

**EFFECT OF Nb, Cr and W ON THE HIGH TEMPERATURE OXIDATION
BEHAVIOR OF Ti-Al ALLOYS.**

By

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LIST OF ABBREVIATION

Ti-Al	Titanium Aluminides
VCR	Valence-Control Rules
ICDD	International Centre for Diffraction Data
HV	Hardness Vickers
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray spectroscopy
XRD	X-Ray Diffractometer
SiC	Silicon Carbide
FL	Fully Lamellar
NG	Near Gamma
NL	Near Lamellar
DP	Duplex
FCC	Face Centered Cubic
BCC	Body Centered Cubic
HCP	Hexagonal Close Packed

LIST OF SYMBOLS

γ	Gamma
α	Apha
β	Beta
O_2	Oxygen
W	Weight gain per unit area
K_L	Linear rate constant
t	Time
k_p	Parabolic rate constant
k_0	Related to the pre-exponential factor of the effective diffusion coefficient and to density of the scale
Q_{eff}	Activation energy
N_{Al}	Al Content
N_O	Oxygen Solubility
D_{Al}	Diffusivities of Al
D_O	Diffusivities of Oxyen
V_M	Volumes of TiAl per mole of Al
V_{OX}	Volumes Al_2O_3 per mole of Al
g	Conversion factor
wt	Weight
at	Atomic
λ	Wavelength
2θ	Diffraction angle
d	Lattice spacing
\AA	Armstrong
ρ	Density
m	Mass
V	Volume
F	Applied Load
d	Average length of Diagonal
π	phi

KESAN Nb, Cr dan W KE ATAS KELAKUAN PENGOKSIDAAN SUHU TINGGI ALOI Ti-Al

ABSTRAK

Penyelidikan ini memfokuskan kepada intermetalik Ti-Al dan sifat pengoksidaannya untuk digunakan sebagai bahan struktur pada suhu tinggi dalam industri permotoran, aeroangkasa dan turbin gas. Walaubagaimanapun, aplikasi aloi Ti-Al ini terpaksa dihadkan kerana sifat mekanik pada suhu rendah yang lemah dan ketahanan pengoksidaannya tidak bersesuaian untuk suhu melebihi 700-850°C. Bagi menghasilkan aloi Ti-Al untuk kegunaan pada suhu tinggi, penambahan unsur pengaloian seperti Nb, Cr dan W telah diberi perhatian. Di dalam kajian ini, aloi Ti-Al dihasilkan menggunakan relau arka peleburan. Kehadiran fasa, kajian mikrostruktur dan ujian kekerasan dianalisis menggunakan XRD, FESEM/EDX, ujian kekerasan Vickers dan ujian ketumpatan. Setelah dianalisis, sampel dipotong pada saiz 5x5x1 mm dan kemudiannya dioksidakan pada suhu 900°C selama 10, 30, 50, 80, 100 dan 200 jam. Perubahan berat selepas pengoksidaan akan diambil untuk melihat kadar pengoksidaan. Keputusan XRD menunjukkan kehadiran fasa γ -TiAl dan α -Ti₃Al sebagai fasa utama dan β -Ti and Al₂Ti sebagai fasa sampingan. Lapisan oksida yang terbentuk terdiri dari lapisan luar (TiO₂), lapisan pertengahan (rich in Al₂O₃) dan lapisan dalam (campuran TiO₂ + Al₂O₃ dengan unsur pengaloian yg ditambah). Penambahan (2 dan 10 at. %) Nb didalam siri 2 dan (2 at. %) W memberikan kesan yang baik terhadap peningkatan rintangan pengoksidaan. Manakala, penambahan 4 at. % Cr (siri 4) tidak memberi kesan malahan merbahayakan. Penambahan Nb dan Cr bersama di dalam Ti-48Al-Nb-Cr (siri 5) juga tidak menunjukkan kesan yang baik terhadap rintangan pengoksidaan. Kerintangan oksida yang paling tinggi dapat dilihat dalam siri 6 (Ti-48Al-Nb-W).

EFFECT OF Nb, Cr and W ON THE HIGH TEMPERATURE OXIDATION BEHAVIOR OF Ti-Al ALLOYS

ABSTRACT

This research is focused on intermetallic TiAl and their oxidation behavior for structural materials at high temperatures in automotive, aerospace and gas turbine industries. However, the commercial application of Ti-Al is currently limited by their insufficient oxidation resistance at temperature above 700-850°C. The addition of alloying elements such as Nb, Cr and W is significant in producing good Ti-Al alloys for high temperature applications. Ti-Al alloys were fabricated using arc- melting furnace. Then the phases present, microstructure evaluation and hardness test were characterized using XRD, FESEM/EDX and Vickers hardness. After the analysis, alloy samples were cut into size of 5x5x1 mm and then oxidized at 900°C for 10, 30, 50, 80, 100 and 200 hours. The weight gain was calculated in order to see the oxidation rate. XRD result shows γ -TiAl and α -Ti₃Al exists as major phases and β -Ti and Al₂Ti exists as a minor phases. The oxide scales formed is composed of outer layer (consist of TiO₂) intermediate layer (rich in Al₂O₃) and inner layers (consist of TiO₂ + Al₂O₃ mixed oxide with small amount of alloying element). The addition of (2 and 10 at.%) Nb in series 2 and (2 at.%) W in series 3 is effectively in increasing the oxidation resistance. Meanwhile, addition of 4 at.% Cr (series 4) does not give beneficial effect and it is harmful to substrate alloy. Addition of Nb and Cr together in quaternary Ti-48Al-Nb-Cr (series 5) also not give significant effect to oxidation resistance. The highest oxidation resistance is observed in series 6 (quaternary Ti-48Al-Nb-W).

CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter comprises of four subtitles which are background, problem statement, objective and scope of work. The background and problem statements lead to why this study is claimed out and what the advantages as well as the benefit of this study. The objectives are laid out and finally, the scope of work to summarize the work done in this thesis.

