FORMATION AND GROWTH MECHANISMS OF A HIGH TEMPERATURE INTERFACIAL LAYER BETWEEN Al AND TiO$_2$

Jairaj J. Payyapilly

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Materials Science and Engineering

Dr. Kathryn V. Logan, Committee Chair
Dr. David E. Clark
Dr. William T. Reynolds, Jr.
Dr. Michael J. Kelley

19$^{th}$ November 2008
Blacksburg, Virginia.

Keywords: interface reaction, liquid aluminum, titanium dioxide, titanium aluminide, oxidation-reduction, growth mechanism

Copyright © 2008
FORMATION AND GROWTH MECHANISM OF A HIGH TEMPERATURE INTERFACIAL LAYER BETWEEN Al AND TiO₂

JAIRAJ PAYYAPILLY

ABSTRACT

The product of interaction between Al and TiO₂ at elevated temperature has a wide range of applications in refractory, structural and electronics industries (refractory tiles, tank armor, fuel cells, and microelectronic devices). This research attempts to understand the extent of interaction between Al and TiO₂ when the reactant surfaces are in contact at elevated temperature and normal atmospheric pressure. The interfacial region between the reactant compounds is examined using analytical techniques; and the formation of TiAl as the interfacial compound is described. The thermodynamics of the Al – Ti – O system is explained as it relates to the particular conditions for the Al – TiO₂ reaction research. Thermodynamic principles have been used to demonstrate that the formation of TiAl is favored instead of other TiₓAlᵧ compounds for the set of conditions outlined in this thesis. A study of the mechanism of interactions in the interfacial region can help towards being able to determine the reaction kinetics that lead to the control of microstructure and thus an improvement in the material performance. An appropriate model that describes the formation of TiAl at the interface is described in this study. The formation of TiAl at the interface is a result of the reduction reaction between TiO₂ and Al. The O released during the reduction of TiO₂ has been investigated and demonstrated to partly remain dissolved in TiAl at the interfacial region. Some O reacts with Al as well to form crystalline Al₂O₃ in the interfacial layer.
ACKNOWLEDGEMENTS

The author wishes to thank his advisor, Dr. Kathryn Logan for the encouragement, and belief in his ability as a researcher. He would also like to extend his gratitude to Dr. William Reynolds Jr., Dr. David Clark, and Dr. Michael Kelley for their participation in this study and serving as committee members of the author’s dissertation. The author would also like to thank Dr. William Reynolds Jr. for the lengthy discussions in the evenings. The author gained enormously from his thoughts and suggestions. The author would also like to acknowledge the help from Dr. Reynolds and Dr. Claudia Rawn (Oak Ridge National Laboratory) in several characterization techniques during this study. The author wishes to extend his acknowledgement to Dr. Stephen Kampe and Dr. Kelley for their critiques that have helped to improve certain aspects of the thesis.

Special thanks to the National Institute of Aerospace, Hampton, for funding this project and also for sheltering the author’s office during his stint at Hampton. The author would like to thank Dr. Nagraj Kulkarni for his constant encouragement throughout the course of this work. The author extends many thanks to the MMRG group for the constant encouragement and constructive criticism towards this project.

The author thanks his wife for her patience and understanding during the course of this work. Finally, the author would like to acknowledge the support and encouragement from his parents, siblings, and friends.
# TABLE OF CONTENTS

ABSTRACT ............................................................................................................. ii

ACKNOWLEDGEMENTS ......................................................................................... iii

TABLE OF CONTENTS .......................................................................................... iv

LIST OF FIGURES ................................................................................................ vi

LIST OF TABLES ...................................................................................................... ix

1.0 INTRODUCTION ............................................................................................ 1

1.1 REACTION SYNTHESIS OF INTERMETALLIC - CERAMIC COMPOSITES ................................. 1

1.2 JUSTIFICATION OF RESEARCH ........................................................................... 2

1.3 OBJECTIVE OF RESEARCH ................................................................................ 3

2.0 BACKGROUND AND LITERATURE REVIEW ....................................................... 4

2.1 SHS REACTION .................................................................................................. 4

2.2 SHS REACTANT COMPONENTS .......................................................................... 6

2.3 Al-TiO₂ SYSTEM AND APPLICATIONS .................................................................. 8

2.4 INTERACTION BETWEEN AL AND TiO₂ ................................................................ 10

2.5 Ti – Al – O THERMODYNAMICS ......................................................................... 13

2.5.1 Binary Systems ............................................................................................... 13

2.5.1.1 Al – O .......................................................................................................... 13

2.5.1.2 Ti – O .......................................................................................................... 16

2.5.1.3 Ti – Al .......................................................................................................... 18

2.5.2 Ternary Phases .............................................................................................. 22

2.6 AN EXPLANATION FOR THE OXYGEN RELEASED DURING THE Al - TiO₂ REDUCTION REACTION ........................................................................................................... 29

3.0 EXPERIMENTAL APPROACH ........................................................................... 32

3.1 THEORETICAL DETERMINATION OF POSSIBLE INTERFACIAL COMPOUND(S) ................................................................. 32

3.2 EXPERIMENTAL REACTION MODEL PARAMETERS ............................................... 34

3.3 DIFFUSION COUPLE SUBSTRATE STRUCTURE ................................................... 35

3.4 IDENTIFICATION OF INTERFACIAL COMPOUND USING XRD ............................. 36

3.5 MORPHOLOGICAL UNDERSTANDING OF THE INTERFACE .............................. 39

3.5.1 Diffusion Couple Samples: Film – Substrate Structure .................................... 39

3.5.2 Powder Mixture Sample .................................................................................. 39

3.6 HIGH RESOLUTION IDENTIFICATION OF THE INTERFACIAL PHASE(S) AND COMPOUND(S) .................................................................................................................... 40

4.0 RESULTS AND DISCUSSION .......................................................................... 45
LIST OF FIGURES

CHAPTER 2
2.1 Microstructure of the reaction product having high aspect ratio crystals formed at a lower heating rate as observed by Logan .........................................................5
2.2 Al-O binary phase diagram. .................................................................14
2.3 Ti-O binary phase diagram. .................................................................16
2.4 Ti-O binary phase diagram showing the Magnelli phases. .....................17
2.5 Ti-Al binary phase diagram by Massalski. .............................................19
2.6 Ti-Al Gibb’s free energy diagram calculated at 1100°C by Li et. al. Calculated values by Murray and Dew-Hughes are used for comparison. .................20
2.7 Calculated isothermal section (at Ti-rich regions) of the Ti-Al-O ternary phase diagram at (a) 500°C and (b) 700°C. .........................................................24
2.8 Calculated isothermal section of Ti-Al-O phase diagram at 800°C by Luthra et al. .................................................................24
2.9 Two possible isothermal sections of the Ti-Al-O ternary system calculated by Tressler et al. .................................................................................25
2.10 Isothermal section of the Ti-Al-O ternary system at 900°C calculated by Rahmel et al. .........................................................................................25
2.11 945°C isothermal section of the Ti-Al-O ternary system based on experimental evaluations on the base diagram calculated by Murray et al., Kattner et al. and Wriedt et al. .................................................................26
2.12 Isothermal section of the Ti-Al-O as calculated by Li et al. with Ti-Al2O3 diffusion paths superimposed. .........................................................28
2.13 Isothermal section of the Ti-Al-O as calculated by Lee et al. .................29

CHAPTER 3
3.1 Schematic of the interfacial region as the area of interest for the study. ......34
3.2 Schematic of 4-5 µm Al film sputter deposited on TiO2 substrate sample. ....35
3.3 Schematic of two film – substrate Al – TiO2 samples sandwiched one on top of the other .................................................................37
3.4 The FIB – SEM position of sample relative to the two beams. ....................40
3.5 Platinum strip deposited on the surface of the sample for FIB ..................41
3.6 Material milled away from both the sides of the platinum-strip using FIB. ....42
3.7 OmniProbe® is attached to the area of interest after which the sides are cut. ....42
3.8 Stages of attachment of the sample strip onto grid using OmniProbe® and platinum using the FIB. .................................................................43
3.9 Side view of thinned sample showing the platinum layer, the thin film layer, the interface and the substrate attached to the grid. .........................44
3.10 Top view of sample thinned to about 150 nanometers. .........................44

CHAPTER 4
4.1 (a) Alumina substrate surface evenly covered with aluminum before heating; (b) Exposed alumina substrate surface after heating to 700°C; (c) EDS spectra at the dark and bright regions from b. .........................................................46
4.2 Interface between substrate and film identified for a fractured sample. ......47
4.3 Features on the surface of Al particle after heating to 1300° .................48
4.4 Hollow Al_2O_3 shell that contained Al particle before heating to elevated temperature. .................................................................49
4.5 X-ray diffraction spectrum for 4:3 molar ratio of Al:TiO_2 powder heated to 700°C for 9 hours. .............................................................50
4.6 (a) Slow and (b) ultra slow X-ray diffraction spectra respectively of Al and TiO_2 powder heated to 700°C for 9 hours. .........................51
4.7 X-ray diffraction spectrum of an unheated Al-TiO_2 film-substrate sample. ......52
4.8 X-ray diffraction spectrum of Al-TiO_2 film-substrate sample heated to 700°C, soaked for 9 hours showing peaks of Al_2O_3. ..............................53
4.9 X-ray diffraction spectra of Al-TiO_2 sample heated from room temperature to 700°C in-situ. .................................................................55
4.10 Interface of an unheated Al-TiO_2 sample. ....................................56
4.11 Cross section of fractured Al-TiO_2 film-substrate sample heated to 700°C for 9 hrs and (EDS) of the corresponding regions. .........................57
4.12 Two unheated film-substrate samples in sandwich structure to measure the Al-film thickness. ...............................................................58
4.13 Two heated film-substrate samples in sandwich structure to measure the Al-film thickness. ...............................................................58
4.14 Surfaces of Al particles that were heated with TiO_2 powder in (a) air and (b) He at a low heating rate 10°C per minute. ..............................60
4.15 Surfaces of Al particles that were heated with TiO_2 powder in (a) air and (b) He at a more rapid heating rate 40°C per minute. .............................60
4.16 Cross-section of the Al particle milled from the surface towards the interior for sample heated at (a) 10°C/minute and (b) 40°C/minute. ..............60
4.17 TEM micrograph of the interface of an unheated Al-TiO_2 film-substrate sample. .63
4.18 TEM micrograph of the interface of the Al-TiO_2 film-substrate sample heated for 9 hours at 700°C. ............................................................64
4.19 Comparison of the interface region between an unheated and a heated Al-TiO_2 film-substrate sample. ....................................................65
4.20 STEM micrograph of the interface using the FEI TITAN. The inset is the image at the same location on 420 Philips TEM both showing the wavy interface on one side and almost straight on the other. ...........................................66
4.21 TEM micrograph showing the thinner and thicker regions of interface. ......67
4.22 Part of the interfacial region protruded into the Al layer. The circle marks the region where the aperture was placed for electron diffraction. ..........68
4.23 (a) Indexed electron diffraction pattern of the circled region on Figure 4.28; (b) (11-1) plane displaced to the center for dark field imaging on the 420 Philips TEM. ...69
4.24 (a) Dark field TEM micrograph of the (11-1) grain that is indexed from images in Figures 4.22. (b) Low magnification dark field micrograph of the interface that highlights the interface that contains the TiAl phase. ..................70,71
4.25 Bright field TEM micrograph of the interfacial region showing few grains protruding into the Al side. The circle marked shows the area selected for electron diffraction. .........................................................72
4.26 TEM dark field image of the marked plane from inset. The dotted line shows the TiO$_2$/interfacial region. .................................................................72

4.27 (a) TEM Bright field micrograph of interfacial region with inset showing indexed electron diffraction pattern of marked area; (b) TEM dark field micrograph with (02-1) plane lit-up at the interface. ......................................................73

4.28 Regions I, II and III along the interface of the Al-TiO$_2$ film-substrate sample that was exposed for 9 hours at 700ºC that was used to prove the presence of an interfacial compound between the film and the substrate. .......................75

4.29 Possible reactions at Al-TiO$_2$ interface. ......................................76

4.30 TiO$_2$ –free energy curve superimposed on Ti-Al Gibbs free energy diagram calculated at 1373 K by Li et al.$^{66}$ for explanation of the preference of formation of TiAl compound. ..................................................80

4.31 Schematic of melted Al in contact with TiO$_2$ substrate. Surface grain of TiO$_2$ has stacking faults. .................................................................82

4.32 The TiO$_2$ grain at the surface of the substrate in contact with the Al-film. The surface grain has stacking faults that are present at the surface and run into the interior of the grain. .........................................................83

4.33 Schematic showing Al diffusing into the TiO$_2$ substrate through stacking faults 84

4.34 Interface of Al-TiO$_2$ sample exposed to 700ºC for 9 hours. Several stacking faults were observed on the TiO$_2$ side. ........................................85

4.35 EDS line spectrum with Al/Ti intensity ratio superimposed on STEM micrograph (from marked region in Figure 4.34). ........................................86

4.36 (a) Bright field micrograph representing the interfacial region of Al-TiO$_2$ film-substrate sample soaked for 36 hours at 700°C.; (b) Micrograph in STEM mode of the marked area in (a). The red line indicates the EDS line scan. ..........87

4.37 Al/Ti and O/Al intensity ratio from EDS line scan superimposed on STEM micrograph. .................................................................................88

4.38 Schematic that summarizes the mechanism of formation of TiAl at regions close to the stacking faults in Step III. ........................................89

4.39 Schematic showing the growth of TiAl into the TiO$_2$ grains in Step IV. ... 90

4.40 (a) A Straight interface of the unheated sample; (b) wavy interface at the TiO$_2$/interfacial boundary in the Al-TiO$_2$ sample, soaked for 9 hours at 700ºC. ... 91

4.41 (a) Large pores at the interface for Al-TiO$_2$ sample soaked for 36 hrs at 700ºC; (b) Pores along the boundary between the interfacial region and TiO$_2$. ..........92

4.42 Schematic of the interface between Al and TiO$_2$ after the interaction between Al and TiO$_2$. .................................................................93

4.43 Schematic showing possibility of the presence of oxygen in the interfacial layer containing TiAl. .................................................................95

4.44 Points from the EDS line scan beginning from the TiO$_2$ side through TiAl interface into Al for the Al-TiO$_2$ sample soaked for 9 hours at 700ºC. .................96

4.45 EDS spectra from points 1 to 20 on Figure 4.44. ................................97

4.46 O/Al and Ti/O EDS intensity ratios superimposed on TEM microstructure at the interface of the Al-TiO$_2$ sample soaked for 9 hours at 700ºC. .................98

4.47 Schematic showing possibility of presence of oxygen in the Al layer on the top surface. ...........................................................................100
4.48 Schematic showing possibility of the presence of oxygen at various interfaces and TiAl grain boundaries. ................................................................. 101
4.49 Schematic showing possibility of the presence of Al₂O₃ grains in the interfacial region containing TiAl grains. ................................................................. 102
4.50 Micrograph of interfacial region showing grain-like features in Al-TiO₂ sample soaked for 9 hours at 700°C as seen in 420 Philips TEM. .............................. 103
4.51 TEM micrograph of a grain observed at the interfacial region containing TiAl shown in Figure 4.50. ................................................................. 104
4.52 High resolution lattice image of region 1 in Figure 4.51. Inset is the indexed ‘Fourier transformed’ pattern. ................................................................. 105
4.53 High resolution lattice image of region 2 in Figure 4.51. Inset is the indexed ‘Fourier transformed’ pattern. ................................................................. 106
4.54 High resolution lattice image of region 3 in Figure 4.51. Inset is the indexed ‘Fourier transformed’ pattern. ................................................................. 107

LIST OF TABLES

2.1 Available literature on X-Phase ................................................................. 22
3.1 Theoretical Determination of Possible Interfacial Compound(s) ............... 32
4.1 Free Energy Comparison of Compounds at 700°C ................................ 79
1.0 INTRODUCTION

The current chapter describes the importance of and explains the common route to synthesize a TiAl – Al₂O₃ composite. The chapter outlines the motivation for the topic of research and the main research objectives.

1.1 Reaction Synthesis of Intermetallic – Ceramic Composites

TiAl based intermetallics have useful properties like low density (3.7 – 3.9 gm/cm³ as compared with superalloys having 8.3 gm/cm³), high oxidation limit of 900°C (as compared to 650°C for Ti₃Al based alloys); high strength value of 400 – 650 MPa; and adequate creep resistance at temperatures to 1000°C (compared with Ti₃Al (760°C). Mechanical properties of γ-TiAl alloys are sensitive to microstructure. The microstructure of γ-TiAl alloys has been reported to vary appreciably with small changes in alloy composition and processing parameters.

