**	77.6
Ti-20Mg	85.3	86.6	**69.8**	68.9
TiO_2-Mg	99.3	46.8	**31.2**	22.9
MgO	78.8	41.3	**12.5**	0.2