1.1 Background

Ti-Al alloys are one of the most important elements in today's material industries and show excellent potential for use as high temperature structural material for automotive, aerospace and other applications. These alloys have been studied extensively over the past 30 years and draw much attentions due to their excellent properties such as high yield strength at elevated temperatures, low density, advanced creep characteristics and excellent resistance to oxidation and corrosion as well as unique anomalous strengthening behavior (i.e strength increases with temperature). (Kim et al., 1995; Mishin and Herzig, 1999; Song et al., 2002; Yang and Wu, 2003; Peng et al., 2008). These combinations of properties make them very attractive to be widely used as components in turbine blades, turbine wheels, high-pressure compressor blades, impellers, exhaust valves, springs, driving shaft and rotating part of engine. Examples of several applications especially in automotive and aero-engine are shown in Figure 1.1 (Mishin and Herzig, 1999; Lutjering and William, 2003; Hu, 2001; Ngnekou et al., 2010).

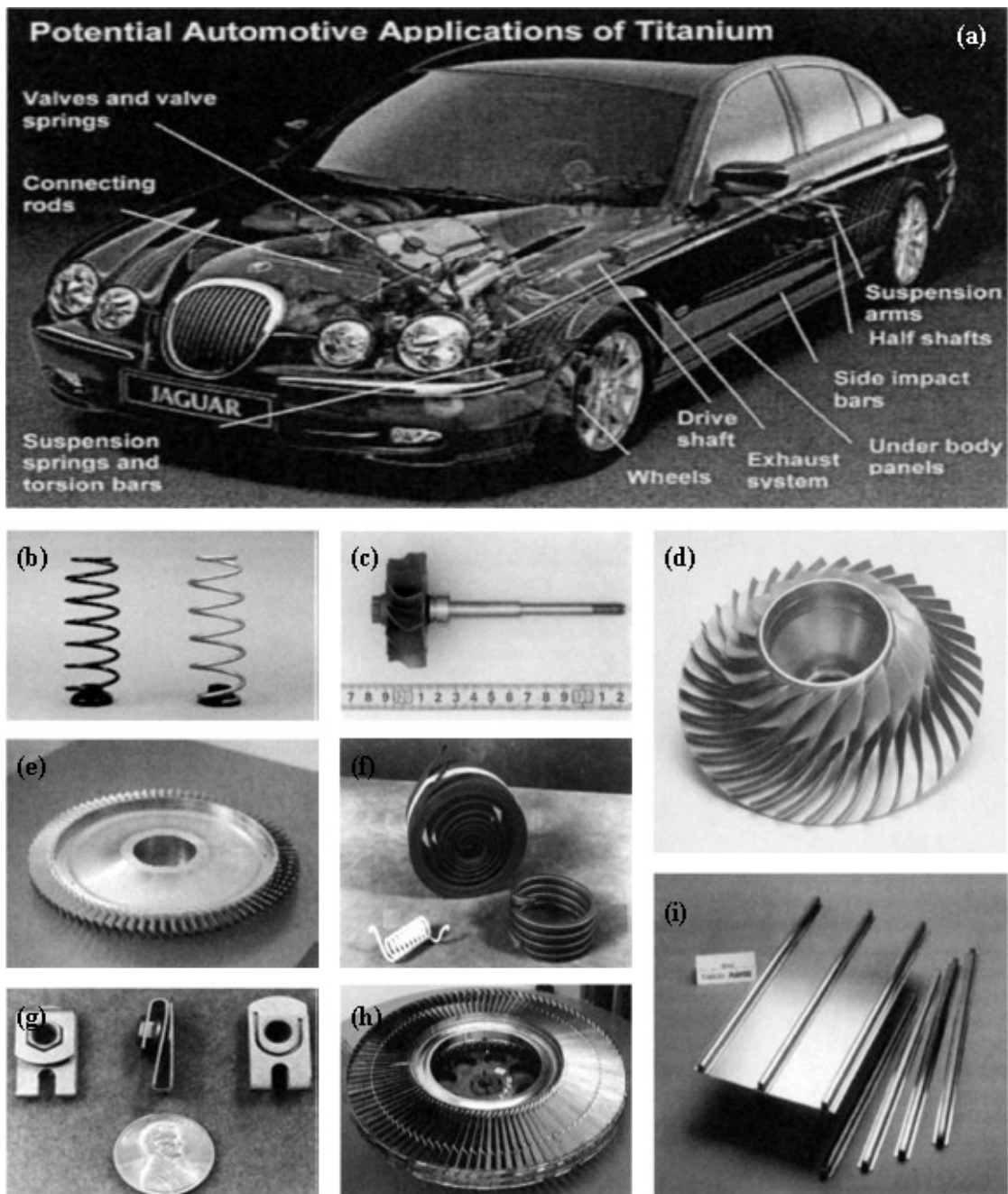


Figure 1.1: Example of several application of Ti-Al alloys in aerospace and automotive industries (a) potential automotive application of titanium demonstrated on a Jaguar S-type (b) suspension spring (c) turbocharger rotor (d) impeller used in small engine (e) high pressure compressor blisk (f) aircraft spring (g) nut clips used in air craft (h) low pressure turbine rotor (i) high stiffness structural panel (Lutjering and William, 2003).