Toughness of TiAl based intermetallic alloys at ambient temperatures could be improved by the introduction of matrix based composites (TiAl-matrix reinforced with SiC, Al₂O₃ or TiB₂ particles or fibers). Al₂O₃ has been identified as a thermodynamically stable reinforcement phase for a γ-TiAl matrix. Intermetallic – oxide interpenetrating phase composites have been proposed for better mechanical properties for structural applications. Several processing techniques have been suggested by various authors for the synthesis of a TiAl – Al₂O₃ composite.

One of the most common ways used for synthesis of such interpenetrating phase composites is by infiltrating liquid metal into a porous ceramic preform. The liquid metal infiltration method is however limited to the manufacturing of Al – containing
composites whose high temperature applications are limited by the low melting point of Al. An *in-situ* process is needed\(^9\) to counter such problems. Matrices and reinforcements that could be formed by *in-situ* reactions of completely different starting materials was suggested by Subramanian *et al.*\(^9\) Subramanian *et al.*\(^9\) demonstrated the formation of an iron aluminide matrix composite reinforced with alumina particles that was synthesized by an *in-situ* displacement reaction between Fe-Al powder and Fe\(_2\)O\(_3\) powder. A similar *in-situ* displacement reaction to synthesize TiAl-Al\(_2\)O\(_3\) composite was performed by Horvitz *et al.*\(^6\) Horvitz *et al.*\(^6\) blended a 70:30 molar ratio of Al and TiO\(_2\) powders. The powders were compacted by cold pressing. A compacted powder sample was placed between preheated (800 – 1000°C) rams of an Instron test machine. When the temperature of the sample was sufficiently high, the powder mixture reacted by a thermal explosion. Horvitz *et al.*\(^6\) explained that the thermal explosion is the result of the moderately exothermic 3TiO\(_2\) + 7Al → 2Al\(_2\)O\(_3\) + 3TiAl self-propagating high temperature synthesis (SHS) reaction. Other researchers have reported the use of such SHS reaction technique for the synthesis of intermetallic – ceramic composites.

### 1.2 Justification of Research

The 10Al + 3TiO\(_2\) + 3B\(_2\)O\(_3\) → 5Al\(_2\)O\(_3\) + 3TiB\(_2\) SHS reaction at standard atmospheric pressure was shown by Logan\(^10\) to produce a composite 5Al\(_2\)O\(_3\) + 3TiB\(_2\) as the reaction product. After the SHS reaction involving the reactant powder mixture was initiated, the reaction front propagated with a speed ranging from 2.4 mm/sec to 7.5 mm/sec depending on the nature of powder packing.\(^10\) The temperature change during the SHS reaction was recorded to be 50°C/min. A unique microstructure with
high aspect ratio grains was obtained by *Logan* \(^{11}\) at 10ºC/min. Neither the mechanism, nor the factors responsible for the unique microstructure have been explained in the literature.

An effective way to affect the rate of change in temperature during the SHS reaction could be by the self-formation of an interfacial compound between the reacting species that would act as a barrier. \(^{12,13,14}\)

Knowledge of the interaction between individual reactant components would be necessary to determine whether a barrier could be made to form between the reactant pairs. The SHS interaction between Al and B\(_2\)O\(_3\) has been studied previously and reported by McLemore. \(^{15}\) McLemore \(^{15}\) reported that the interaction between Al and B\(_2\)O\(_3\) yielded 2Al\(_2\)O\(_3\).B\(_2\)O\(_3\) at 870ºC in some cases, and 9Al\(_2\)O\(_3\).2B\(_2\)O\(_3\) in others. Al\(_2\)O\(_3\) was reported to have formed at 1035ºC for every experiment reported by McLemore. \(^{15}\) The reaction between Al and TiO\(_2\) at elevated temperatures is documented as a common route to synthesize a TiAl – Al\(_2\)O\(_3\) composite. \(^{7}\) Knowledge of the mechanism of reaction component interactions causing the composite formation can provide a basis for prediction and control of product characteristics.

### 1.3 Objective of Research

The objective of my research is to understand the interactions and mechanisms that lead to a possible interface between Al and TiO\(_2\) when the two components are in contact with each other at 700ºC isothermal condition and standard atmospheric pressure. Advanced analytical techniques and thermodynamics will be used to understand the growth mechanism of the resultant interface.
2.0 BACKGROUND AND LITERATURE REVIEW

The current chapter explains the necessary concepts and relevant findings from the literature pertaining to the current research. In particular, thermodynamics of the Ti-Al-O system that is reported in literature is explained.

2.1 SHS Reaction

An SHS reaction involving aluminum, anatase and anhydrous boron oxide powders forms a composite of alumina and titanium diboride as given by Equation (2.1). Information about formation of product phases other than the stoichiometric reaction product as given by Equation (2.1), has not been generally reported.

\[
3\text{TiO}_2 + 3\text{B}_2\text{O}_3 + 10\text{Al} \rightarrow 3\text{TiB}_2 + 5\text{Al}_2\text{O}_3 \quad (2.1)
\]

Logan\textsuperscript{11} has observed that compounds and phases that form at the SHS reaction heating rate (~50°C/min) are different from products that form during the lower reaction heating rates (~10°C/min) involving the same reactants. Some compounds and phases that form at a lower heating rate have a high-aspect ratio morphology compared with products that form at a higher heating rate, as shown in Figure 2.1.\textsuperscript{11} Materials with high aspect ratio morphology could potentially be used for structural applications with improved properties such as toughness\textsuperscript{17,18} and strength\textsuperscript{17}.
A brief outline of events that take place during an SHS reaction that produce the Al$_2$O$_3$-TiB$_2$ composite product follows:\textsuperscript{16}

- A stoichiometric proportion [as shown in Eq. (2.1)] of Al, TiO$_2$ and B$_2$O$_3$ powders are mixed to form a reactant mixture.
- The reactant mixture is placed in a refractory crucible and heat is supplied from an external source to initiate the reaction.\textsuperscript{10}
- The B$_2$O$_3$ powder begins to melt as the temperature of the powder mixture reaches 450°C.
- The melted B$_2$O$_3$ coats the small particles of TiO$_2$ as it spreads into the interior of the sample by capillary action and also coats the Al particles.\textsuperscript{19}
- The Al and TiO$_2$ particles are isolated from the atmospheric oxygen as a consequence of the molten B$_2$O$_3$ coating.
- Al reduces the oxides of Ti and B to elemental metals\textsuperscript{19} and in the process forms Al$_2$O$_3$. Oxygen required for the oxidation of Al is obtained from the

---

**Figure 2.1:** Microstructure of the reaction product having high aspect ratio crystals formed at a lower heating rate as observed by Logan.\textsuperscript{11} (printed with permission)
reduction of the oxide reactants and a small amount from the ambient air. The exothermic nature of the reaction causes an increase in temperature of the reactants.\textsuperscript{19} As the heat evolved from the reaction increases, Al expands because of its higher coefficient of thermal expansion, while Al\textsubscript{2}O\textsubscript{3} does not expand to the same extend due to its relatively low coefficient of thermal expansion. The difference in thermal expansion coefficients causes the surface oxide layer to crack and continuously expose fresh elemental Al.

- When the temperature reaches 660°C, Al melts and begins to flow out of the oxide shell. Al is directly exposed to B\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}.

At about 1060°C the two oxide components and Al react to form titanium diboride (TiB\textsubscript{2}) and negligible amounts of Al\textsubscript{18}B\textsubscript{4}O\textsubscript{33}.\textsuperscript{20} Near stoichiometric amounts of Al\textsubscript{2}O\textsubscript{3} and TiB\textsubscript{2} are the final products of the SHS reaction as shown in Eq. (2.1).\textsuperscript{10}

2.2 SHS Reactant Components

Depending on the SHS reaction conditions, some stable and metastable compounds could form between the reacting compounds. The final SHS reaction product is a mixture of Al\textsubscript{2}O\textsubscript{3} – TiB\textsubscript{2}. Binary or ternary reactant systems comprising a combination of Al, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, and B\textsubscript{2}O\textsubscript{3} react among themselves until equilibrium is attained to form the final stoichiometric compound.

A list of the potential reactant pairs involved in the Al\textsubscript{2}O\textsubscript{3} – TiB\textsubscript{2} SHS reaction system (Equation 2.1) are:

i. Al – TiO\textsubscript{2}

ii. Al – B\textsubscript{2}O\textsubscript{3}

iii. TiO\textsubscript{2} – Al\textsubscript{2}O\textsubscript{3}
iv. TiO$_2$ – B$_2$O$_3$

v. Al$_2$O$_3$ – B$_2$O$_3$

A passive layer of Al$_2$O$_3$ forms on the surface of Al. Interaction of Al with either oxygen or an oxygen-containing compound forms a stable Al$_2$O$_3$. Al – Al$_2$O$_3$ is not considered a reactant pair since Al$_2$O$_3$ is a stable compound formed by oxidation of Al; although some interaction is possible.

Particle – particle interaction between the individual components was studied and reported by Logan et al.$^{22,10}$ Logan et al.$^{10}$ investigated particle size and powder compaction effects on the initiation temperature for the following powder mixtures: (i) 4Al + 3TiO$_2$, and (ii) 2Al + B$_2$O$_3$ in order to study the SHS produced Al$_2$O$_3$ – TiB$_2$ product.

Logan et al.$^{10}$ found that the reaction between an Al and TiO$_2$ loose powder mixture ignited from room temperature proceeded in a slow and controlled manner at about 0.4 mm/sec. It was reported that the Al – TiO$_2$ SHS reaction would not initiate when pressed pellets of the Al and TiO$_2$ powder mixture were used. $\alpha$–Al$_2$O$_3$ and TiN were the major products and small amounts of TiO$_2$ were detected.

It was interesting to note that only pressed pellets of the Al – B$_2$O$_3$ powder mixture would initiate.$^{10}$ It was further noted that the pellets containing coarse Al and coarse B$_2$O$_3$ powders initiated but would not self–propagate.$^{10}$ The combustion front of the Al – B$_2$O$_3$ SHS reaction propagated in a spiral oscillation from the top to the bottom at about 1.0 mm/second. The product of the reaction was reported to be largely $\alpha$–Al$_2$O$_3$ and small amounts of Al, B$_2$O$_3$ and a solid solution of 9Al$_2$O$_3$.2B$_2$O$_3$. McLemore$^{15}$ determined the activation energy for the formation of
$2\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3$ from the reaction between Al and B$_2$O$_3$ to be between 120 and 165 kcal/mol. The activation energy for the formation of Al$_2$O$_3$ from the same reactants was determined to be between 210 and 235 kcal/mol.

The remaining three reactant pairs TiO$_2$ – Al$_2$O$_3$, TiO$_2$ – B$_2$O$_3$ and Al$_2$O$_3$ – B$_2$O$_3$ are nonreactive and therefore are not relevant to this investigation.

### 2.3 Al – TiO$_2$ System and Applications

Al interaction with TiO$_2$ could be a rate determining factor that would be useful in the control of the Al+TiO$_2$+B$_2$O$_3$ SHS reaction kinetics. Diffusivity of a species into a compound could have significantly different values depending on the phase of the compound encountered by the diffusing species.\textsuperscript{23} A study of the individual reactant components would help to determine the rate limiting step. Such a study that involves the examination of the interface between the reactants would be difficult using small spherical particles (powder samples); since the interface between the two particles would be difficult to examine using an area specific characterization technique like the SEM or the TEM. The interface between the two components would also be difficult to study if one of the reactants is in the liquid state at the temperature of interest. A diffusion couple study is a conventional route to study the interface between two reactants.\textsuperscript{24} A film-substrate structure would ensure easy accessibility to examine the interface. The compound having the lower melting point could be chosen to be deposited as the film over a substrate (compound with the higher melting point). Heating a film-substrate (Al – TiO$_2$) structure could result in the formation of an interfacial compound(s) for the Al-Ti system. It is possible that oxygen would diffuse from the oxide (TiO$_2$) to form Al$_2$O$_3$ and Al would diffuse from the Al film to form
either an Al - Ti intermetallic or Al2O3 or both. Intermetallic compound phases have been identified for the Al-Ti system having different structures: Ti3Al(α2), TiAl(γ), Al2Ti (HfGa2 type tetragonal), Al3Ti (simple tetragonal) and other possible metastable phases.25,6

Titanium aluminides form having high melting temperature, good oxidation resistance and low density suitable for high temperature applications when Al and TiO2 react. Al2O3 has been reported as a second phase formed within the titanium aluminides. Techniques like gas-pressure infiltration,26,27 liquid metal infiltration into porous preforms,8 reactive melt infiltration,28,29 directed metal oxidation,30,31 and hot isostatic pressing have been used to synthesize the combination of intermetallic-ceramic composites. The aluminide – alumina mixture has been used as reinforcement for *in-situ* Al based alloy metal matrix composites.32,33,34 Titanium aluminide composites are used as binders along with carbides or Al2O3 for structural applications, even when the aluminide is the minor component of the composite.35 The combination of TiAl or Ti3Al, and Al2O3 are used for the production of *in-situ* aluminide – alumina composites for various applications.36,37,38 The Al-TiO2 system has been used for producing *in-situ* metal matrix composites by vortex casting33,39 and *in-situ* intermetallic matrix composites by squeeze casting40,41,42. Feng *et al.*34 have indicated that there are often intermediate steps between the starting compounds and the final product after a reaction occurs in such systems. Insufficient knowledge of the intermediate steps hinders the optimization of properties of the composite products formed by such reactions. The advantage of such an intermetallic system is that the thermo-mechanical properties, such as wear resistance, environmental
stability and high temperature strength, are dominated by Al₂O₃ while the intermetallic phase significantly improves the toughness of the component through a crack-bridging mechanism. The TiAl phase is usually the preferred intermetallic reinforcement due to a combination of properties like low density, high melting temperature and excellent oxidation resistance.⁶

2.4 Interaction between Al and TiO₂

The interaction between Al and TiO₂ has been studied previously under various conditions of temperature and pressure⁴³,⁴⁴,⁴⁵,⁴⁶ yielding a composite TiAl₃ and Al₂O₃ as the final product. The experiments have all involved some form of pressurization of the reactant mixture at some point in time. Example experiments that involve interaction between Al and TiO₂ as reported in the literature are explained below.

Feng et al.³⁴ used an Al - TiO₂ powder mixture with a weight percentage mixture of 88.33:16.67 Al:TiO₂ that was initially milled, then uniaxially cold-pressed to form green compact pellets. The samples were heated to 1100°C at 10°C per minute, and then cooled to room temperature at 10°C per minute. TiAl₃ and α-Al₂O₃ were reported to have been the final product. Intermediate γ-Al₂O₃ and TiO phases were also reported to have formed during heating that were not present when the reaction was cooled to room temperature. The authors have hypothesized three steps during the reaction that lead to the formation of the final product mixture. The first step involved the formation of TiO and γ-Al₂O₃ intermediate phases. The second and third steps involved formation of α-Al₂O₃ and TiAl₃. Evidence of the presence of TiAl₃ and TiO has been derived from X-ray diffraction analysis. γ-Al₂O₃ has also been reported to have formed as determined by X-ray diffraction analysis. Pan et al.⁴⁷ reported the
presence of $\gamma$-Al$_2$O$_3$ using high resolution TEM. Both authors have reported that $\gamma$-Al$_2$O$_3$ forms as an intermediate phase that either transforms to the more stable $\alpha$-Al$_2$O$_3$; or the $\gamma$-Al$_2$O$_3$ reacts with another compound to form a ternary compound. For example $\gamma$-Al$_2$O$_3$ reacts with Mg to form MgAl$_2$O$_4$. The presence of TiAl$_3$ has also been reported from the X-ray diffraction analysis.

The interaction between TiO$_2$ and Al have been reported by Gheorghe et al.$^{46}$ during pressure infiltration; and by Pan et al.$^{47}$ during squeeze casting processes of a TiO$_2$ pre-form with Al. TiAl$_3$ and $\alpha$-Al$_2$O$_3$ were reported as the final product. TiAl$_3$, TiAl or Ti$_3$Al could form as part of the final product during the reaction between Al and TiO$_2$, depending on the volume of the reactants consumed during the reaction as stated by Pan et al.$^{47}$. Criteria for the formation of each of the three compounds were unclear from the explanation in the report. In other words, the ratio of Al:TiO$_2$ consumed during the reaction was not reported, possibly since it was not known. The report also suggested that the pores at the reaction interface were due to the volume shrinkage between the reactant and product compounds. Gheorghe et al.$^{46}$ and Pan et al.$^{47}$ also hypothesized a three step product-formation process that was derived from results from the experiments.

Run-hua Fan et al.$^7$ have recently reported the formation of $\gamma$-TiAl and Al$_2$O$_3$ when reacting Al with TiO$_2$ during a non-isothermal reaction. The work demonstrated that two modes of reaction stages were possible depending on the rate of heating of the reactant components for the reaction $3\text{TiO}_2 + 7\text{Al} \rightarrow 3\text{TiAl} + 2\text{Al}_2\text{O}_3$. A mole fraction ratio of 7:3 Al:TiO$_2$ powder mixture was mixed in a planetary mill and then cold pressed into 10 mm diameter pellets under a uniaxial pressure of 100 MPa. The
pellet samples were heated at different heating rates and held for a specific soaking period to study the characteristics of the synthesis reaction. $\gamma$-TiAl and Al$_2$O$_3$ were found as products after the reaction at higher heating rates (15 K/minute). During the interaction, $fcc$-TiAl was reported to have formed initially which later transformed to the more stable $\gamma$-TiAl by ordering.

Horvitz et al.$^6$ reported the formation of TiAl and Al$_2$O$_3$ as the outcome of the interaction between Al and TiO$_2$ under various conditions of temperature and pressure. The authors reported TiAl and Al$_2$O$_3$ as the main products and small amounts of Ti$_3$Al after the SHS reaction of the reacting components. The product of reaction after thermal explosion was reported to be similar in composition to the TiAl – Al$_2$O$_3$ SHS reaction. The reaction between Al and TiO$_2$ could be controlled since an interfacial layer of Al$_2$O$_3$ formed between the two reactants, thereby slowing the reaction.$^6$

A reaction was not observed between Al and TiO$_2$ when the reactant component mixture was held at 800°C between press-rams. X-ray diffraction of the resultant mixture showed only the reactants. However, when the reactant component mixture was held at 800 °C for about 20 minutes, a mixture of TiAl$_3$ and Al$_2$O$_3$ was formed and small amounts of TiO and Ti$_2$O$_3$ were observed. When the samples were held at 875 °C and 950 °C between the press-rams, thermal explosions occurred and the final reaction mixture contained TiAl, Ti$_3$Al and Al$_2$O$_3$. When samples were constrained under the press-rams to 50 MPa at 950 °C, TiAl and Al$_2$O$_3$ were formed with small amounts of Ti$_3$Al. When the reactant component mixture was reactive hot pressed (RHP) at 950 °C for one hour, a complete reaction was not observed. The end
products did not reveal remains of reactants after the reaction: but large amounts of intermediate compounds, like TiO, Ti$_2$O and TiAl$_2$ were observed besides the usual TiAl, Ti$_3$Al and Al$_2$O$_3$.

The outcome of the interaction between Al and TiO$_2$ is dependent on conditions like temperature, pressure and composition as reported by Feng et al., Pan et al., Gheorghe et al., Run-hua Fan et al., and Horvitz et al. The outcomes of interaction between Al and TiO$_2$ at the temperature range of 660°C (melting point of Al) to 850°C (a reported thermite reaction to form TiAl$_3$) has not been reported in the literature.

2.5 **Ti – Al – O Thermodynamics**

The Ti-Al-O system has been partially studied from the point of view of the thermodynamics of the ternary system. Attempts to calculate the Ti-Al-O phase diagram at temperatures of significance for applications of interest are listed below.

2.5.1 **Binary Systems**

The binary systems of interest here are Al – O, Ti – O and Ti – Al.

2.5.1.1 **Al – O**

Equilibrium phases in the Al-O binary phase diagram are (i) liquid Al at the high temperature Al-rich end, (ii) liquid Al$_2$O$_3$ near the high temperature O-rich end, (iii) solid fcc-Al at low temperature with very small solubility of O, (iv) hexagonal Al$_2$O$_3$ (α-Al$_2$O$_3$ or corundum) that is commonly believed to have small but unknown deviation from the stoichiometry, and (v) the gas phase.
shows the Al-rich side of the Al-O phase diagram. It is noted that the solubility of O in pure Al is shown to be low at the temperature range of 700ºC.

Besides the thermodynamically stable α-Al₂O₃, Al₂O₃ has several polymorphs that are metastable. The thermodynamically metastable Al₂O₃ polymorphs are divided into two broad categories: (i) fcc and (ii) hcp, based on location of the oxygen anions. The γ, η (cubic), θ (monoclinic), and δ (either tetragonal or orthorhombic) polymorphs are based on the fcc structure.

![Al-O binary phase diagram](image)

**Figure 2.2: Al-O binary phase diagram**

The α (trigonal), κ (orthorhombic), and χ (hexagonal) phases are based on the hexagonal closed packed (hcp) structure. New monoclinic phases have been identified by Levin *et al.*
Some researchers have reported the presence of metastable Al$_2$O$_3$ phases, during the interaction between Al and TiO$_2$ as a transition phase before the more stable $\alpha$-Al$_2$O$_3$ is formed; while others have obtained the stable phase directly.$^{51,51,46,47,53,54,55}$

The discrepancy revolving around the rate of oxidation of Al to form alumina is worthy of mention. Doremus$^{56,57}$ reported that the oxidation of alloys containing Al to form an Al$_2$O$_3$-scale is much faster than the calculated values of the diffusivities of Al and O. The activation energy measured for the oxidation is less than that for diffusion. Doremus$^{56}$ thus claims that Wagner’s theory of oxidation does not hold true for oxidation of Al. An alternative model suggested by Doremus involves diffusion of uncharged ‘AlO molecules’. The author further claims that it is possible to find reasonable diffusivity values for AlO molecules that correspond to the measured oxidation rates. However, neither a direct measurement of the concentration of the diffusing species has been made nor has the transport of AlO molecules been verified.$^{56}$

Pint et al.$^{58}$ is of the opinion that formation of alumina scales satisfied Wagner’s theory of oxidation. Pint et al.$^{58}$ reported that extrapolated grain-boundary diffusivity relations are consistent with the oxidation rates. Pint et al.$^{58}$ further refute the mechanism of transport by AlO molecules using the argument that reported experimental results were inconsistent with the growth of alumina scales by uncharged species. Also, the growth rate of such scales can be altered by an applied current.$^{58}$
The above explanation is part of the reason why the current research does not include the study of the interaction between Al and Al₂O₃. The explanation about the solubility of O in Al at 700°C is relevant to the discussion about oxygen released during the Al – TiO₂ reaction. When Al alloys were oxidized in air, web-like structures were observed by Nychka and Clarke,⁵⁹ on the surface of the Al particles. Nychka and Clarke,⁵⁹ have explained the formation of such structures by the diffusion of Al towards the oxide shell occurring more rapidly at the Al₂O₃ grain boundaries compared to within the grains. Al that is diffused outward is oxidized at the surface to form Al₂O₃ which appears as a web-like structure over the surface of grains.

2.5.1.2 Ti – O

Figure 2.3 shows the Ti – O phase diagram that was reported by Massalski.⁴⁸
At low temperatures, as shown in Figure 2.3, the $\alpha$-Ti (hexagonal close packed structure) shows a high solubility of oxygen. Dissolved oxygen is probably responsible for stabilization of the high temperature $\beta$-Ti (fcc). The $hcp$ phases Ti$_2$O and Ti$_3$O are reported at low temperatures. Peritectoid reactions $\alpha$-Ti + Ti$_2$O$_3$ $\rightarrow$ Ti$_2$O at $\sim$600°C and $\alpha$-Ti + Ti$_2$O $\rightarrow$ Ti$_3$O at $\sim$500°C are responsible for the formation of Ti$_2$O and Ti$_3$O respectively. For both reactions the components $\alpha$-Ti, Ti$_3$O$_2$, Ti$_2$O and Ti$_3$O are seen to have a high solubility of oxygen ($\sim$17 to 40 atomic percent oxygen). A peritectic reaction L + $\alpha$-Ti $\leftrightarrow$ $\gamma$-TiO at 1770°C forms $\gamma$-TiO that has 34.5 atomic percent of oxygen. $\gamma$-TiO transforms to $\beta$-TiO at $\sim$1250°C. $\alpha$-TiO forms by a peritectoid reaction at 940°C.
where the oxygen content in $\alpha$-TiO is 50 atomic percentage. At the higher oxygen content side of the Ti-O phase diagram, $\beta$-Ti$_3$O$_5$, $\beta$-Ti$_2$O$_3$ and TiO$_2$ form by a peritectic and two different congruent reactions. The congruent reactions to form $\beta$-Ti$_2$O$_3$ and TiO$_2$ occur at 1842°C and 1870°C respectively. Waldner et al. have shown the occurrence of the Magnelli phases (Ti$_{n}$O$_{2n-1}$) also at the higher oxygen side of the calculated phase diagram as shown in Figure 2.4.

**2.5.1.3 Ti – Al**

Equilibrium phases in the Ti-Al system are as follows:

(i) liquid

(ii) disordered solution phases

(iii) $hcp-(\alpha Ti)$ – maximum solubility of Al is ~45%

(iv) $bcc-(\beta Ti)$ – maximum solubility of Al is ~48%

(v) $fcc-Al$ – maximum solubility of Ti is ~0.7%$^1$

(vi) ordered intermetallic compounds [Ti$_3$Al (ordered hcp structure), $\gamma$-TiAl and TiAl$_3$ (both have ordered $fcc$ superstructure), TiAl$_2$ and $\delta$- phases both having bcc structure].

*Figure* 2.5 shows the calculated Ti-Al phase diagram compiled by Massalski. Discrepancies still appear to be present between some phases in the Ti-Al system which indicate that the system is not well calculated and optimized. Kaufman was first to investigate the Ti-Al system. Early attempts by Kaufman to calculate the Gibb’s free energy of formation of the ordered compounds Ti$_3$Al, TiAl and TiAl$_3$ were carried out by assuming that the compounds were line compounds.$^{66}$
The phase diagram calculated by Murray\textsuperscript{67} took into consideration the homogeneity range of Ti\textsubscript{3}Al and TiAl. The model that was used by Murray\textsuperscript{65} combined the description of the sublattices of the compounds and used the Bragg-Williams approximation. Li \textit{et al.}\textsuperscript{68} calculated Gibb’s free energy of the Ti-Al system using Ti\textsubscript{3}Al data generated by Murray\textsuperscript{67} and also included the thermodynamic data for the phases: $\alpha$-Ti(Al), $\beta$-Ti(Al) solid solutions and TiAl\textsubscript{2}. Li \textit{et al.}\textsuperscript{68} used a polynomial expansion for the excess free energy of the Ti\textsubscript{3}Al and TiAl in the known homogeneity range\textsuperscript{68}. Parameters of the polynomial expression for Gibb’s free energy were calculated by using lattice stability of Ti and Al.

Figure 2.5: Ti-Al binary phase diagram by Massalski\textsuperscript{48}.  

![Ti-Al binary phase diagram](image_url)
established by Dew-Hugues and Kaufman. The resultant free energy diagram at 1100°C is shown in Figure 2.6.

![Figure 2.6: Ti-Al Gibb’s free energy diagram calculated at 1100°C by Li et. al.](image)

Work by Li et al. shows that the TiAl phase has a lower Gibb’s free energy than Ti₃Al and TiAl₃ at atmospheric pressure and 1100°C. Section 2.5 explains the reports that describe the interaction between Al and TiO₂ under various conditions of pressure and temperature. The interaction yields TiAl₃ as part of the product. Work by Li et al. indicates that at 1100°C, the Gibb’s free energy of TiAl is lower than TiAl₃.

Kattner et al. used experimental data from Murray and Mishurda and Perepezko for optimization of the thermodynamic quantities for the Ti-Al system. The sections of interest in the current research are the ordered
intermetallic compounds Ti$_3$Al, TiAl and TiAl$_3$. Kattner et al.\textsuperscript{62} used random mixing of Ti and Al atoms on each sublattice to derive the analytical Equation 2.5.1.

\[ G = x_{Ti} * G_{Ti}^n + x_{Al} * G_{Al}^n \]

\[ + R * T \left\{ n_{Ti}^1 * \ln(n_{Ti}^1) + n_{Al}^1 * \ln(n_{Al}^1) + n_{Ti}^2 * \ln(n_{Ti}^2) + n_{Al}^2 * \ln(n_{Al}^2) - N^1 * \ln N^1 - N^2 * \ln N^2 \right\} \]

\[ + \Delta G^f + n_{Ti}^2 * G_{Ti}^2 + n_{Al}^1 * G_{Al}^1 + n_{Ti}^1 * n_{Al}^1 * \left\{ G_0^1 + (n_{Ti}^1 - n_{Al}^1) * G_1^1 \right\} \]

\[ + n_{Ti}^2 * n_{Al}^2 * \left\{ G_0^2 + (n_{Al}^2 - n_{Ti}^2) * G_1^2 \right\} + n_{Ti}^2 * n_{Al}^2 * G^{12} \]  

(2.5.1)

where \( x_{Ti} = n_{Ti}^1 + n_{Ti}^2 \) \hspace{1cm} \( x_{Al} = n_{Al}^1 + n_{Al}^2 \)

\( N^1 = n_{Ti}^1 + n_{Al}^1 \) \hspace{1cm} \( N^2 = n_{Ti}^2 + n_{Al}^2 \)

\( n_{Ti}^1, n_{Al}^1, n_{Ti}^2, \) and \( n_{Al}^2 \) are the mole fractions of Ti and Al atoms on Ti (1) and Al (2) sublattices. \( N^1 \) and \( N^2 \) are the site fractions of Ti and Al sublattices respectively. \( G_{Ti}^n \) and \( G_{Al}^n \) are the Gibb’s free energy at the reference state for Ti and Al respectively. \( \Delta G^f \) represents the Gibbs free energy per mole of the perfectly ordered phase at the stoichiometric composition. \( G_{Ti}^2 \) and \( G_{Al}^1 \) are the Gibbs free energy of formation of one mole of substitutional Ti and Al atoms on the Al and Ti sublattices. \( G_0^1, G_1^1, G_0^2 \) and \( G_1^2 \) are coefficients of polynomial interaction terms between atoms on the same sublattice. \( G^{12} \) represents the term for the coefficient of interaction between the substitutional atoms on the different sublattices.
2.5.2 Ternary Phases

Free energy equations, solubility limits of the components, and other thermodynamic information of the ternary phases in the Ti-Al-O system are not well documented in the literature compared to the other phases (unary and binary). The literature shows only three ternary phases that are recorded, the X-phase, Al$_2$TiO$_5$, and Al$_6$Ti$_2$O$_{13.6}$.\(^6\)\(^1\),\(^7\)\(^1\)

High temperature applications involving titanium aluminides depend on the oxidation resistance of the $\gamma$-TiAl phase. Al$_2$O$_3$ forms a continuous layer on the $\gamma$-TiAl surface depleting the sub-surface layer of Al. A stoichiometric ternary phase known as the X-phase forms as a result.\(^6\)\(^1\) Kussmaul et al.\(^7\)\(^2\) has summarized details of results from the work on the X-phase as shown in Table 2.1.\(^7\)\(^3\),\(^7\)\(^4\),\(^7\)\(^5\)

Table 2.1: Available Literature on X-Phase

<table>
<thead>
<tr>
<th>Ti:Al:O (at. %)</th>
<th>Symmetry</th>
<th>Lattice Parameters</th>
<th>Oxidation of $\gamma$-TiAl</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:30:20</td>
<td>Cubic</td>
<td>$a = 0.69$ nm</td>
<td>900°C, Ar + 20% O$_2$</td>
</tr>
<tr>
<td>37.5:25:37.5 ±10 at. % O</td>
<td>Cubic</td>
<td>$a = 0.69$ nm</td>
<td>1000°C, O$_2$</td>
</tr>
<tr>
<td>37.5:25:37.5 ±5 at. % O</td>
<td>Cubic</td>
<td>$a = 0.69$ nm</td>
<td>900°C, air</td>
</tr>
</tbody>
</table>

Seifert and Aldinger\(^7\)\(^6\) reported decomposition of Al$_2$TiO$_5$ to form TiO$_2$ and Al$_2$O$_3$ at a temperature below 1300°C; while there are others who reported the decomposition to take place at temperatures between 1200°C and 1280°C.\(^5\)\(^8\) Seifert and Aldinger\(^7\)\(^6\) suggest that Al$_2$TiO$_5$ is a stoichiometric phase at high oxygen partial pressure; but as oxygen partial pressure decreases, stoichiometric Al$_2$TiO$_5$...
decomposes to form a reduced form of the $\text{Al}_2\text{TiO}_5$, $\text{Al}_2\text{O}_3$ and $\text{O}_2$ is liberated. A further decrease in $\text{O}$ pressure leads to decomposition of the reduced $\text{Al}_2\text{TiO}_5$ phase to form $\text{Al}_2\text{O}_3$ and $\text{Ti}_2\text{O}_3$.$^{76}$ Thermodynamic information for $\text{Al}_6\text{Ti}_2\text{O}_{13}$ is not reported since the compound has been recently discovered.$^{71}$

Thermodynamics of the Ti-Al-O ternary system have been calculated at isothermal conditions for various elevated temperatures; but very little experimental data are available to complete the ternary phase diagram. A detailed literature search has revealed that attempts have been made to calculate the ternary Ti-Al-O phase diagram at 500ºC, 700ºC, 800ºC, 871ºC, 900ºC, 945ºC and 1100ºC.