There are four binary intermetallic compounds which are of interest in the Ti-Al system; Ti_3Al (α_2), TiAl (γ), TiAl_2 and TiAl_3 . From the point of view of structural-insensitive properties (the ratio of melting point to density), the attention has now been focused on γ -TiAl which is the most potential among the Ti-Al binary alloys phases. This new group of alloys seems to promise better oxidation resistance and mechanical strength at high temperature. The advantage of lighter density makes Ti-Al alloys ($4\text{-}7\text{g/cm}^3$) one of the potential candidates to replace steel and nickel based superalloys ($8\text{-}8.5\text{g/cm}^3$) in gas turbine engine applications (Lasalmonie, 2006). The γ -TiAl alloys (with compositions in the range 45-50at.% Al) are now used in practical applications in selected areas, mostly based on two-phase mixture of γ -TiAl and a small volume fraction of the α_2 - Ti_3Al phase. The two-phased mixtures of α_2 and γ have great potential due to their superior ratio of strength to density and good oxidation resistance at elevated temperature. Even though γ -TiAl alloys possess good high temperature properties, they often suffer in ductility at low temperatures, poor fabricability and insufficient oxidation resistance at temperatures beyond 700 - 850°C and thus limit their applications (Sunderkotter et al., 1997; Frohlich et al., 2006; Lu et al., 2007). A great deal of research effort has been directed towards improving these properties by adding ternary and quaternary alloying elements. The results presented in those studies for several elements appear to improve the high temperature oxidation resistance of Ti-Al alloys. Consequently, research is still needed to find a correct balance between the composition of Ti-Al-X (X=alloying elements) in order to fulfill their limitation and it can be used for specific well-defined applications.

There is several elements that can work as an alloying element such as niobium(Nb), tungsten(W), chromium(Cr), molybdenum(Mo), zirconium(Zr),

chlorine(Cl), phosphorus(P), boron(B), vanadium(V) and silicon(Si). Among these elements, Nb was identified as the most effective alloying element. Recent developments have shown that alloy containing 5-10 at.% Nb improve room temperature ductility and toughness, creep resistance and good oxidation resistance (Yoshihara and Muira, 1994; Jiang et al., 2002; Zhang and Appel, 2002; Liu et al., 2002). Meanwhile, addition of above 8-10 at.% Cr exhibit excellent oxidation resistance (Brady et al., 1995). However, some researchers reported that even at addition of above 4 at.% Cr can be beneficial to oxidation resistance and smaller amount of Cr (<4 at.%) are detrimental to the oxidation resistance (Fergus et al., 2002). Addition of W is also effective for improving the high temperature oxidation resistance of Ti-Al alloys. Ti-Al alloy containing 2 wt.% W exhibited a protective oxidation layer even after long-term oxidation up to 1000 hour at 900°C (Yang and Wu, 2003).

This study focused only on three alloying addition (Nb, Cr and W) in order to improve the oxidation resistance. According to previous works, the fundamental aspects of the oxidation behaviors, such as oxidation kinetics and oxide scale morphology of binary Ti-Al alloys have been investigated. The investigations revealed that oxidation of Ti-Al alloys generally leads to a formation of complex scale and have some unknown information about oxide scale. The microstructure evolution of Ti-Al alloys was also investigated where is the types of microstructures have been found to display different properties and strongly depend on chemical and phase composition. Generally, the microstructures of Ti-Al alloys formed in four types; single phase near γ , duplex, near lamellar and fully lamellar (Stroosnijer et al., 1997; Lamirand et al., 2002). The addition of various alloying element are essential to

obtain required types of microstructure and good balance of alloys properties (Chraponski, 2006). Thus, further investigation in the distribution of alloying element after oxidation is still needed (Lu et al., 2007).

In this present study, the work will consist of two major sections which are specimen fabrication using powder metallurgy method and experimental investigation to evaluate the properties of sample. Ti-Al alloys samples were produced by arc-melting process with several compositions (by adding alloying elements: Nb, Cr and W). All these alloys then went for oxidation test to determine the oxidation exposure for 50 and 200 hours. Characterization in order to observe microstructures, phase identification, cross-sectional of oxide scale, mass gain, hardness and density of the alloys were carried out.

1.2 Problem Statement

Owing to their low density and their good mechanical properties, Ti-Al alloys are considered having good potential for applications as structure materials. However, the oxidation resistance is still not sufficient for temperature above 750°C (Sunderkotter et al., 1997; Frohlich et al., 2006; Lu et al., 2007). Fox-Rabinovich et al., (2004) claimed that the mechanism of oxidation behavior of these alloys is very complicated and not very well understood. There are several factors mainly affecting the oxidation resistance such as types of microstructure, phases present, alloying composition, fabrication process and oxidation environment. In this study, the effect of ternary and quaternary alloying elements on the microstructure, phase present and oxide scales formation will be focused in order to overcome the limitation. At elevated temperature, layers of the oxides growth by the competitive oxidation of Ti

and Al which prevent the formation of continuous Al_2O_3 layer that would provide an effective oxidation barrier. Thus, the addition of Nb, Cr, W, Nb/Cr and Nb/W element into Ti-Al alloys is expected to promote the Al_2O_3 layer and improve the properties of Ti-Al alloys as well as oxidation resistance.

1.3 Objectives

The present work is conducted based on the following objectives:

1. To fabricate ternary and quaternary Ti-Al alloys with addition of (4- 10 at. %) Cr, (2-10 at. %) Nb and (0.5-10 at. %)W.
2. To investigate the effect of Nb, Cr and W addition to the oxidation behavior of Ti-Al alloys.

1.4 Scope of Work

This research focus on addition of different percentage of alloying element (Nb, Cr and W) into Ti-Al alloys in order to get the best composition for oxidation resistance. The experimental work involves several steps. The Ti-Al alloys were prepared by mixing using ball milling for 4-5 hours. The well-mixed powder was compressed into pellet and melted in arc-melting furnace to make ingot alloy. The ingot alloy was cut to square shape with dimension of 5x5x1 mm followed by oxidation exposure for 10, 30, 50, 80, 100 and 200 hours at 900°C inside muffle furnace. The phases present, microstructure examination and formation of oxides scales were studied using XRD and FESEM/EDX. After oxidation exposure, the weight gain of alloys was calculated in order to see the oxidation kinetic of Ti-Al alloys. The hardness value was determined using Vickers hardness.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter focuses on the theories and information related to Ti-Al alloys and their oxidation behavior. An introduction to Ti-Al is given at the beginning of the chapter, and followed by fundamental of oxidation behavior.