Not much information is available for the Ti-Al-O ternary at 500ºC and 700ºC as is seen in Figure 2.7. Lee et al.$^{77}$ have calculated the phase diagram of the ternary system at 500ºC and 700ºC. The difference in the slope of the curve seems to be different at both temperatures which indicate the higher solubility of Al in Ti with an increase in oxygen at 700ºC. Luthra$^{78}$ calculated the ternary phase diagram at the isothermal 800ºC section as is shown in Figure 2.8. Luthra$^{78}$ did not consider $\text{Ti}_3\text{O}$ (a metastable phase) for equilibrium diagram calculations. It is noted that $\text{Ti}_3\text{O}$ is not expected to form at temperatures above 500ºC as per the binary phase diagrams.
Figure 2.7: Calculated isothermal section (at Ti-rich regions) of the Ti-Al-O ternary phase diagram at (a) 500°C and (b) 700°C (Lee et al.\textsuperscript{77})

Figure 2.8. A calculated isothermal section of Ti-Al-O phase diagram at 800°C (Luthra\textsuperscript{78})
Tressler et al.\textsuperscript{79} made one of the earliest evaluations of the Ti-Al-O ternary system at 871\textdegree C. Tressler et al.\textsuperscript{79} proposed two possible sections of the ternary as shown in Figure 2.9. The two sections are almost identical except that there are differences in the equilibrium between TiAl, TiO, and Ti$_2$O$_3$ in one case, and between Ti$_3$Al, TiO, and Ti$_2$O$_3$ in the other. It is of interest to note that the authors were investigating the reaction path between Ti and Al$_2$O$_3$ at 871\textdegree C. The reaction path was determined to be Al$_2$O$_3$ → TiO → Ti$_3$Al → $\alpha$-Ti as the layers of compounds from Al$_2$O$_3$ to $\alpha$-Ti.

The reaction sequence was verified by preparing diffusion couples and heating the couples for extended periods of time at 871\textdegree C. The TiO phase was not detected by the X-ray diffraction technique, but was claimed to be present by the reflection electron diffraction technique. Later it was suggested by Choi et al.\textsuperscript{80}, Li et al.\textsuperscript{68} and Zhang et al.\textsuperscript{81} that the TiO phase was incorrectly identified and could instead be the TiAl.
phase. Zhang et al.\textsuperscript{81} stated that the sequence with TiO as represented above is not thermodynamically possible since Al would have to diffuse from a higher activity in Al\textsubscript{2}O\textsubscript{3}, to a low value in TiO, and again to a high value in Ti\textsubscript{3}Al.

At 900\textdegree C, Rahmel et al.\textsuperscript{82} calculated the Ti-Al-O phase diagram considering Ti\textsubscript{3}Al, TiAl and TiAl\textsubscript{3} as line compounds (shown in Figure 2.10). Rahmel et al.\textsuperscript{82} assumed that the compounds had no solubility for any species in order to simplify calculations.

Figure 2.10: Isothermal section of the Ti-Al-O ternary system at 900\textdegree C calculated by Rahmel et al.\textsuperscript{82}
Kelkar et al.\textsuperscript{83} assessed parts of the Ti-Al-O ternary system. Figure 2.11 shows the 945\textdegree C isothermal section of the ternary system calculated by Kelkar et al.\textsuperscript{83} based on the boundary conditions evaluated by Murray et al.\textsuperscript{84}, Kattner et al.\textsuperscript{62} and Wriedt et al.\textsuperscript{85} for the Ti-O, Ti-Al, and Al-O systems respectively. Regions in the phase diagram having a three phase field are represented with filled circles, and the two phase fields with open circles. Tie-lines established by Kelkar et al.\textsuperscript{83} are represented by solid lines; and the ones previously established are represented by dashed lines. Single phase regions are represented as shaded areas and the three-phase regions are marked with Roman numerals. The tie-lines with alternating long and short dashed lines are based on diffusion couple experiments with two phase samples. The phase diagram also shows a single phase field representing the ternary phase Al\textsubscript{2}TiO\textsubscript{5}.

Figure 2.11: 945\textdegree C isothermal section of the Ti-Al-O ternary system based on experimental evaluations on the base diagram calculated by Murray et al.\textsuperscript{84}, Kattner et al.\textsuperscript{62} and Wriedt et al.\textsuperscript{85}
Figures 2.12 and 2.13 show isothermal sections of the Ti-Al-O phase equilibrium at 1100°C as calculated by Li et al.\textsuperscript{68} and Lee et al.\textsuperscript{77} respectively. It is noted that the TiAl phase region on both phase diagrams (Figures 2.12 and 2.13) have very little solubility of oxygen at 1100°C.

Figure 2.12: Isothermal section of the Ti-Al-O as calculated by Li et al.\textsuperscript{68} with Ti-Al\textsubscript{2}O\textsubscript{3} diffusion paths superimposed.
2.6 An Explanation for the Oxygen Released During the Al – TiO₂ Reduction Reaction

Al is expected to reduce TiO₂ at elevated temperatures to form titanium aluminides. Reduction of TiO₂ results in the liberation of oxygen. There are discrepancies about what happens to the liberated oxygen as explained below. Some reports revealed that Al₂O₃ was formed as dense crystalline particles by the oxidation of Al that reduced TiO₂.⁴⁴,⁴⁶,⁴⁷,⁵⁵ Some reports suggested that oxygen was trapped in the intermediate layer since the mobility of oxygen and other diffusing species was low and hence formation of Al₂O₃ did not take place.⁴⁴
It has been suggested by Zhang et al.\textsuperscript{44} that O\textsuperscript{2-} liberated during the reduction of TiO\textsubscript{2} stayed in the TiAl\textsubscript{3} grains as a supersaturated solid solution. Zhang et al.\textsuperscript{44} suggested that O\textsuperscript{2-} ions do not have mobility at the temperature range around 800ºC to be able to combine with Al\textsuperscript{3+} ions formed by the oxidation reaction to form any polymorph of Al\textsubscript{2}O\textsubscript{3}. The O\textsuperscript{2-} and Al\textsuperscript{3+} ions required a period of time (incubation time) to nucleate to stable compounds. The incubation time was significantly reduced at 1000 ºC so that α-Al\textsubscript{2}O\textsubscript{3} nucleated and grew at the elevated temperature.\textsuperscript{44}

Zhang et al.\textsuperscript{44} reported that the reaction:

\[
3\text{TiO}_2 + 13\text{Al} \rightarrow 3\text{TiAl}_3 + 2\text{Al}_2\text{O}_3 \quad (2.6)
\]

was possibly responsible for the formation of the aluminide when the reactants interacted at elevated temperature. Based on Equation 2.6, 33% of the volume of the product would be Al\textsubscript{2}O\textsubscript{3} assuming that all the oxygen produced by the reduction of TiO\textsubscript{2} was converted to Al\textsubscript{2}O\textsubscript{3}. An explanation for the significant amount of oxygen has not been reported. Lefebvre et al.\textsuperscript{86} developed a theoretical model that showed that the equilibrium solubility of oxygen in titanium aluminide phases was not much, and that the solubility decreased significantly with an increase in Al content in the phases. The model suggested that the decrease in solubility of oxygen was primarily due to the decrease in number of suitable interstitial sites in the crystal when the Al content was increased. According to the model\textsuperscript{86}, the solubility of oxygen in the γ-TiAl phase that contains 50 at% Al, was about zero. The TiAl\textsubscript{3} phase had a higher Al content than TiAl; therefore, the solubility of oxygen was lower. The report stated that if the O\textsuperscript{2-} ions exist, they were in a highly metastable state in the TiAl\textsubscript{3} phase. Zhang et al.\textsuperscript{42} suggested that Al\textsuperscript{3+} and O\textsuperscript{2-} ions that were present in the titanium
aluminide grains as a metastable solution could precipitate as fine Al₂O₃ particles in the aluminide phase by low temperature aging. Further research would be needed to study and prove it.

Oxygen could possibly be present in the Al layer. As observed in the Al-O phase diagram in Figure 2.2 in Section 2.5.1.1, Al does not have much solubility (close to zero) for oxygen at the temperature range of 700ºC. Levis and Kaplan⁸⁷ and Das et al.⁶¹ have also shown that the solubility of oxygen in Al was very low. It has also been reported by Kubaschewski and Hopkins⁸⁸ that oxygen has very small solubility (close to zero) in Al at 700ºC and above. One of the reasons for the limited solubility could be that the equilibrium partial pressure of oxygen for the oxidation reaction of Al is tens of orders of magnitude lower than the partial pressure of oxygen found in most experimental and industrial applications.⁸⁹ Due to such conditions, Al tended to oxidize to form an oxide rather than form a solid solution of oxygen in Al.
3.0 EXPERIMENTAL APPROACH

Determination of the interface between Al and TiO$_2$ was approached experimentally and the mechanism of formation and growth of the interface was determined by use of theoretical calculations and analytical tools.

3.1 Theoretical Determination of Possible Interfacial Compound(s)

Table 3.1: Possible compounds expected to form in the Ti-Al-O system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Structure</th>
<th>Crystallographic Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>Hexagonal closed pack</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>--</td>
</tr>
<tr>
<td>Aluminum oxides</td>
<td>$\alpha$-Al$_2$O$_3$</td>
<td>Hexagonal closed pack</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>Titanium aluminides</td>
<td>TiAl$_3$</td>
<td>Tetragonal</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-TiAl</td>
<td>Tetragonal</td>
</tr>
<tr>
<td></td>
<td>Ti$_3$Al</td>
<td>Hexagonal closed pack</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>TiO$_2$ (rutile)</td>
<td>Tetragonal</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ (anatase)</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Magnelli phase</td>
<td>Ti$_2$O$_3$</td>
<td>Hexagonal closed pack</td>
</tr>
</tbody>
</table>

Possible compounds and phases in the Al-Ti-O system that could form by the interaction between Al and TiO$_2$ are listed in Table 3.1. Formation of an interfacial compound was assessed using thermodynamic principles. Standard thermodynamic principles were used with appropriate assumptions to determine the lowest energy
state of the existing system by calculating free energy states of possible compounds in association with the interacting components of Al and TiO$_2$. The compounds resulting in the lowest energy state were the ones that were expected to form during the reaction. Elements and compounds of interest during the interaction between Al and TiO$_2$ are listed in Table 3.1.

Thermochemical data of the relevant compounds of interest at specific temperatures and other thermodynamic parameters are not available. Gibb’s free energy equations listed by $FactSage^{TM}$ were checked for validity by using the equations at specific temperature values. The free energy values were compared with those from the JANAF-Thermochemical Tables (the more widely accepted thermochemical data). Calculations that show the verification of thermochemical data from $FactSage^{TM}$ with that from the JANAF-Thermochemical Tables are presented in Appendix I. It was shown that the values obtained by using the equations in $FactSage^{TM}$ compared well with the values reported in the JANAF-Thermochemical Tables and were thus used for calculations.

The experiments performed were largely classified into two categories:

- The first set of samples was the powder samples used for preliminary X-ray diffraction analysis.
- The second set of samples was the film-substrate samples that were treated to specific conditions.

The treated samples were further characterized to explain the results obtained using suitable analytical tools.
3.2 Experimental Reaction Model Parameters

The region of interest in the current research was exclusively the interface between Al and TiO₂ as is shown in Figure 3.1. The isothermal temperature chosen for the current study was 700°C due to the reason stated in Section 2.6. Samples that were treated to elevated temperature were soaked for an extended period of time so that the interaction between film and substrate could generate a sufficiently wide interfacial region to allow investigation.

![Diagram of interfacial region](image)

Figure 3.1: Schematic of the interfacial region as the area of interest for the study.

3.3 Diffusion Couple Substrate Structure

The experiments were designed to study the extent of interaction between Al and TiO₂ particles. A diffusion couple experiment is the conventional way to study particle – particle interaction; therefore, a simple system consisting of a flat interface between the starting materials in the form of a diffusion couple was chosen. Vacuum deposition grade TiO₂ (99.9 % pure/ CERAC Inc.) was used as a 10 - 12 mm diameter
x 4 - 5 mm thick substrate. An aluminum (99.9% pure, CERAC Inc.) film about 4-5 μm thick was sputter deposited (Innovative Coatings LLC.) on the rutile substrate. Surface roughness of the substrates was less than one μm as was determined using AFM. The surface texture allowed adequate adherence of the film to the substrate after deposition. It is noted here that grains of TiO2 usually have stacking faults present at the surface of the grains that run into the interior of the grains;\textsuperscript{91,92} and the stacking faults usually terminate within the grains.

Figure 3.2 shows a schematic of Al deposition on a TiO\textsubscript{2} substrate. The film thickness of 4-5 μm was chosen so that the area of interaction of the X-ray beams would include the interface between Al and TiO\textsubscript{2}. 

![Figure 3.2. Schematic of 4-5 μ Al film sputter deposited on TiO\textsubscript{2} substrate sample.](image)
The film-substrate samples were treated at elevated temperatures for extended periods (9 and 36 hrs) of time. The diffusivity of O at 700°C into Al₂O₃ (1.8×10⁻²³ m²/second) was used to calculate the depth of diffusion for either of the diffusing species by using the well known equation:

\[ l = \sqrt{Dt} \]  \hspace{1cm} (3.3)

where \( l \) is the depth of diffusion for the diffusing species, \( D \) is the diffusivity of the diffusing species into substrate and \( t \) is the time required for diffusion. It was calculated that the diffusing species (oxygen) would travel a depth of about 50 nm, and 100 nm by exposing the sample to 700°C for 9 hours, and 36 hours respectively.

### 3.4 Identification of Interfacial Compound(s) Using XRD

Samples of powdered Al (atomized 325 ALCOA) were mixed thoroughly with TiO₂ (anatase) powder (Fisher Scientific Inc.) in a 4:3 molar ratio of Al:TiO₂. The 4:3 molar ratio of Al:TiO₂ was used so that there would be sufficient Al to reduce TiO₂ completely in the event that the oxidation-reduction reaction would go to completion as shown by Equation 3.4. Batches 15 mg in size were prepared by mixing 4.65 mg of Al powder with 10.34 mg of TiO₂ powder. The powder sample mixture was then loaded in a furnace maintained at 700°C in air. The powder sample was held at 700°C in the furnace for 9 hours to allow the TiO₂ to interact with the Al.

\[ 4Al + 3TiO₂ \rightarrow 2Al₂O₃ + 3Ti \]  \hspace{1cm} (3.4)

The powder mixture was loaded into the sample tray of the Philips X’Pert Pro MPD X-ray diffractometer for analysis. Powder diffraction was conducted in triplicate on different samples to check for repeatability. Diffraction scans ranged...
between 20 values 20° and 90°. The step size was 0.0167°; the time per step was 100.33 seconds; and the scan speed was 0.012° per second. The total time of scan per sample was 56 minutes and 53 seconds. Slow scans were performed between 20 values 36° and 40° to resolve closely spaced peaks. The film-substrate [Al-TiO₂ (rutile)] samples were analyzed using X-ray diffraction to determine the presence of new phases or compounds; either at the surface, or at the interface of the film-substrate samples. It was observed earlier that when the film-substrate samples were heated at elevated temperatures (700°C) the melted Al rolled off the surface resulting in a large loss of Al. Two film-substrate samples were then sandwiched together (see Figure 3.3) before heat treatment. The sandwiched samples were heated in a furnace preheated to 700°C and held at 700°C for 9, or 36 hours. The samples were cooled to room temperature by furnace cooling. The samples were gently detached from the sandwich arrangement, and the Al sides of the samples were used for X-ray diffraction analysis.