2.1 Introduction to Intermetallic Compounds

In general, intermetallic compounds is a structure in which the two or more metal constituents are in relatively fixed abundance ratios and are usually ordered on two or more sublattices, each with its own distinct population of atoms (Westbrook and Fleischer, 2000). They are also called, preferably, intermetallic phases. Their properties cannot be transformed continuously into those of their constituents by changes of composition alone, and they form distinct crystalline species separated by phase boundaries from their metallic components and mixed crystals of these components; it is generally not possible to establish formulas for intermetallic compounds on the sole basis of analytical data, so formulas are determined in conjunction with crystallographic structural information.

2.1.1 Titanium (Ti) and Aluminium (Al)

Titanium and its alloys are among the important elements in today's material industries and has become the new group of engineering materials that posses an extraordinary combination of properties. It has a low density (4.5g/cm^3), high melting point (1668°C), good strength, easily fabricated and excellent corrosion resistance

(Callister, 2000). Pure titanium exhibit an allotropic phase transformation from hcp (α) to bcc (β) as its temperature is raised at 882°C (Lutjering and William, 2003). The oxidation of Ti at high temperature is very difficult to understand due to the presence of oxide such as TiO, TiO₂ and Ti₂O₃.

Al and its alloys are among the practical elements to use in material industries because of their low density (2.7g/cm³), high electrical and thermal conductivities, and high corrosion resistance especially in some common environments (Callister, 2000). Al is light, non toxic, non-magnetic and easily formed by virtue of high ductility. Since Al has fcc crystal structure, the ductility is retained even at very low temperature. However, the low melting temperature which is about 660°C has restricted the maximum temperature usage of Al. In order to improve the lack of strength, this material can be alloyed with small amount of copper (Cu), magnesium (Mg), silicon (Si), manganese (Mn), chromium (Cr), titanium (Ti) and other elements that can improve the mechanical properties.

2.1.2 Titanium Aluminides (Ti-Al)

Ti-Al alloys show excellent potential for use in numerous aerospace and automotive applications due to their attractive mechanical and physical properties. It has been recognized that Ti-Al intermetallic alloys have low density, high modulus and also attractive high temperature mechanical properties such as tensile and creep strength (Dudziak et al., 2009). The oxidation resistance of the alloys can be improved by addition of third and fourth alloying element such as Nb, Cr and W. This part will be discussed in detail in section 2.4.

Due to low density and high melting point, this material has great potential to be used in advanced structural applications such as aircraft systems, or in any high temperature moving parts such as turbochargers for passenger vehicle diesel engines (Yang and Wu, 2003). This low density materials are important since they are used in advanced aerofoil design to reduce the structural weight of all other engine components design to support the load rotating blade set. Hence, there have been a great deal of works on these compounds beginning in 1953 and continuing up until now (Lutjering and William, 2003).

2.2 Titanium Aluminides System

2.2.1 Binary system

The intermetallic Ti-Al binary alloys receive a lot of interest because they offer good combination of high oxidation resistance and good mechanical properties at temperatures higher than those possible with conventional titanium alloys. In general, about 60-70 at.% Al is needed to form protective alumina layers during oxidation in air. However, these binary alloys are extremely brittle and this limits their applications (Moskalewicz et al., 2007). This observation is also reported by most of the researchers that reduction of Al content tends to increase the strength level but at the same time it decreases the ductility and oxidation resistance. Figure 2.1 shows widely accepted phase diagram of Ti-Al binary alloys (Mishin and Herzig, 2000).

There are four intermetallic compounds of interest in the Ti-Al system which are α_2 -Ti₃Al, γ -TiAl, Ti₃Al and TiAl₂ (Yang and Wu, 2003). The γ -TiAl intermetallics are most promising among these Ti-Al due to good high temperature

properties and already in use for automotive and aircraft application. Most of γ -TiAl alloys contained 47-56 at% of Al. These alloy phases will be discussed further in section 2.2.2.

Hu, (2001) reported that in Al-lean composition; binary compounds form as a result of solidification or heat-treatment. The solidification path of binary Ti-Al based alloys can be divided into three categories as state below:

- | | |
|--|--------------------|
| $L \rightarrow [\beta] + L \rightarrow [\beta+\alpha] \rightarrow [\alpha] \rightarrow [\alpha_2] \rightarrow [\alpha_2+\gamma]$ | ≤ 45 at. % Al |
| $L \rightarrow [\beta] + L \rightarrow [\beta+\alpha] + L \rightarrow [\beta + \alpha] + \gamma \rightarrow [\alpha] + \gamma \rightarrow [\alpha_2+\gamma]$ | 46 – 49 at. % Al |
| $L \rightarrow [\alpha] + L \rightarrow [\alpha] + \gamma \rightarrow [\alpha_2] + \gamma$ | 49 – 55 at. % Al |

The portion of Ti-Al binary phase diagram relevant to solidification is schematically shown in Figure 2.1 (Mishin and Herzig, 2000).

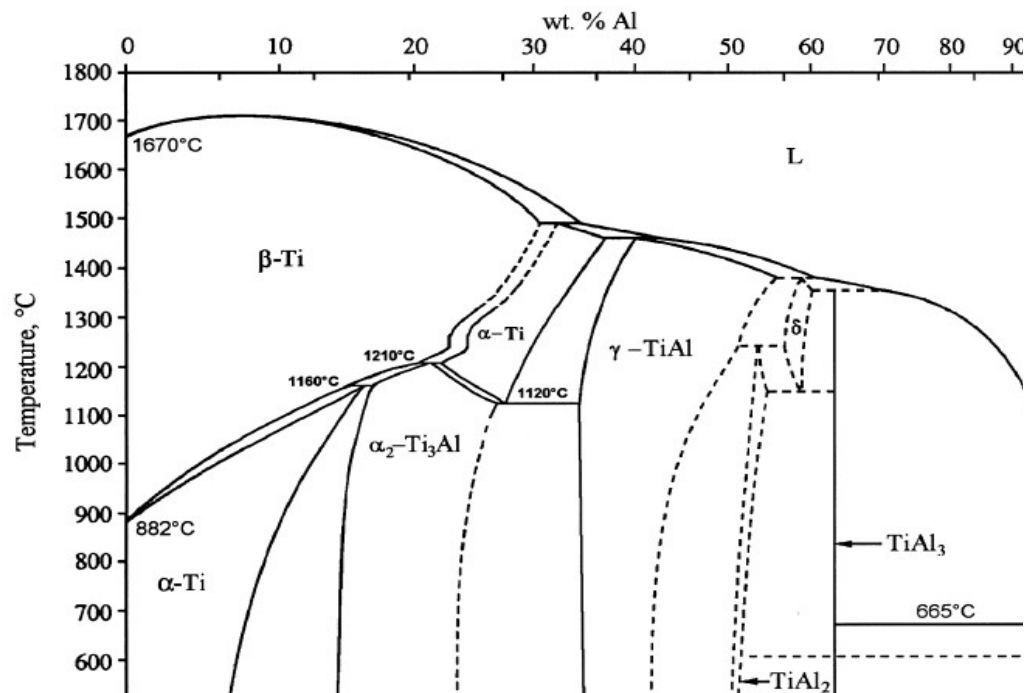


Figure 2.1: Ti-Al binary system phase diagram (Mishin and Herzig, 2000)

Higher concentration of Al is needed to achieve a protective Al_2O_3 scales. However, increasing of Al concentration is technologically not desired for the loss of ductility by the formation of brittle TiAl_3 . The addition of ternary and quaternary element to Ti-Al binary is an effective method to improve the oxidation resistance (Yang and Wu, 2003). Alloying elements like Nb, W, Ta and Hf can influence the kinetics of phase transformation and improve greatly the oxidation and creep resistance (Hu, 2001).

In this study, the improvement of oxidation resistance is focused on addition of alloying element in Ti-Al binary and the formation of protective Al_2O_3 scale. A large fraction of Al (48 at. %) have been used to accomplish the target. From Bhattacharya et al., (2004), alloys closed to the nominal composition $\text{Ti}_{52}\text{Al}_{48}$ (at.%) with a dual phase microstructure comprising 88 % γ -TiAl and 12 % α_2 - Ti_3Al are presently believed to offer the best combination of strength, ductility and creep resistance.

2.2.2 Phases in Ti-Al System

Ti-Al phase diagram has four binary compounds in the system which is α_2 - Ti_3Al , γ -TiAl and TiAl_3 and TiAl_2 (Okafor and Reddy, 1999). Among these, only Ti_3Al (α_2) and TiAl (γ) has been intensively studied. Ti-Al alloy with this two-phase mixture (α_2 and γ) have attracted a lot of attention due to the improvement offered and was achieved by microstructure control and alloying addition. The α_2 - Ti_3Al has a hexagonal DO_{19} structure. Meanwhile, γ -TiAl phase has a tetragonal L1_0 ordered face-centered tetragonal structure. In both cases these compounds exhibit limited ductility at room temperature, particularly in the binary state.

The research focus on Ti₃Al based systems to develop α_2 and super α_2 alloys in the 1970s. The development of these alloys has been driven by the need to bridge the gap in temperature capability between current conventional near- α titanium alloys (550-600°C) and nickel based super alloys (650-800°C) (Westbrook and Fleischer, 2000). Although encouraging results were obtained, no application was really successful because the gain was marginal and the experimental difficulties were enormous (Lasalmonies, 2006). The alloyed versions can exhibit quite high strength particularly in the temperature range 550-650°C where conventional Ti alloys begins to rapidly weaken with increasing temperature.

In the 1980s, the interest switch to γ -Ti-Al which has creep and oxidation properties better than α_2 pushing its temperature capability up to 750°C (Lasalmonies, 2006). γ -TiAl alloys have the potential to be the high temperature engineering material because of their superior properties such as low density, high melting point, high strength and an adequate creep resistance at high temperature (Kainuma et al., 2000). The potential applications were found in industries such as automotive and nuclear industries. Some properties α_2 , γ and super alloys are shown in Table 2.1.

Recently, many studies have been carried out in the Ti-Al-X system and it has been reported that the addition of Nb, Mo, W, Ta, Cr, V and Mn are useful to improve fracture toughness, ductility and corrosion or oxidation resistance in these alloys (Wang et al., 2005; Yang and Wu, 2003). However, there is still possibility for alloys development to optimize the $\alpha_2+\gamma$ microstructures in these alloys. In view of this, quantitative data on phase relations among the α (A3), α_2 (Ti₃Al:D0₁₉), β (A2 or B2) and γ phases in several ternary alloys would be very important. The phase equilibrium

between α_2 and γ phases in Ti-Al-X ternary systems has been briefly reviewed and from a practical point of view, there is considerable interest in knowing how different alloying elements changes the $\alpha_2+\gamma/\gamma$ boundary and partition between the two phases in the Ti-Al based ternary system (Lutjering and William, 2003).

2.2.3 Microstructures

The properties of Ti-Al alloy are strongly controlled and affected by their microstructures (Sauder, 1995; Hu, 2001). Type of microstructure can be readily obtained by wrought processing of ingots or rapid solidification. These processing approaches break up the solidification structure and achieve homogeneity and grain refinement through rapid solidification or work induced recrystallization (Westbrook and Fleischer, 2000).