An unheated film-substrate sample was heated in-situ in an X-ray diffractometer and scanned by the X-ray diffractometer at regular intervals of temperature (400°C,
600°C, 650°C and 700°C). An in-situ scan experiment while heating samples in the X-ray diffractometer was performed to detect possible interactions between the film and substrate that could potentially result in the formation of a new metastable compound. The new compounds could later transform to a more stable state at equilibrium when cooled to room temperature. A Philips X’Pert Pro MPD X-ray diffractometer was used with an Anton PAAR XRK-900 high temperature stage to continuously monitor the film-interface-substrate at various elevated temperatures in air at near isothermal conditions. The objective of the experiment was to determine the temperature at which another phase could originate. Data about possible transformation of new phases and their transformation to more stable phases could be obtained. The continuous scan mode using a Cu $K_\alpha$ radiation with a step interval of 0.02° ($2\theta$) and a count time of one second/step was used to collect the data. The experiments were carried out in air. The PANalytical X-Pert Plus software was used to evaluate the peaks obtained from the diffraction spectra.
The Al – TiO₂ samples were loaded onto the high temperature stage of the Philips X’Pert Pro MPD X-ray diffractometer. The high temperature stage used a muffle furnace that heated the small sample space to a maximum of 900°C. The thermocouple used to measure the temperature of the sample was situated close to the surface of the sample. Also, the heating chamber had a relatively small volume that ensured the temperature measurement would be as close to accurate as possible.

3.5  Morphological Understanding of the Interface

3.5.1 Diffusion Couple Samples: Al – TiO₂ Film – Substrate Structure

A LEO model 1550 Field Emission Scanning Electron Microscope at 5 kV was used to investigate the two types of samples (film-substrate and powder samples).

The surface of the Al – TiO₂ (film – substrate) sample that was held at 700°C for 9 hours was compared to the surface of the unheated Al – TiO₂ (film – substrate) sample using the SEM. The morphology of the substrate-interface-film regions was compared before and after the samples were heated to an elevated temperature.

3.5.2 Powder Mixture Samples

The second set of samples was a mixture of Al powder and either Al₂O₃ powder, or TiO₂ powder. Al/Al₂O₃ and Al/TiO₂ powder mixture samples were heated to 1200°C in either air (oxidizing environment), or He (non-oxidizing environment) (99.999% purity). The Al – Al₂O₃ powder interfaces were investigated using the SEM. The Al/A₂O₃ powder samples were studied using the
SEM to check whether the Al$_2$O$_3$ shell outside the Al particles would break to allow liquid Al to interact with the particles outside of the shell.

3.6 High Resolution Identification of the Interfacial Phase(s) and Compound(s)

The interface of the film-substrate samples was investigated using the TEM to compare morphology before and after heating to an elevated temperature for different periods of time. Cross-sectional slices were prepared from both heated and unheated samples, then Focused Ion Beam (FIB) was used to mill thin sections at the sample interface. The sample preparation procedure is explained below in this section.

Attempts were made to prepare samples for TEM studies by the traditional route (dimpling followed by ion milling); but a significant amount of copper re-deposited onto the dimpled surface. The deposited copper interfered with the existing material; so it was decided to use the FIB to prepare the samples for the TEM study. The procedure for TEM sample preparation using FIB is explained below.

Figure 3.4. The FIB – SEM position of sample relative to the two beams.
The FEI HELIOS NANOLAB 600 dual beam focused ion beam was used here to mill small slices at the interface of the sample treated to elevated temperature. *Figure 3.4* shows the sample with two beams in the FIB system: one beam is used to mill material from the surface of the sample; while the other is used like an SEM to scan the working surface.

A suitable spot on the sample containing the interface was selected. The platinum FIB probe was then inserted and the required amount of platinum was deposited on the surface of the sample (see *Figure 3.5*). An Ar-ion beam was used to mill material on both sides of the platinum strip as shown in *Figure 3.6*. The sideways-cut that was employed to mill material from both sides of the platinum strip is called a “staircase cut” (see *Figure 3.6*). A “cleaning cut” was then used to clean the edges on both sides of the platinum strip and remove most of the re-deposited material from the area of interest.

![Figure 3.5. Platinum strip deposited on the surface of the sample to be FIBed.](image)
Figure 3.6. Material milled away from both the sides of the platinum strip using the FIB.

Figure 3.7. OmniProbe® is attached to the area of interest after which the sides are cut.
The bottom of the strip was detached from the bulk sample using the “undercut” beam. The sample strip of interest was attached to the bulk only at the sides. Figure 3.7 shows an OmniProbe® attached to the area of interest after the sides of the strip were milled with the ion beam. The strip of interest was supported only by the OmniProbe® and was entirely detached from the bulk sample. The sample was next attached to a grid using platinum as shown in Figure 3.8 and was then ready to be thinned as required for TEM applications [regular Bright Field (BF) and Dark Field (DF) imaging, lattice imaging, STEM etc.]

Material was removed from either side of the sample slice to make it thinner. A lower current ion beam was employed for this purpose so as to avoid excessive erosion that could damage, or even destroy, the sample beyond use for TEM investigation. Figure 3.9 shows the side view of a thinned sample and Figure 3.10 shows the top view. The sample was thinned to about 150 nanometers to make it suitably electron transparent to be probed with the TEM, and was then ready to be studied.

Figure 3.10. Stages of attachment of the sample strip onto grid using the OmniProbe® and platinum using the FIB.
Figure 3.9. Side view of thinned sample showing the platinum layer, the thin film layer, the interface and the substrate attached to the grid.

Figure 3.10. Top view of sample thinned to about 150 nanometers.
4.0 RESULTS AND DISCUSSION

Al is usually covered with a thin passive layer of Al₂O₃ due to oxidation. The current chapter explains the results obtained from experiments when Al₂O₃ in contact with Al was heated to elevated temperatures (1000°C to 1300°C). Film-substrate and Al powder samples covered with Al₂O₃ were studied and results at elevated temperature are explained here.

This chapter also describes the results obtained during the high temperature experiments when Al and TiO₂ interacted for extended periods of time. Formation of the interfacial region and identification of the interfacial compound(s) are explained. A theoretical model for the formation and growth of the interfacial compound is postulated and proof of various elements of the model are explained in this chapter using thermodynamics and analytical tools like the SEM, FIB and TEM.

4.1 Effect of Temperature on the Al₂O₃ Shell around Al

The surfaces of alumina substrates coated with Al were compared before and after heating to elevated temperatures. The surfaces appeared to be different after being heated to 700°C. The surface of the sample before it was heated to 700°C was uniformly covered with aluminum as shown in Figure 4.1 (a). After the sample was heated to an elevated temperature, the surface of the sample was observed to have some regions that were not evenly covered with Al as shown in Figure 4.1 (b). At about 660°C, aluminum melts. It was observed that the Al apparently melted and formed into spheres of different sizes on the Al₂O₃ substrate surface as seen in Figure 4.1 (b). During cooling to room temperature there was no means to observe morphological changes on the substrate and interface.
Figure 4.1 (c) shows the EDS spectra from the dark and bright areas in Figure 4.1 (b) of the Al₂O₃ (substrate) – Al (film) samples. The EDS spectra showed that the dark area contained significantly more oxygen than the bright areas indicating that the dark areas (substrate) were not entirely covered with Al (metal) after the sample was heated to 700°C. The interface between the Al₂O₃ substrate and the Al film was identified from a fractured sample (Figure 4.2) after the sample was heated and cooled. The region between the substrate and the interface in one case, and the film
and the interface in the other, were not easy to observe using the SEM. The thickness of the film was observed to be reduced from 4 – 5 µm to about 2 - 3 µm after heat treating and cooling as measured by SEM.

![Figure 4.2. Interface between substrate and film identified for a fractured sample.](image)

Al powder samples having an average particle size of 50 µm diameter were heated in air. Figure 4.3 (a) and (b) are microstructures of the surface of an Al particle after the sample was heated to 1300°C at a heating rate of 10°C per minute. The surface showed several web-like structures. The web-like structure on the surface of the Al powder sample seemed much like the ones observed by Nychka and Clarke as described in Section 2.5.1.1.

The oxide shell was apparently broken (Figure 4.3) due to the difference in the coefficient of thermal expansion between Al and Al₂O₃. The Al₂O₃ layer on Al would not have expanded at the same rate as Al. The coefficient of thermal expansion of Al and Al₂O₃ are 24×10⁻⁶ /°C and 8×10⁻⁶ /°C respectively at room temperature. Hence Al would have expanded more rapidly than Al₂O₃ at elevated temperature. It was
interesting to observe the texture on the surface of the Al₂O₃ shell [Figure 4.3 (b)] around the Al particle which is indicative of the direction of growth of the oxide on the metal surface. Figure 4.4 shows an Al particle after it was heated to 1300°C and cooled to room temperature. The Al₂O₃ outer shell was observed to be ruptured and only the hollow remains of the shell was observed. After the Al₂O₃ shell ruptured, it would be possible for the liquid Al to flow out of the shell at the elevated temperature and interact with the components outside the shell.

![Figure 4.3: Features on the surface of Al particle after heating to 1300°C.](image)

The Al that is usually covered with a layer of Al₂O₃ would then be in contact with the compounds that are not encompassed by the Al₂O₃ passivating shell and could thus interact at elevated temperature.
4.2 High Temperature Interaction between Al and TiO₂

4.2.1 Identification of Interfacial Compound(s) Using XRD: Powder Samples

*Figure 4.5* shows the X-ray diffraction pattern of a powder mixture (4:3 mole ratio of Al:TiO₂) soaked for 9 hours at 700°C and cooled to room temperature by furnace cooling. The spectrum in *Figure 4.5* shows peaks corresponding only to the reactants Al and TiO₂. There was no indication of any other phases in this spectrum.
A slow scan X-ray diffraction was performed between 2-θ values 25º and 50º in an attempt to resolve peaks that were either close to one another or those that were superimposed on another. Figure 4.6 (a) shows the slow scan X-ray spectrum. Additionally, an ultra slow scan [Figure 4.6 (b)] was performed to resolve the peak at 38.5º. Both slow scan attempts failed to reveal any other phase or compound other than the reactants Al and TiO₂.

Figure 4.5. X-ray diffraction spectrum for 4:3 molar ratio of Al:TiO₂ powder heated to 700ºC for 9 hours.
Figure 4.6 (a) Slow and (b) ultra slow X-ray diffraction spectra respectively of Al and TiO₂ powder heated to 700°C for 9 hours.
4.2.2 Identification of Interfacial Compound(s) Using XRD: Film – Substrate Samples

The XRD spectrum of the unheated film-substrate sample is shown in Figure 4.7. The spectrum shows only Al and TiO₂ peaks as was expected. The film-substrate sample was heated to 700°C, soaked for 9 hours and cooled to room temperature by furnace cooling. The sample surface was then scanned using the X-ray diffractometer.

Figure 4.7. X-ray diffraction spectrum of an unheated Al-TiO₂ film-substrate sample.

The XRD spectrum of the unheated film-substrate sample is shown in Figure 4.7. The spectrum shows only Al and TiO₂ peaks as was expected. The film-substrate sample was heated to 700°C, soaked for 9 hours and cooled to room temperature by furnace cooling. The sample surface was then scanned using the X-ray diffractometer.
Figure 4.8 shows the diffraction pattern of the heated sample. α-Al₂O₃ peaks were observed in the spectrum along with the Al and TiO₂ peaks.

The volume of interaction of the X-ray beam incorporates the surface of the film, the interface between the film and the substrate, and a part of the substrate. α-Al₂O₃ could have formed on the surface of the sample (Al-side) that is exposed to air or it could form at the interface between Al and TiO₂ during the oxidation-reduction reaction between the reactants at elevated temperature. XRD data is not sufficient to determine the details about the formation of the observed α-Al₂O₃. X-ray diffraction is not an appropriate technique to determine the location of oxide formation.
Figure 4.9 shows the X-ray diffraction spectra of a sample that was scanned at several temperature intervals while heating to 700ºC. It was observed that Al peaks disappeared from the scans at 650ºC and above. Since Al melts at about 660ºC and is no longer in the crystalline state, the peaks representing certain planes of Al atoms disappeared beyond the melting point of Al. There was no indication of new phases or transition phases forming as the Al peaks disappeared.

A possible explanation for the absence of a new phase can be explained by a small amount of interfacial compound (if it exists) constituting the thin interfacial region. The interfacial region can occupy only a fraction of the volume of interaction between the X-ray beam and sample volume. The X-ray detector receives the majority of the diffracted beam signal from the film or substrate region. The small fraction of the diffracted beam would not be significant compared to the diffracted beams from the other areas. Therefore, a bulk characterization technique like X-ray diffraction is not a suitable characterization technique to analyze the interface for determination of the existence of an interfacial compound. A more location specific analytical tool is required to examine the interface and determine the interfacial compound.
4.3 Morphological Understanding of the Interfaces

4.3.1 Diffusion Couple Film – Substrate Structure

The unheated film-substrate Al-TiO$_2$ sample was fractured and the cross section was studied (Figure 4.10) using SEM to compare nature and morphology of the interface with a sample that was heated to 700°C and soaked for 9 hours.
The demarcation at the interfacial region, shown in Figure 4.10, which separates the film from the substrate in an unheated sample, is well defined. The Al deposited on the substrate is in the form of a columnar structure.

Figure 4.10. Interface of an unheated Al-TiO₂ sample.

Figure 4.11 shows the fractured surface of a film-substrate Al-TiO₂ sample that was heated to 700°C and soaked for 9 hours. The interface between the film and the substrate was clearly visible. The thickness of the film was reduced after the sample was soaked for 9 hours at 700°C as observed in the micrograph in Figures 4.12 and 4.13. Electron dispersive spectroscopic (EDS) analysis at the substrate, interface and film semi-quantitatively revealed the atomic composition at the respective locations after the sample was heated at 700°C for 9 hours. EDS data confirmed that the film had Al and little Ti while the substrate side had Ti. The interface contained a significant amount of both Al and Ti.
The sandwich structures for the unheated and the heated samples were prepared as shown in Figures 4.12 and 4.13. The thickness of the film was measured before and after soaking at 700°C. It was observed that the thickness of Al on the surface of the TiO₂ substrate was reduced after the sample was heated to 700°C and cooled to room temperature.

Figure 4.11. Cross section of fractured Al-TiO₂ film-substrate sample heated to 700°C for 9 hrs and electron dispersive spectra (EDS) of the corresponding regions.
The interface between the Al film and TiO₂ substrate is clearly identified in both unheated and heated samples. The interface appears to be a defined demarcation at the resolution offered by the SEM.
4.3.2 Surface and Interfacial Morphology for Powder Mixture Sample

An Al and TiO$_2$ powder mixture was heated under oxidizing (air) and non-oxidizing conditions (flowing He). It was observed that the Al film was not entirely reacted for the formation of the oxide even when the sample was heated in air; proof of which is also shown in Section 4.4.

The surfaces of Al powder particles that were heated in air were compared with those heated in He at 10ºC per minute to an elevated temperature (shown in Figure 4.14). Figure 4.15 shows the surfaces of two similar samples heated to a temperature range between 700ºC and 1000ºC at 40ºC per minute in both air and He. The small TiO$_2$ particles were observed on the surface of the large Al particles in all cases after the powder mixture was heated to the elevated temperature and cooled to room temperature. The surfaces of all four samples had web-like structures. The lines (of web-like structures) were thicker on the samples heated in air than on the ones heated in He (Figure 4.14) possibly due to greater oxidation occurring along the grain boundaries (represented by web) when heated in air. Another observation is that more TiO$_2$ particles seemed to be adhered to the Al particles heated at the faster heating rate when heated in air. Not much difference in surface morphology was observed for samples heated at a slow or fast heating rate when in a He environment.
It is thus observed that experiments performed in air and He are similar as far as interaction between Al and TiO$_2$ are concerned; except that the extent of interaction appeared greater in air as compared to a He environment. Figure 4.16 shows micrographs of the cross sections of an Al particle that was heated with TiO$_2$ powder and FIBed from the surface towards the interior of the sample.
The surface of Al is observed to be flatter for the sample heated at 10ºC/minute (lower heating rate) than the surface of Al for the sample heated at 40ºC/minute (faster heating rate). The interface region was observed to be too thin to allow determination of the composition using EDS with either SEM or FIB. The interface between the Al film and TiO₂ substrate was identified for both the unheated sample and heated sample, using SEM and FIB. It was concluded that the interface appeared to be a ‘line’ at the resolution limit offered by the SEM. It was also concluded that area specific techniques with better resolution was needed to further study the interface to identify the compound at the interface and also determine the nature of the interface.