As a result of solid-state phase equilibrium shown in Figure 2.1, basically the microstructures of Ti-Al alloys exist in these four types; single phase near γ , duplex, near lamellar and fully lamellar (Stroosnijder et al., 2007; Lamirand et al., 2007; Hu, 2001). The classification of various microstructures is primary based on phase equilibrium as a function of alloy composition and heat-treatment temperature. The microstructure has been studied due to its balance properties in terms of creep, ductility and strength. Figure 2.2 shows some type of the typical wrought microstructures of Ti-Al alloys (Westbrook and Fleischer, 2000). Alloys with above 52 at.% Al generally lie in the single phase γ field during heat-treatment and are single phase γ after cooling to room temperature (see Figure 2.2a). For alloys between 46 and 50 at.% Al, heat-treatment in the $\alpha + \gamma$ phase field results in a two-phase structure upon cooling (see Figure 2.2b). This structure consists of γ grains and grains of a lamellar

structure. The lamellar grains contain alternating α_2 and γ plates which form as result of transformation from the primary α during cooling to room temperature. This structure is referred to as a duplex structure. The alloys below 48 at.% Al that are heat-treated in the single phase α field can form the fully lamellar structure as shown in Figure 2.2 (c).

The four types of microstructures reported by Stroosnijder et al., (1997) are described as follow:

- a. *Near γ structure*: consists of equiaxed γ -grains and α_2 -particles on grain boundaries and triple point.
- b. *Duplex structure*: consists of γ -grains and lamellar colonies of alternating layers of γ and α_2 platelet.
- c. *Near lamellar*: the size of the lamellar grains is larger than that of γ grain.
- d. *Fully lamellar*: compose of γ and α_2 lamellar

In the last few years, great effort has been focused on producing refined fully lamellar which is the most promising type of microstructure of Ti-Al alloys (Hu et al., 2001). The fully lamellar microstructure composed of γ and α_2 lamellar seem to be better than the other microstructure by offering high strength, high creep resistance, good fatigue strength and high fracture toughness but usually has poor tensile ductility at room temperature (Hu et al., 2001; Wang et al., 2005; Maziasz et al., 1997; Stroosnijder et al., 1997; Zhengfang et al., 2008; Lamirand et al., 2007). Lamellar microstructures can be formed by heating the alloys into the α phase region and then cooling through $\alpha + \gamma$ phase region to form γ lamellar. The residual α trapped between these growing γ lamellar then transfers to ordered α_2 phase below the eutectoid

temperature (Maziasz et al., 1997). The lamellar colonies in grain-refined alloys are randomly oriented after solidification (Hu et al., 2001).

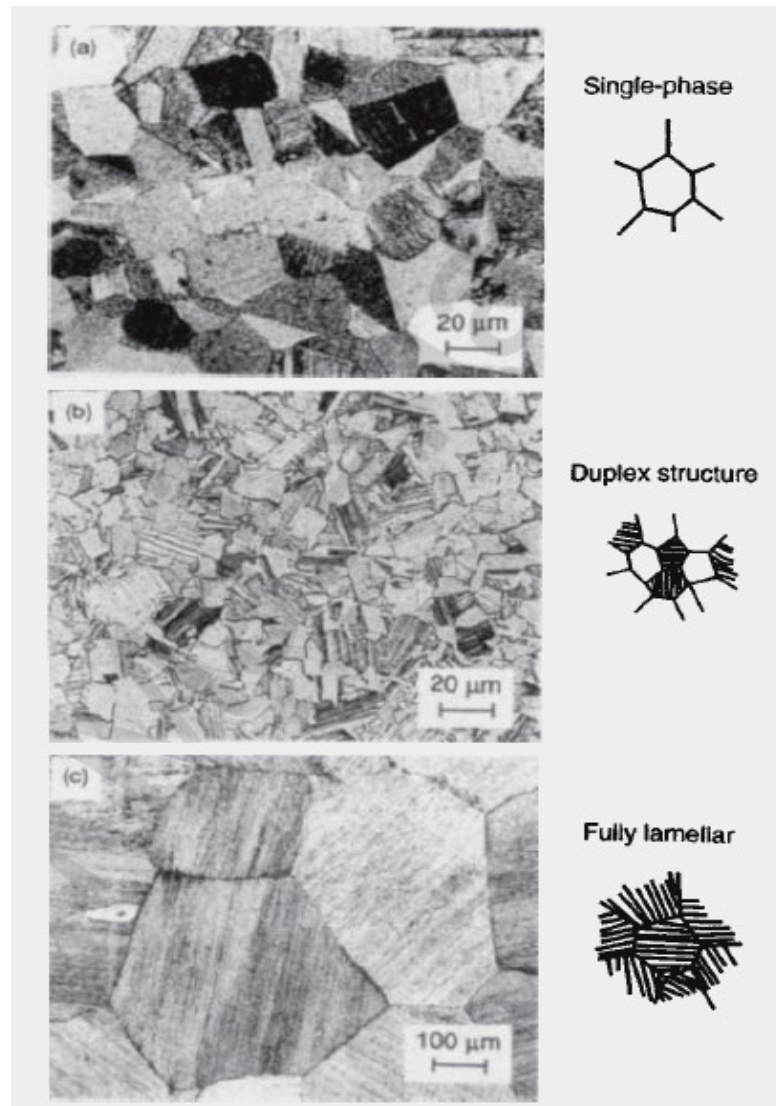


Figure 2.2: Typical wrought microstructure of (a) single phase- γ , (b) duplex of γ and lamellar and (c) fully lamellar (Westbrook and Fleischer, 2000).

2.2.4 Physical and Mechanical Properties

The oxidation resistance behavior typically depends on the physical structure of the different oxidation phases of the Ti-Al alloys. The Ti-Al alloys with a two-phase mixture of α_2 and γ have attracted great attention during the past decade due to their superior ratio of strength to density, and good oxidation resistance at elevated temperature. The disadvantages of Ti-Al alloys due to poor ductility at room temperature and low creep resistance at elevated temperature. Table 2.1 and 2.2 show the properties of Ti-Al alloys compare to superalloys and other structural metallic materials based on Fe, Ni, and Al. As evidence from Table 2.1 and 2.2, Ti-Al alloys exhibit a significant density advantage over the current used superalloys and have potential to for replacing superalloys at temperature up to 900°C (Yang and Wu, 2003; Lasalmonie, 2006).

Leyens and Peters (2003), to generally improve the properties of Ti-Al alloys, there are essential two ways to proceed which are alloying and processing. Alloying lays the basic for an increasing in strength (e.g solid-solution strengthening, age hardening), allows the generation of ordered structure (e.g intermetallic compound of Ti-Al), determines most of alloys properties (e.g density, elastic modulus, CTE), and large controls in the chemical resistance of the materials (corrosion, oxidation). Processing allows the careful balancing of the material's properties. Depending on the specific property profile required for the final application, different microstructures can be generated for Ti-Al alloys to optimize the properties.

Table 2.1: Properties of the α_2 , γ and superalloys (Westbrook and Fleischer, 2000).

Property	α_2 alloys	γ alloys	superalloys
Density (g/cm ³)	4.1-4.7	3.8-4.0	8.3
Young's modulus (GPa)	120-145	160-175	206
Ductility (%)	2-5	1-3	3-5
Yield Strength (Mpa)	700-990	400-650	1100
Thermal Conductivity (W/mK)	7	22	11
Phase Stability Limit (°C)	1180	1440	1450
Creep Limit (°C)	750	900	1090
Oxidation Limit (°C)	650	900	1090

Table 2.2: Properties of titanium and titanium based alloys compared to other structural metallic materials based on Fe, Ni, and Al (Lutjering and William, 2003).

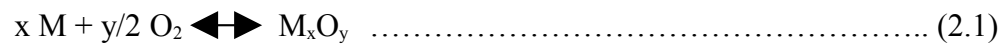
Properties	Ti	Fe	Ni	Al
Melting temperature (°C)	1670	1538	1455	660
Allotropic Transformation (°C)	$\beta \xrightarrow{882} \alpha$	$\gamma \xrightarrow{912} \alpha$	-	-
Crystal Structure	Bcc \rightarrow hex	fcc \rightarrow bcc	fcc	fcc
Room Temperature E (GPa)	115	215	200	72
Yield Stress Level (MPa)	1000	1000	1000	500
Density (g/cm ³)	4.5	7.9	8.9	2.7
Comparative Corrosion Resistance	Very High	Low	Medium	High
Comparative Reactivity with Oxygen	Very High	Low	Low	High
Comparative Price of Metal	Very High	Low	High	Medium

2.3 Theory of Oxidation

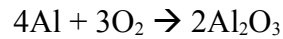
2.3.1 Introduction

Oxidation is the conversion of the surface portion of metal to the metal's oxide form, upon being heated in air or oxygen. It occurs whenever there is an increase in valency state of the metal. In a simple chemical reaction, oxidation of a metal (M) in

pure oxygen (O₂) forming an oxide M_xO_y as a reaction product can be described by the following equation:



For example: $Ti + O_2 \rightarrow TiO_2$



Oxidation is an important aspect to analyze when assessing metal resistance in high temperature environment. The oxygen always needs two electrons from the metal with which it react in order to reach stability. Metal has to donate two electrons from its outer shell to oxygen atom, so that stability could be achieved. When oxygen and metal react together, oxide starts to grow in proportion to the oxygen exposure and increased temperature on the surface of metal. This oxide growth actually is faster in some elements than others. For example, in pure Al and Al alloys, the oxidation is faster than other metals since they have high electron affinity with oxygen. It can be seen that if there are metallic compounds in chemical reaction with oxygen, some of the compounds is going to convert to oxidized metal.

In this part, the theory of oxidation is focused on the Ti-Al alloys in order to improve the oxidation of these alloys. As mentioned before, the oxidation resistance is still a critical factor for Ti-Al alloy to be used at high temperatures (above 800°C) for a long time.

2.3.2 Oxidation Kinetics

Considering a pure metal surface, the formation of an oxide scale can be divided by into four steps (Leyens and Peters, 2003):

- a) Oxygen adsorption at the surface
- b) Oxide nucleation

- c) Lateral growth of the nuclei
- d) Formation of a compact oxide scale

Figure 2.3 shows the model of oxide scale formation on a metallic surface. When lateral growth of nuclei is accomplished, the metal surface is completely covered with a thin film and thus the metal is separated from the gaseous environment. At elevated temperatures and sufficiently high oxygen partial pressures, steps (a)-(c) in Figure 2.3 occur very rapidly, hence having only a minor effect on the oxidation kinetics. When compact film has been formed on the metal surface, further oxide growth is controlled by mass transport through the oxide scale.

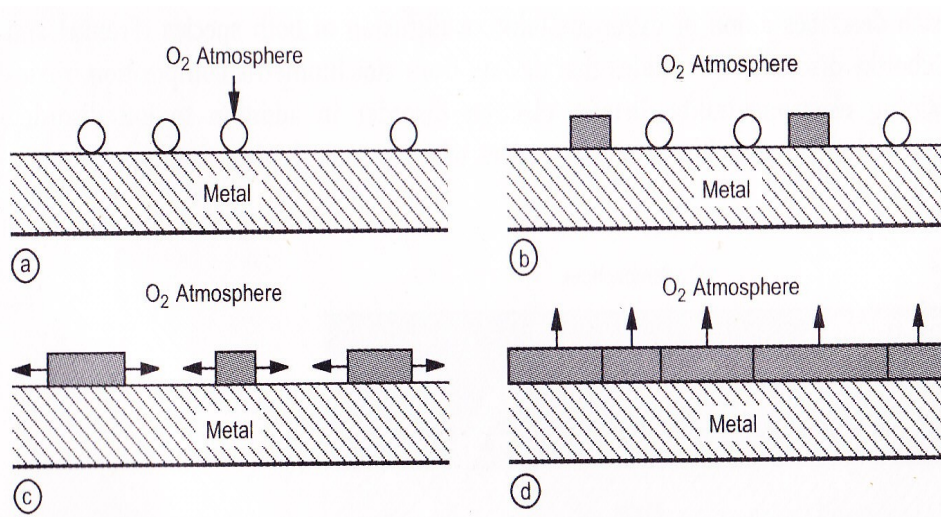


Figure 2.3: Model of oxide scale formation on a metallic surface. (a) Oxygen adsorption at the surface, (b) formation of nuclei, (c) lateral growth of nuclei and (d) growth of the compact oxide scale (Leyen and Peters, 2003).