Figure 4.16. Cross section of the Al particle milled from the surface towards the interior for sample heated at (a) 10ºC/minute and (b) 40ºC/minute.

The surface of Al is observed to be flatter for the sample heated at 10ºC/minute (lower heating rate) than the surface of Al for the sample heated at 40ºC/minute (faster heating rate). The interface region was observed to be too thin to allow determination of the composition using EDS with either SEM or FIB. The interface between the Al film and TiO₂ substrate was identified for both the unheated sample and heated sample, using SEM and FIB. It was concluded that the interface appeared to be a ‘line’ at the resolution limit offered by the SEM. It was also concluded that area specific techniques with better resolution was needed to further study the interface to identify the compound at the interface and also determine the nature of the interface.
An analytical technique like transmission electron microscopy (TEM), was required to determine the compound formed at the interface and to explain the mechanisms involved in the formation of the interfacial compound. The selective area electron diffraction (SAED) analysis capability that is area specific was an added advantage to the high resolution imaging on the TEM.

4.4 High Resolution Identification of the Interfacial Phase(s) and Compound(s)

Details about the nature of the interface, particularly the morphology, continuity of the interfacial region, shape of the edges on both sides of the interfacial region, and the compound(s) that form the interfacial region was studied using the TEM.

4.4.1 Interface Comparison

The interface of an unheated Al-TiO₂ film-substrate sample was considered the basis of comparison with a similar sample treated to 700°C for 9 hours. A small section of the interface between the film and the substrate (that contains the interface and parts of the film and the substrate) was milled using a focused ion beam; and the interface was examined to study the morphology of the interface using TEM. Figure 4.17 shows the TEM micrograph of the unheated sample milled at the interface.
The film (having columnar grains of Al) above the boundary of the interface, was confirmed to be $fcc$-Al by electron diffraction of a selected area on the film within the dark dotted circle shown in Figure 4.17. Bright rings (shown in the upper right inset in Figure 4.17) resulted from electron diffraction of several grains of $fcc$-Al with different orientations. An area on the other side of the interfacial boundary was selected, as shown by the white dotted circle in Figure 4.17 for electron diffraction. The diffraction pattern showed a dot pattern (lower left corner inset in Figure 4.17) that was indexed to the [213] zone of the tetragonal TiO$_2$ rutile structure. The indexed diffraction patterns from the regions separated by the boundary of the interface (as shown in Figure 4.17) on the micrograph confirmed that the two regions were the film and substrate.
respectively for the unheated sample. The interface was a clear thin boundary that separated the film from the substrate.

Figure 4.18: TEM micrograph of the interface of the Al-TiO$_2$ film-substrate sample heated for 9 hours at 700°C.

The interface for the Al-TiO$_2$ film-substrate sample that was soaked for 9 hours at an isothermal condition of 700°C is shown in Figure 4.18. The top dark region in the micrograph is the platinum that was deposited to facilitate milling of the material for the TEM sample preparation using a FIB. The dark dotted circle indicates the area that was selected for electron diffraction using a suitable aperture on the TEM. The dot pattern shown in the inset (bottom left corner) was the indexed diffraction pattern representing $f$cc-Al. A similar region (Al-film) for the unheated sample, as shown in Figure 4.17, showed a ring pattern of various $f$cc planes of Al. Al would have melted on the substrate when the sample was heated to a temperatures beyond 660°C and on cooling it would have re-solidified as large grains. The area selected for diffraction on the upper side of the interface
was perhaps a single large grain and not several grains as in the unheated sample (Figure 4.17). This explains why a dot pattern was obtained in the heated sample while a ring pattern was obtained for an unheated sample. Similarly, the diffraction pattern of a selected area (shown by the white dashed circle) from an area below the interface was indexed to the tetragonal-TiO₂ structure as shown in Figure 4.18.

The film and the substrate regions were clearly identified for the treated sample. The difference in the nature of the interface between the unheated and the heated sample as observed in the microstructures (in Figure 4.19) was that the interface in the unheated sample was a clear line of demarcation while that for the heated sample was an area with a finite width.

Figure 4.19: Comparison of interface regions between the unheated and heated Al-TiO₂ film-substrate samples.
Figure 4.20 represents a Scanning Transmission Electron Microscopy (STEM) micrograph (obtained on FEI TITAN TEM) of the interface of the Al-TiO₂ film-substrate sample that was soaked for 9 hours at 700°C. The inset shows the same interfacial region using an objective lens in a 420 Philips TEM. The white dotted lines in both micrographs indicate the boundary between the interfacial region and the TiO₂ substrate. The boundary between the interfacial region and the TiO₂ substrate was distinctly wavy in shape; while the boundary between the interfacial region and the Al film (indicated by solid line) was more or less straight, except for the small rugged edges that protruded from the
interfacial region into the Al side. The nature and occurrence of the upper boundary is explained in the latter part of this chapter. The interfacial region was continuous at the interface between the film and substrate. Certain regions in the interface were observed to be thin while other regions appeared to be thick as shown in Figure 4.21. The sites where the interfacial region rise to the highest point (blue arrows) were the thinnest regions at the interface; while the sites where the wavy region dipped to form a concave curve (green arrows) were thick regions as shown in Figure 4.21. Although the interface seemed smooth with one straight boundary and one wavy boundary as shown in the side view (Figure 4.21), it was observed that the interface was not as smooth throughout as was observed at a different location at the interfacial region (Figure 4.20).

4.4.2 Interface Compound Identification

The interfacial region was clearly located as explained in the previous section and information about the nature of interface was described in Section 4.4.1. The
current section describes the identification of the compound present in the interfacial region.

*Figure 4.22* shows a specific site of the interfacial region where the interfacial compound(s) protruded into the Al film above the interfacial layer.

![Figure 4.22](image)

**Figure 4.22:** Part of the interfacial region protruded into the Al layer. The circle marks the region where the aperture was placed for electron diffraction.

*Figure 4.23 (a)* shows an electron diffraction pattern of the circular area marked on *Figure 4.22*. The pattern was indexed to the [213] zone of a tetragonal TiAl compound, commonly known as the TiAl phase. The McTempas® software was used to generate an electron diffraction pattern that matched within reasonable limits with the one shown in *Figure 4.23 (a)*. Parameters used for generation of the pattern were obtained from the JCPDS file number 00-005-0678. The lattice parameters were: \(a = b = 3.976 \, \text{Å}, \ c = 4.0490 \, \text{Å}; \ \alpha = \beta = \gamma = \)
90°. The calculated d-spacing for generated planes, as shown in Figure 4.23 (a), were $d(\overline{1}1\overline{1}) = d(11\overline{1}) = 2.31 \text{ Å}$, $d(1\overline{2}0) = 1.78 \text{ Å}$, $d(2\overline{2}0) = 1.63 \text{ Å}$. Figure 4.23 (b) represents translation of the $(1\overline{1}1)$ plane (encircled white dot) to the center for dark field imaging.

Figure 4.23. (a) Indexed electron diffraction pattern of the circled region on Figure 4.22; (b) $(1\overline{1}1)$ plane displaced to the center for dark field imaging on the 420 Philips TEM.

Figure 4.24 (a) represents a dark-field image of the $(1\overline{1}1)$ plane marked on Figure 4.23 (b). All the grains that were oriented in the $(1\overline{1}1)$ direction are highlighted in the micrograph. Thus it was concluded that the grain in Figure 4.22 that protruded out of the interfacial region was the TiAl grain having a $(1\overline{1}1)$ orientation. It was important to know whether the presence of the TiAl phase was an isolated occurrence or whether more regions of the interface contained the TiAl phase. In order to verify the presence of additional TiAl along the interface,
the low magnification dark-field TEM micrograph of the same plane [(1\bar{1}1) plane] was observed to check whether more regions along the interface were highlighted. 

Figure 4.24 (a) is the dark-field high magnification TEM micrograph of the protruded grain shown in Figure 4.22. Figure 4.24 (b) represents the low magnification dark-field TEM micrograph (1\bar{1}1) at the interface. It was interesting to note that regions all along the interface were highlighted. It was also noted that there were certain areas [as shown in Figure 4.26 (b)] within the TiAl interfacial region that were dark. It is possible that the dark regions could be one of the two:

(i) dark regions were the TiAl compound with an orientation other than (1\bar{1}1).

(ii) a different compound formed at the interface other than the TiAl, eg. Al₂O₃ that was also expected to form due to the release of oxygen during the reduction of TiO₂ by Al.

The presence of the dispersed dark regions in the TiAl interface is explained later in this chapter.
Figure 4.25 shows the bright-field TEM micrograph of a second region along the interface between the film and the substrate of the same sample as mentioned above. The micrograph shows a grain that protruded from the interface into the Al film. An area (circular mark) on the protruded grain as shown in Figure 4.25 was selected using the selective area aperture on the TEM for electron diffraction. The inset in Figure 4.26 shows the ‘selective area diffraction pattern’ from the marked area in Figure 4.25. The dotted line represents the boundary between the TiO$_2$ substrate and the interfacial region. The solid line represents the boundary between the Al film and the interfacial region.
Figure 4.25: Bright field TEM micrograph of the interfacial region showing few grains protruding into the Al side. The circle marked shows the area selected for electron diffraction.

Figure 4.26: TEM dark field image of the marked plane from inset. The dotted line shows the TiO$_2$/interfacial region.
The diffraction pattern obtained from the circled region in Figure 4.25 did not have a low index of symmetry (simple symmetry); therefore it was not indexed. It was interesting to note that the boundaries on both sides of the interfacial region were consistent with previously explained observations. The interaction was consistent along the interface.

Figure 4.27: (a) TEM Bright field micrograph of interfacial region with inset showing indexed electron diffraction pattern of marked area; (b) TEM dark field micrograph with (02-1) plane lit-up at the interface.

The diffraction pattern obtained from the circled region in Figure 4.25 did not have a low index of symmetry (simple symmetry); therefore it was not indexed. It was interesting to note that the boundaries on both sides of the interfacial region were consistent with previously explained observations. The interaction was consistent along the interface.
Another region along the interface on the same Al-TiO$_2$ film-substrate sample is shown by the TEM micrograph in Figure 4.27 (a). The two interfaces are marked with dotted and solid lines as shown in the micrograph. The width of the interface measured from 200 to 250 nm. The interface seemed to be continuous. The inset shown in Figure 4.27 (a) is the indexed selective area diffraction pattern of the circular area marked (within the interfacial region) in the figure on the left side.

The diffraction pattern in the inset of Figure 4.27 (a) was indexed to the [021] zone of the tetragonal $\gamma$-TiAl phase. The McTempas® software was used to generate an electron diffraction pattern that matched within reasonable limits to the one shown in Figure 4.27 (a). The parameters used to generate the pattern were obtained from JCPDS file number 00-005-0678. The lattice parameters used from the JCPDS file were: $a = b = 3.976$ Å, $c = 4.0490$ Å; $\alpha = \beta = \gamma = 90^\circ$. The calculated d-spacing of the generated planes, as shown in Figure 4.29 (a), were $d(02\bar{1}) = d(02\bar{1}) = 1.78$ Å, $d(12\bar{1}) = d(12\bar{1}) = d(1\bar{2}\bar{1}) = d(1\bar{2}\bar{1}) = 1.63$ Å, $d(2\bar{1}\bar{1}) = 1.63$ Å, $d(\bar{1}00) = 3.98$ Å. The circled spot in the inset in Figure 4.27 (a) represents the shifting of the $(02\bar{1})$ plane (circle marked on white spot) to the center for dark field imaging.

Figure 4.27 (b) shows the dark field image of the $(02\bar{1})$ plane marked in Figure 4.27 (a). The image highlights all the grains that are oriented in the $(02-1)$ direction. Thus it was concluded that the grains shown in Figure 4.27 (b) are the TiAl grains having (02\bar{1}) orientation.
Figure 4.28 collectively showed the different regions (Regions I and III) that show the presence of TiAl at the interface. It was concluded that the interface between the Al film and TiO₂ substrate for a heated sample was not a defined boundary but a ‘region’ with a definite width. It was concluded from the TEM results that the interfacial region was continuous along the interface, though not uniform in thickness. It was also concluded that the interfacial region consisted of TiAl and possibly a second phase.

Figure 4.28: Regions I, II and III along the interface of the Al-TiO₂ film-substrate sample that was exposed for 9 hours at 700°C.
4.5 Theoretical Determination of Possible Interfacial Compound(s)

Chapter 2 (Section 2.5) described the results reported for the reaction between Al and TiO$_2$ for various conditions of temperature, pressure and sample preparation history. Some researchers have reported the formation of a TiAl$_3$ phase while others have reported the formation of a $\gamma$-TiAl phase. The current section employs thermodynamic principles to explain the formation of a TiAl phase instead of the other competing ordered phases (Ti$_3$Al, TiAl$_3$ and the Al dissolved Ti phases).

4.5.1 Free Energy Calculations (assuming stoichiometry in compounds)

\[
\Delta G^\circ = 2[G^\circ_{Al_2O_3(973)}] + 3[G^\circ_{Ti(973)}] - 4[G^\circ_{Al(973)}] - 3[G^\circ_{TiO_2(973)}] = -448153 \text{ Joules}
\]

\[
\Delta G^\circ = -306640 \text{ Joules}
\]

\[
\Delta G^\circ = -648733 \text{ Joules}
\]

\[
\Delta G^\circ = -812677 \text{ Joules}
\]

Figure 4.29: Possible reactions at the Al-TiO$_2$ interface.
Four possible reactions at the interface are listed below as shown in Figure 4.29.

\[ 4\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Ti} \quad 4.5.1 \]

\[ 5\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + \text{Ti}_3\text{Al} \quad 4.5.2 \]

\[ 7\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{TiAl} \quad 4.5.3 \]

\[ 13\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{TiAl}_3 \quad 4.5.4 \]

Equation 4.5.1 represents the complete reduction reaction of TiO\(_2\) by Al to form Ti and Al\(_2\)O\(_3\). Equations 4.5.2, 4.5.3 and 4.5.4 represent the formation of Al\(_2\)O\(_3\) and Ti\(_3\)Al, TiAl or TiAl\(_3\) respectively when Al and TiO\(_2\) react at 700ºC. The free energy calculations shown in Figure 4.29 assumed that the compounds were stoichiometric and were perfectly ordered compounds; although in reality, that may not be the case. The phrase “compounds are stoichiometric” in the above statement means that the sublattices are precisely determined by the stoichiometry. For example, if the compound TiAl was assumed to be stoichiometric, it would be assumed that a 1:1 ratio of Ti:Al atoms was maintained in the compound. The phrase “perfectly ordered compound” for TiAl means that the Al and Ti species strictly occupy the Al and Ti sites respectively and no other sites. The above explanations suggest that deviation from “stoichiometry” and from “perfect ordering” would result in the formation of substitutional atoms in the compound structure. Free energy values for the
compounds were calculated as described in Chapter 3. Polynomial equations obtained from FactSage™ used for the free energy calculations were first tested by comparing the values obtained. Values of temperatures were used in the polynomials and the resulting free energy values were compared with values listed in the JANAF tables. The reference state chosen for all the free energy calculations was 298.15°K at atmospheric pressure. Free energy calculation for the random mixing of Ti and Al on each sublattice was described by Kattner et al. as was shown in Section 2.7.1.3. Useful information for the solution of Equation 2.6.1 was found in the report by Kattner et al. Certain information about calculating the free energy for any composition of Al and Ti in the TiₙAlₘ system that is critical in obtaining the quantities \( n_{Ti}^{1}, n_{Al}^{1}, n_{Ti}^{2}, \) and \( n_{Al}^{2} \) (from Equation 2.1) was not available. The above mentioned data was the only missing information that was needed to plot free energy of the ordered Ti-Al intermetallic compounds as a function of composition at any temperature.

The free energy for the reaction represented by Equation 4.5.4 seemed to be the most negative. Caution should be exercised before concluding that the TiAl₃ phase is thermodynamically favorable to form by the reaction represented by Equation 4.5.4. It is inappropriate to compare the free energy of reactions involving different amounts of reactants as shown in Figure 4.29. A fair comparison of the free energy of the above mentioned reactions was made possible by considering the free energy of a reaction per mole of the reactant consumed. The free energy of each reaction was divided by the respective number of moles of combined reactants as is listed in Table 4.1. The comparison was
legitimate since in each case, the free energy was normalized to the amount of the reactants consumed. The reaction represented by Equation 4.5.3, has the highest negative value of free energy and therefore was the most energetically favorable for formation. Results from the thermodynamic calculations are listed in Table 4.1 and are in agreement with experimental findings described in the current research as explained in section 4.4.

Table 4.1: Free energy comparison of reactions at 700ºC.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta G^\circ$ per mole of combined reactant consumed</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5.1</td>
<td>- 64000</td>
</tr>
<tr>
<td>4.5.2</td>
<td>- 38300</td>
</tr>
<tr>
<td>4.5.3</td>
<td>- 64800</td>
</tr>
<tr>
<td>4.5.4</td>
<td>- 50800</td>
</tr>
</tbody>
</table>

4.5.2 Formation of the Thermodynamically Favored $\text{Ti}_x\text{Al}_y$ Compound

Li et al.\textsuperscript{66} reported the calculated free energy as a function of composition at 1100ºC K as shown in \textit{Figure 2.6} in \textit{Section 2.7.1.3}. The free energy (without the assumption of perfectly ordered Ti-Al compounds (Ti$_3$Al, TiAl and TiAl$_3$) could not be calculated at 700ºC due to lack of key information. The thermodynamics of the Ti-Al system is solved and reported at 1100ºC by Li et al. An explanation for the preference of formation of the TiAl phase at 1100ºC can be presented using the thermodynamic data by Li et al. Data was not reported at 700ºC.

A free energy curve for TiO$_2$ (green curve) was superimposed on \textit{Figure 2.6} shown in \textit{Chapter 2} (see \textit{Figure 4.30}). The lateral position of the free energy curve for TiO$_2$ was significant due to the small amount of Al dissolved in TiO$_2$ at
elevated temperatures. The vertical position of the curve is not significant for the explanation below, hence the free energy curve for TiO₂ was chosen as shown in Figure 4.30.

![Figure 4.30: TiO₂ –free energy curve superimposed on Ti-Al Gibbs free energy diagram calculated at 1100°C by Li et al. for explanation of the preference of formation of TiAl compound.](image)

The point on the free energy curve of TiO₂, through which the tangent passes, defines the amount of Al dissolved in TiO₂ (about one mole percent) as shown by the dotted line extended to the X-axis in Figure 4.30. Tangents on the free energy curves of Ti-Al compounds are shown by blue lines in Figure 4.30. Blue tangents (on free energy curves of Ti-Al compounds) are parallel to the tangent to the free energy curve for TiO₂. The red arrows represent the drop in the free energies due to the formation of the respective compounds. The magnitude in the free energy drop due to the formation of the Ti-Al compound is indicated by the red curly
bracket on the right hand side of Figure 4.30. The TiAl compound has the maximum drop in free energy among the other shown Ti\textsubscript{x}Al\textsubscript{y} compounds and hence was most energetically favorable for formation. In other words free energy change for the formation of TiAl (\(\Delta G_{\text{TiAl}}\)) is greater than the free energy change for the formation of Ti\textsubscript{3}Al (\(\Delta G_{\text{Ti3Al}}\)) and \(\alpha\)-Ti (\(\Delta G_{\alpha\text{Ti}}\)) in that order. Theoretical calculations show that TiAl is most favored for formation at 1100°C. A similar proof is not furnished at 700°C in this thesis. There is no published literature that suggests transformation of a formed Ti\textsubscript{x}Al\textsubscript{y} compound to another compound unless a change of composition in the system is forced. Thus the result of the calculation at 1100°C, indicating the formation of TiAl, would be true at 700°C (as was observed experimentally in Section 4.4).

It was concluded from theoretical calculations that TiAl was the interfacial compound energetically favored for formation at elevated temperature by using thermodynamic principles and making appropriate assumptions. At elevated temperature, the formation of TiAl was favored over the formation of other Ti\textsubscript{x}Al\textsubscript{y} compounds and is in agreement with the experimental results.

4.6 Mechanism of Interaction at the Interface: A Proposed Model

The interaction between Al and TiO\textsubscript{2} yields TiAl and possibly another compound at the interface. The interfacial layer was found to be continuous; but the thickness was not uniform. The interfacial region physically separated the surfaces that were in contact with each other. Such an interfacial layer could act as a self-formed barrier against the diffusion of the reacting species towards each other; for example, the diffusion of Al towards the TiO\textsubscript{2} substrate, and the diffusion of Ti or O towards the
Al film. The self formation of the diffusion barrier between the reacting components would be useful in structural applications and in electronic device applications. It was necessary to understand the nucleation and growth of the interfacial compound that would be the outcome of the interaction between the two surfaces in contact at elevated temperature.

4.6.1 Nucleation and Growth Model

The current section describes a model to explain the formation and growth of TiAl at the interface under the conditions explained above. The mechanism of formation and growth of TiAl can be explained by four steps. Each step is described in detail below.

4.6.1.1 Step 1

![Figure 4.31: A schematic of melted Al in contact with TiO$_2$ substrate. Surface grain of TiO$_2$ has stacking faults.](#)

The TiO$_2$ grains at the interface are such that part of the grain is exposed to the Al-film as shown in Figure 4.31. The ‘purple’ lines that run from the interface (surface of TiO$_2$ grains) into the substrate represent stacking faults in the TiO$_2$
grains as shown in Figure 4.31. The stacking faults were present at the surface and they run towards the interior of the grains and terminate within the grain (usually observed for stacking faults). Figure 4.31 illustrates a schematic of the interface that corresponds to the TEM micrograph (Figure 4.32). The schematic shows a TiO$_2$ grain at the interface between the substrate and the film. The stacking faults are shown to initiate at the surface and terminate in the interior of the grain. Al, in contact with the substrate would have melted when the temperature of the sample reached 660ºC.

![Figure 4.32: The TiO$_2$ grain at the surface of the substrate in contact with the Al-film. The surface grain has stacking faults that are present at the surface and run into the interior of the grain.](image)

4.6.1.2 Step II

Liquid Al on the surface of the TiO$_2$ substrate diffuses towards the interface and into the TiO$_2$ grains. The diffusing species usually prefers high diffusivity paths because of the higher energy involved. The stacking faults are high energy
paths that are present on the surface of the TiO$_2$ grains. The second step involves diffusion of Al into the TiO$_2$ grains through the stacking faults (preferred high energy diffusivity paths) as shown in the schematic above (Figure 4.33).

![Figure 4.33: A schematic showing Al diffusing into the TiO$_2$ substrate through stacking faults.](image)

Although the stacking faults seem an obvious route for Al to diffuse into TiO$_2$ grains, it has yet to be proven that stacking faults are indeed the path that Al would take to diffuse into TiO$_2$. Figure 4.34 shows the interfacial region of the Al-TiO$_2$ film-substrate sample that also shows several stacking faults on the TiO$_2$ side of the interface. The micrograph in Figure 4.34 was obtained through STEM mode on the FEI TITAN.

The stacking faults are marked by blue dotted lines and labeled in the micrograph in Figure 4.35. Some stacking faults were observed to pass through the area marked with dotted circles as shown in Figure 4.35. An electron energy loss spectroscopy (EDS) line scan was performed along the red line (shown in Figure 4.35) to semi-quantitatively determine the atomic composition at the
points along the line. The EDS data was superimposed on the micrograph as shown in Figure 4.35.

![Figure 4.34: Interface of Al-TiO₂ sample exposed to 700°C for 9 hours. Several stacking faults are observed on the TiO₂ side.](image)

Some of the common problems encountered while using EDS data from the TEM and the steps taken here to counter those problems are described. TEM samples were prepared by milling a thin region at the interface between two surfaces using the focused ion beam. The FIB used gallium ions as the milling material. Usually some of the milled material re-deposited on the surface of the sample. Although a “cleaning cut” was employed to clean the re-deposited material, it did not always clean the surface completely. Unwanted oxygen-containing material could be left behind on the surface of the TEM sample that could render the results of the EDS scan useless if the data is not used carefully. It is common to have a slight variation in the thickness of the sample over short
distances. The differences in the thickness of the sample are usually sensitive to data counts for EDS scans even over a few nanometers. The data would show that the relative amount of a particular element would be greater in a thicker region even though the percent element concentration is uniform over the entire sample. In order to counter such problems a couple of steps were taken:

i. An EDS scan was performed at the Al-film region (where no oxygen was expected to be found) and at the oxide region. The scan did not show any trace of oxygen on the Al-film side; while it showed a significant amount of oxygen on the oxide side. This indicated that the sample surface did not have re-deposited oxide-containing material and was clean for EDS.

ii. A ratio of intensities was used that would account for the varying thicknesses from one point on the sample to the other.

Figure 4.35: EDS line spectrum with Al/Ti intensity ratio superimposed on STEM micrograph (from marked region in Figure 4.34).
The blue dashed lines in Figure 4.35 trace the stacking faults in TiO\textsubscript{2} grains. The plot superimposed on the micrograph as shown in Figure 4.35 shows the variation of intensity ratio of Al/Ti along the distance. The data at the dotted circular marked regions showed a higher intensity of Al/Ti compared to the other regions with data points indicating a high Al concentration at the marked regions at the stacking faults. The result validates Step II of the model that explained the stacking faults as high diffusivity paths for diffusion of Al into TiO\textsubscript{2} grains. The stacking faults, in a similar sample that was exposed to 700\textdegree C for 36 hours, were inspected for consistency. Figure 4.36 (a) shows a bright-field micrograph of the interface of the sample soaked for 36 hours at 700\textdegree C. Figure 4.36 (b) represents the same location taken in STEM mode.

![Figure 4.36: (a) Bright field micrograph representing the interfacial region of Al-TiO\textsubscript{2} film-substrate sample soaked for 36 hours at 700\textdegree C; (b) Micrograph in STEM mode of the marked area in (a). The red line indicates the EDS line scan.](image-url)
The EDS line scan shown in Figure 4.37 revealed a higher concentration of Al at and near the stacking faults. The data points are marked (dotted circles) in sets (points with similar characteristics) and labeled in Figure 4.37. The marked point 1 indicated a high Al/Ti ratio and very low O/Ti ratio. This showed that the marked point 1 was a high Al-diffusion path. The marked points 2 indicated a very low O/Al intensity ratio but a fairly high Al/Ti intensity ratio. The marked point 2 was thus the TiAl region. The marked points 3 and 4 represent areas in the TiAl region with a higher concentration of Al. The marked point 5 was possibly an unreacted TiO₂ grain with a high O/Al intensity ratio and a low Al/Ti intensity ratio. The marked point 6 represents a TiO₂ grain that possibly had transformed to the TiAl grain but contained an excess amount of oxygen from the local reduction of TiO₂. The marked points 7 possibly indicate the TiAl region similar to the one
described as the point 2. The marked point 8 represents the TiO₂ grain as explained for point 5. The above explained points in the Al-TiO₂ samples soaked for 9 and 36 hours verify that Al chose the stacking faults in the TiO₂ grains as preferred paths for the diffusion into the TiO₂ grains at the elevated temperature.

4.6.1.3 Step III

The Al that diffused into the TiO₂ grains through the stacking faults, as explained above in Step II, reacted with TiO₂ at the stacking fault locations as shown in Equation 4.6.3.1 and Equation 4.6.3.2. The Equations 4.6.3.1 and 4.6.3.2 represent intermediate stages during the reaction between Al and TiO₂.

Step III hypothesized that the reaction sites are close to the stacking faults.

\[
\text{TiO}_2 \xrightarrow{\text{Al}} \text{Ti} + 2\text{O} \quad \ldots \ (4.6.3.1)
\]

\[
\text{Ti} + \text{Al} \rightarrow \text{TiAl} \quad \ldots \ (4.6.3.2)
\]

Figure 4.38: A schematic that summarizes the mechanism of formation of TiAl at regions close to the stacking faults in Step III.

Step III shows the reaction of Al with TiO₂ during the reduction of the TiO₂ to form Ti and O. The Al further reacts with the Ti, which was released by the
reduction of TiO$_2$, to form TiAl. The mechanism explained in Step III is represented in the schematic shown in Figure 4.38.

4.6.1.4 Step IV

Step IV represents the growth of the TiAl compound (the green area represented in Figure 4.39) after formation of the interfacial TiAl compound at the regions close to the stacking faults in the TiO$_2$ grains. The boundary between the interfacial region and the TiO$_2$ substrate was shown to be distinctly wavy.

![Figure 4.39: Schematic showing the growth of TiAl into the TiO$_2$ grains in Step IV.](image)

The mechanism of growth of the TiAl compound at the interface into the TiO$_2$ substrate in Step IV is indicative of the reason for the wavy shape of the TiAl interfacial region (boundary between interfacial region and TiO$_2$ substrate). The region around the stacking faults in the TiO$_2$ grains was occupied by the TiAl compound. The TiAl compound was not expected to form at regions that were isolated from the stacking faults due to the lack of availability of Al at those
regions. Figure 4.40 (a) shows the interface of an unheated sample for the purpose of comparison with the interface of a similar sample that was soaked at 700°C for 9 hours as shown in Figure 4.40 (b). The microstructure shows the wavy boundary between the interfacial region and the TiO₂ substrate and hence is in agreement with the growth mechanism in Step IV.

![Figure 4.40: (a) A straight interface of the unheated sample; (b) a wavy interface at the TiO₂/interfacial boundary in the Al-TiO₂ sample soaked for 9 hours at 700°C.](image)

\[
7\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{TiAl} \quad 4.5.3
\]

Equation 4.5.3 represents the reaction between Al and TiO₂ as explained in Section 4.5. The equation shows that three moles of TiO₂ react with seven moles of Al to form three moles of TiAl and two moles of Al₂O₃. The molar volume of TiO₂ without dissolved Al was calculated to be \(18.8\, \text{cm}^³\). The molar volume of TiAl was calculated to be \(18.7\, \text{cm}^³\). TiAl occupied slightly less volume (\(0.01\, \text{cm}^³\) per mole) than TiO₂. It is possible that the difference in volume can be explained as pores at the interface.
Large pores were present at the boundary between the interfacial region and the TiO$_2$ substrate in the sample that was soaked at 700ºC for 36 hours as shown in *Figure 4.41(a)*. *Figure 4.41(b)* shows a different location along the interface of the same sample. The large pores that were located along the boundary between the interfacial region and the TiO$_2$ substrate were such that the wavy boundary demarcation was distinctly visible as a wide wavy gap (*Figure 4.41*).

**700ºC, 36 hrs**

![Figure 4.41: (a) Large pores at the interface for Al-TiO$_2$ sample soaked for 36 hrs at 700ºC; (b) Pores along the boundary between the interfacial region and TiO$_2$.]

It was thus concluded from the analysis of the interface using the TEM that the formation of the interfacial compound (TiAl) could be described in the following way:

**Step I:** Melted Al was in contact with the TiO$_2$ substrate at elevated temperature.

**Step II:** Al diffused into the TiO$_2$ substrates more quickly through the stacking faults in the TiO$_2$ substrate.
Step III: At the stacking faults, TiO₂ is reduced by Al to form Ti and O. Ti reacts with Al near the stacking fault sites to form TiAl.

Step IV: The interfacial region containing TiAl grows near the stacking fault sites into the TiO₂ substrate.

4.7 An Explanation for the Oxygen Released during the Al – TiO₂ Reduction Reaction

The amount of oxygen that would have been released during the reduction of the TiO₂ would be twice as much as the amount of TiAl formed. The formation of each TiAl molecule would have been preceded by the reduction of one molecule of TiO₂ that would have released one Ti and two O atoms. The current section lists four possible ways to explain the presence of oxygen that would have been released during the reduction of TiO₂. The results thus far indicated that the following equilibrium equation was probably responsible for the interfacial reaction:

\[
7\text{Al} + 3\text{TiO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{TiAl}
\]

Figure 4.42: A schematic of the interface between Al and TiO₂ after the interaction between Al and TiO₂.
There were four possible ways that O released during reduction of TiO$_2$ at the interface as shown in Figure 4.45 could be present:

i. The O could be dissolved in the TiAl layer.

ii. The O released at the boundary between the interfacial region and the TiO$_2$ below could diffuse through the interfacial region and settle as a solution in the Al.

iii. Oxygen could be present at the

- interface between TiAl and TiO$_2$
- interface between TiAl and Al
- grain boundaries between the TiAl grains

iv. The O could combine with the Al that diffuses into the TiO$_2$ grains, to form Al$_2$O$_3$.

4.7.1 Possibility I (Presence of Oxygen in Layer Containing TiAl)

The possibility of the presence of O in the TiAl interfacial layer was considered, as shown in the schematic below (Figure 4.43). Section 2.8 in Chapter 2 explained that a theoretical model has been developed by Lefebvre et al. that indicated that there is little solubility of O in the ordered Ti$_x$Al$_y$ compounds which included Ti$_3$Al, TiAl and TiAl$_3$. The model by Lefebvre et al. calculated the solubility of TiAl and the line compound TiAl$_3$ to be almost “zero”.

Figure 4.43: Schematic showing possibility of the presence of oxygen in the interfacial layer containing TiAl.

The current section explains the results from the analysis to detect the presence of oxygen at the interfacial region. The challenge posed by the analysis was to be able to create a sample that had a sufficient interfacial region that was created by the reaction that could be characterized suitably for the presence of O. Also, a spectroscopic technique like EDS was preferred to a diffraction technique for such an experiment. Figure 4.44 showed a bright-field image at the interface of the Al-TiO\textsubscript{2} film-substrate sample that was soaked for 9 hours at 700\textdegree C. Arrow-tips in the micrograph point to the specific points on the sample where the electron beam from the TEM collected the EDS data to semi-quantitatively determine the composition at each point. Small holes were observed at the end of most arrows that indicated the exact location where the EDS data were collected.
Figure 4.44: Points from the EDS line scan beginning from the TiO$_2$ side through TiAl interface into Al for the Al-TiO$_2$ sample soaked for 9 hours at 700ºC.

The EDS spectra that were collected from the interfacial region (spanning from points 1 to 18) that contained TiAl compound is shown in Figure 4.45.
Figure 4.45: EDS spectra from points 1 to 20 on Figure 4.44.
As explained in Section 4.6.2 in the current chapter, the ratios of the intensities from the EDS data were used to reduce errors due to non-uniform thickness of the TEM samples. Figure 4.46 shows the EDS intensity ratios O/Al and Ti/O that were superimposed on the TEM microstructure at the interfacial region. The appropriate superimposition of the EDS data on the microstructure facilitated an easy comparison of the intensity ratios.

![Figure 4.46: O/Al and Ti/O EDS intensity ratios superimposed on TEM microstructure at the interface of the Al-TiO₂ sample soaked for 9 hours at 700°C.](image)

The interfacial region-TiO₂ boundary (dotted line) is shown at the left side of the micrograph. The right side of the micrograph (dark region) was almost completely Al as is seen from the EDS intensity ratios shown in Figure 4.46. The interfacial layer that contained the TiAl compound clearly showed intermediate levels of the O/Al as well as the Ti/O EDS intensity ratios that indicated the presence of O in the TiAl containing interfacial layer. A very high value of the
O/Al intensity ratio at the left side of the micrograph possibly was due to the proximity to the TiO\textsubscript{2} side. The data points around the vicinity of the points 10 and 15 showed a very high O/Al and very low Ti/O intensity ratios. A careful examination at those regions showed a grain-like structure. The high O content at those regions could have been due to the presence of Al\textsubscript{2}O\textsubscript{3} grains in the interfacial region. The determination of the presence of Al\textsubscript{2}O\textsubscript{3} grains in the interfacial region will be dealt with, in detail in Section 4.7.4.

The current section explains the presence of O in the interfacial layer containing the TiAl compound. Although contrary to the explanation provided by Lefebvre et al., it could be that O would be present in the metastable state in the TiAl compound and not in a “dissolved” state as a solid state solution of O in TiAl. The presence of O in the metastable state could possibly explain the presence of well dispersed Al\textsubscript{2}O\textsubscript{3} grains (if any in the interfacial region) that could have precipitated when the sample was exposed for longer periods of time at an elevated temperature. The O could be in the metastable state thus forcing the formation of Al\textsubscript{2}O\textsubscript{3}.

### 4.7.2 Possibility II (Presence of Oxygen in Al Layer)

*Figure 4.47* represents a schematic of the presence of O in the Al-layer during the interaction of Al with the TiO\textsubscript{2} substrate at 700°C.
The presence of O in the Al-layer as a solid solution of O in Al or otherwise was not thermodynamically favorable as explained in Section 2.7. Section 2.7 described the report by Kubaschewski and Hopkins and Weast about the formation of an oxide that was thermodynamically more favorable than the formation of a solid solution of O in Al. The results from the EDS characterization that was explained in Section 4.8.1 also confirmed that O was not present in the Al layer. The points labeled 19 and 20 in Figure 4.46 showed that very little or no oxygen was dissolved in the Al layer. Due to the above mentioned reasons it was safe to conclude that O would not exist in the Al film layer.
4.7.3 Possibility III (Oxygen at the Interface Boundaries and Grain Boundaries)

Figure 4.48 shows a schematic representation of the presence of O at the interfacial layer-TiO$_2$ substrate boundary, the Al layer-interfacial layer boundary, and the TiAl grain boundaries, during the interaction of Al with TiO$_2$ at an elevated temperature.

Figure 4.48: Schematic showing possibility of presence of oxygen at various interfaces and TiAl grain boundaries.

The boundary between the interfacial region, and Al and the grain boundaries between the TiO$_2$ grains were thin (few nanometers). It was a challenge to focus an electron probe well within the interfacial boundary, or within a TiAl grain boundary in order to characterize the grain boundary composition using the EDS. It is usually challenging to maintain the probe focus within grain boundaries since grain boundaries are not always two dimensional and also they need not
necessarily be straight but could have curves that could render the spectroscopic results invalid. The above mentioned challenges do not rule-out the possibility of the presence of O in the above mentioned regions.

### 4.7.4 Possibility IV (Oxygen Reacts with Al in TiAl to Form Al$_2$O$_3$)

Figure 4.49: Schematic showing possibility of presence of Al$_2$O$_3$ grains in the interfacial region containing TiAl grains.

Figure 4.49 shows the presence of Al$_2$O$_3$ grains schematically in the interfacial region containing TiAl. It has been reported by Zhang et al. (as described in Section 2.8) that Al$_2$O$_3$ grains do not form instantly when Al interacts with TiO$_2$ to form an aluminide.

The small grain-like features observed in Figure 4.44 were examined for the presence of Al$_2$O$_3$. Figure 4.50 shows a region having the grain-like features (curly brackets) at the interface that contained the TiAl grains in the Al-TiO$_2$ sample that was soaked for 9 hours at 700°C.
The usual route to characterize a compound or a phase with such a microscopic size (about one micron) is to select the subject with an aperture in the TEM for electron diffraction. The grains in the Al-TiO$_2$ sample were about an order of magnitude smaller than one micron and hence it would be difficult to select a suitable area on the grain (as in Figure 4.50). An indirect way was thus employed to determine the structure of the grains.

A thin TEM sample was used to examine the grain-like feature at a very high magnification in the FEI-TITAN TEM. The particles were crystalline in nature as a regular lattice arrangement was observed at a high magnification. Figure 4.51
shows the high magnification micrograph of the grain observed using the FEI-TITAN TEM.

![Micrograph of grain observed at the interfacial region containing TiAl](image)

**Figure 4.51**: TEM micrograph of grain observed at the interfacial region containing TiAl shown in Figure 4.50.

The regions marked 1, 2 and 3 are shown in *Figures 4.52, 4.53 and 4.54* respectively at very high magnification. *Figures 4.52, 4.53 and 4.54* are high resolution TEM micrographs that reveal the lattice arrangement of atoms within the crystal structure. A software attachment with the FEI – TITAN allowed for the selection of a square region that showed the lattice image and then processed the image-data using ‘Fourier Transformation’. The software converted the atomic arrangement data to a diffraction-pattern quite similar to the dot-pattern that is usually representative of an electron diffraction pattern. Insets in each of *Figures*
4.52, 4.53 and 4.54 show the ‘Fourier Transformed’ dot-patterns that were indexed as an ordinary electron diffraction pattern would have been indexed.

Figure 4.52: High resolution lattice image of region 1 in Figure 4.51. Inset is the indexed ‘Fourier transformed’ pattern.

The square shaped area that was selected was faintly visible in Figure 4.52. The dot-pattern generated from the selected area by performing a ‘Fourier Transformation’ of the selected area of the image was indexed to the [110] zone of the rhombohedral structure of Al₂O₃. The lattice parameters used for matching the rhombohedral structure of Al₂O₃ were obtained from the JCPDS file # 00-
The lattice parameters were: \( a = b = 4.75 \, \text{Å}, c = 12.97 \, \text{Å}; \alpha = \beta = 90^\circ, \gamma = 120^\circ \).

Figure 4.53: High resolution lattice image of region 2 in Figure 4.51. Inset is the indexed ‘Fourier transformed’ pattern.
The insets in the above two figures are the dot-patterns that were generated by performing a ‘Fourier Transformation’ of the corresponding lattice images from the selected areas in the Figures 4.53 and 4.54. The dot-patterns were indexed to the [113] zone and the [121] zone of the rhombohedral structure of Al₂O₃ respectively. It is thus concluded that Al₂O₃ grains form when Al is in contact with TiO₂ at 700ºC and soaked at the elevated temperature for an extended period of time.
5.0 CONCLUSIONS

The current chapter presents the conclusions drawn from the results discussed in the previous chapter.

5.1 Effect of Temperature on the Al$_2$O$_3$ Shell Around Al

Al particles that are usually covered with a passivating layer of Al$_2$O$_3$ can be quickly heated to allow aluminum to be released and interact with other compounds that are present.

5.2 Morphological Understanding of the Interfaces

The interface between an Al film and TiO$_2$ substrate was identified for both an unheated sample and heated sample using SEM and FIB. It was concluded that the interface appeared to be a defined boundary, a ‘line’, at the resolution limit offered by the SEM.

5.3 High Resolution Identification of the Interfacial Phase(s) and Compound(s)

It was concluded that the interface between the Al film and the TiO$_2$ substrate for a heated sample was not a simple ‘line’, but a region with a definite width. It was concluded from the TEM results that the interfacial region was continuous along the interface, though not uniform in thickness. It was also concluded that the interfacial region consisted of TiAl and possibly a second phase. The second phase was identified to be crystalline Al$_2$O$_3$. 

108
5.4 Theoretical Determination of Possible Interfacial Compound(s)

It was concluded from the theoretical calculations that TiAl was the interfacial compound favored for formation at elevated temperature instead of the formation of other Ti$_x$Al$_y$ compounds and is in agreement with the experimental results.

5.5 Mechanism of Interaction at the Interface: A Proposed Model

It was concluded, from the analysis of the interface using the TEM, that the formation process of the interfacial compound (TiAl) could be described in the following way:

**Step I:** Melted Al was in contact with the TiO$_2$ substrate at elevated temperature.

**Step II:** Al diffused into the TiO$_2$ substrates more quickly through the stacking faults in the TiO$_2$ substrate.

**Step III:** At the stacking faults, TiO$_2$ is reduced by Al to form Ti and O. Ti reacts with Al near the stacking fault sites to form TiAl.

**Step IV:** The interfacial region containing TiAl grows near the stacking fault sites into the TiO$_2$ substrate.

5.6 An Explanation for the Oxygen Released during the TiO$_2$ – Al Reduction Reaction

Contrary to the reports in literature, it was concluded that O was dissolved in TiAl at the interfacial region. It was also concluded that fine crystalline Al$_2$O$_3$ particles were present as a second phase in the interfacial region that contained TiAl.
The current research thus describes the extent of interaction between Al and TiO$_2$ at an elevated temperature and standard atmospheric pressure. The resulting interface is well characterized using suitable analytical techniques in order to satisfactorily identify the interfacial compounds and explain the formation of growth of the interfacial region. Theoretical calculations for the formation of the interfacial compound are in agreement with the experimental results.
6.0 Future Work

The mechanism of formation and growth of a TiAl interfacial layer was determined and understood. It would be useful as future work to employ the self-formation of the interfacial layer in several structural and electronic device applications.

As an example for the structural application, it is suggested to expose an appropriate ratio of a mixture of Al, TiO₂ and B₂O₃ powders to 700°C for an extended period of time before initiating the corresponding SHS reaction. A correlation between preheat time, thickness of interfacial layer, and kinetics of the SHS reaction could be drawn. The resultant SHS reaction product is expected to be significantly different in the morphology of its microstructure if the SHS reaction kinetics were inhibited by the formation and growth of an interfacial layer. Hence a correlation between the microstructure and kinetics of the SHS reaction can be drawn by an appropriate study of the formation and growth mechanisms at the interfacial layer between SHS reactants.

As an example for the electronic device application, it is suggested to expose a film-substrate sample (quite similar to a source-gate in MOSFET devices). Due to the continuing reduction in size of such electronic devices, the interfaces need to be carefully designed so that the diffusion of material from one region into another would prevent a short circuit. A self-formed interfacial layer as explained in the current thesis will help to reduce the harmful effects of diffusion.
REFERENCES


11. K. V. Logan, Private communication.


Validation of the Thermodynamic Parameters from FACTSage™ with the Corresponding Values from JANAF Tables

*FactSage™* (obtained from JANAF-Thermochemical Tables⁹²), a thermochemical software, has documented the free energy of several metallic and ceramic compounds, and the corresponding temperature range at which the equations are valid. Thermodynamic parameters like the $C_p(T)$s (specific heats), $H(T)$ (enthalpy), $G(T)$ (Gibb’s Free Energy) and $S(T)$ (entropy) are listed in *FactSage™*. Thermodynamic parameters are presented as equations for different temperature ranges. For example, the Gibb’s Free Energy $G(T)$ of a compound at a specific temperature range is given by an equation which is a function of temperature.

The calculation for $\Delta H(T)$ in Joules per mole for Al using the equation listed in the JANAF-Thermochemical Table⁹² for temperature range of 298 – 1200ºK is:

$$
H(T) = 5025.23805 + 45.9248180 * T + 5.232429015 * 10^{-6} * T^3 - 2850.41894 * \ln(T) - 0.514611719 * (T^{1.5}) + 2972635.17 * (T^{-2})
$$

Change in enthalpy for Al is calculated at 300K with 298.15K as the reference temperature.

$$
\Delta H(300) = H(300) - H(298.15)
$$

\begin{align*}
\Delta H(300) &= 45.924818[300 - 298.15] + 5.232329015*10^{-6}[300 - 298.15] \\
& \quad - 2850.4184[\ln300 - \ln298.15] - 0.514611719[300^{1.5} - 298.15^{1.5}] + 2972735.17[300^{-2} - 298.15^{-2}] \\
& = 48.44969253 \text{ Joules per mole.}
\end{align*}
The value reported in JANAF-Thermochemical Tables\textsuperscript{93} is 45 Joules per mole at 300K. The error is only 7.6\% of the value reported in the JANAF-Thermochemical Tables\textsuperscript{2} and is used in the calculations shown in Chapter 3.

Calculation of $\Delta H(T)$ in Joules per mole for aluminum using the equation listed in the JANAF-Thermochemical Table\textsuperscript{92} for temperature range of 298 – 1200ºK.

$$H(T) = 5025.23805 + 45.9248180 \times T + 5.232429015 \times 10^{-6} \times T^3 - 2850.41894 \times \ln(T) - 0.514611719 \times (T^{1.5}) + 2972635.17 \times (T^{-2})$$

Change in enthalpy for Al is calculated for 1000K with 298.15K as the reference temperature.

$$\Delta H(1000) = H(1000) - H(298.15)$$

$$\Delta H(1000) = 45.924818[1000 - 298.15] + 5.232329015 \times 10^{-6}[1000 - 298.15]$$

$$-2850.41894[\ln1000 - \ln298.15] - 0.514611719[1000^{1.5} - 298.15^{1.5}] + 2972735.17[1000^{-2} - 298.15^{-2}]$$

$$= 20.22 \text{ kJoules per mole.}$$

The value of enthalpy for Al reported in the JANAF-Thermochemical Tables\textsuperscript{93} is 30.806 kJoules per mole at 1000ºK. The error is 34.36\% of the value reported in the JANAF-Thermochemical Tables\textsuperscript{93} and is used in the calculations shown in Chapter 3.

The values obtained using the equations provided by FACTSage are comparable with the values reported in the widely accepted JANAF-Thermochemical Tables\textsuperscript{92} and hence can be used for calculations shown in Chapter 3.