At low temperatures, mass transport is predominantly influenced by grain boundary diffusion due to its lower activation energy, and by cracks and voids that may provide direct access of oxygen to the metal surface. Meanwhile, at elevated temperatures, mass transport can be dominated by volume diffusion. Along with

temperature, the oxygen partial pressure, oxidation time, surface condition and pretreatment of the metal may substantially affect oxidation kinetics.

The oxidation kinetic is usually measured and expressed as weight gain per unit area. The various growth rate laws are reported in practical applications, some of the cases are shown in Figure 2.4, in which a plot of weight gain per unit area verses time is shown. The simplest empirical relationship is the linear type:

$$W = k_L \cdot t \dots\dots\dots (2.2)$$

where W is the weight gain per unit area, k_L is the linear rate constant and t is the time. Linear oxidation is the characteristic of metals for which a porous or cracked scale is formed, so the scales do not represent a diffusion barrier between the two reactants.

In 1933, Wagner showed that the ideal ionic diffusion controlled oxidation of pure metals should follow a parabolic oxidation rate law:

$$(\Delta W)^2 = k_p \cdot t = k_0 \cdot e^{-Q_{eff}/RT} \cdot t \dots\dots\dots (2.3)$$

Where ΔW is the weight gain per unit initial surface area, k_p is the parabolic rate constant, t is the oxidation time, Q_{eff} is the activation energy, T is the oxidation temperature in degree Kelvin and R is the gas constant. k_0 = related to the pre-exponential factor of the effective diffusion coefficient and to density of the scale.

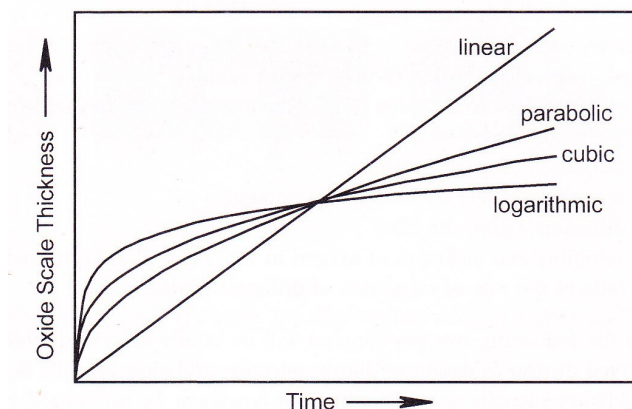


Figure 2.4: Schematic representation of rate laws for oxide scale formation.

(Leyen and Peter, 2003; Yang and Wu, 2003)

2.3.3 Oxidation Mechanism of Ti-Al alloy

The mechanism of oxidation can be divided into three stages according to oxidation rate and the scale structure (Taniguchi and Shibata, 1996). Figure 2.5 shows the schematic oxidation curve. Meanwhile, Figure 2.6 shows the model of transition from stage 1 to stage 3. During stage 1 the scale is very rich in Al_2O_3 and correspondingly the oxidation is slow. This is experienced during heating to test temperatures or during the initial period of oxidation at relatively low temperatures. However, there is the first breakaway to stage II where the oxidation is vigorous with the scale becoming a mixture of TiO_2 and Al_2O_3 . After an extended time at high temperatures the second breakaway takes place (transition from stage II to stage III). This breakaway kinetic was explained in terms of the formation of relatively large cracks in the scales. At high temperatures, small crack can be healed by sintering of outer layer TiO_2 layer, resulting in repeated acceleration for short periods in the oxidation curve. As the oxidation proceeds the flux of oxygen diffusing through the initially formed Al_2O_3 scale exceeds that of Al diffusing towards the scale/substrate. As a result of this, TiO_2 crystals grow at the interface; refer to stage b in Figure 2.6. Another possibility for the transition from stage (a) to (b) is the formation of microcracks in the scale because an oxide scale is usually under-growth stress. The formation of TiO_2 is associated with the large volume increase. This can partially break the Al_2O_3 scale and thus forming the two-layer oxide mounds as shown in stage (c). The subsequent lateral growth of the oxide mounds will lead to the complete coverage of the specimen surface, see stage (d).

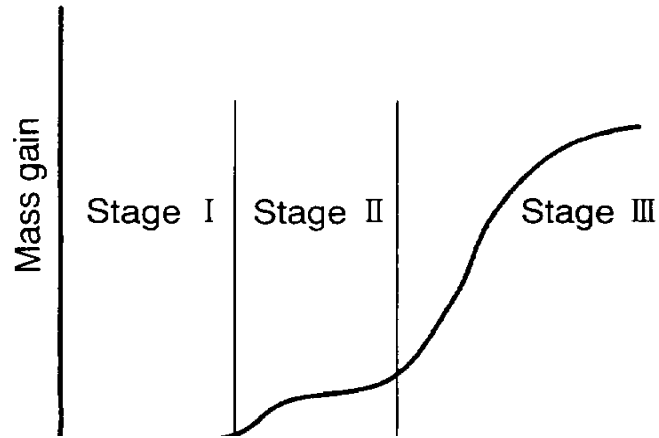


Figure 2.5: Schematic oxidation curve of TiAl consisting of three stages (Taniguchi and Shibata, 1995).

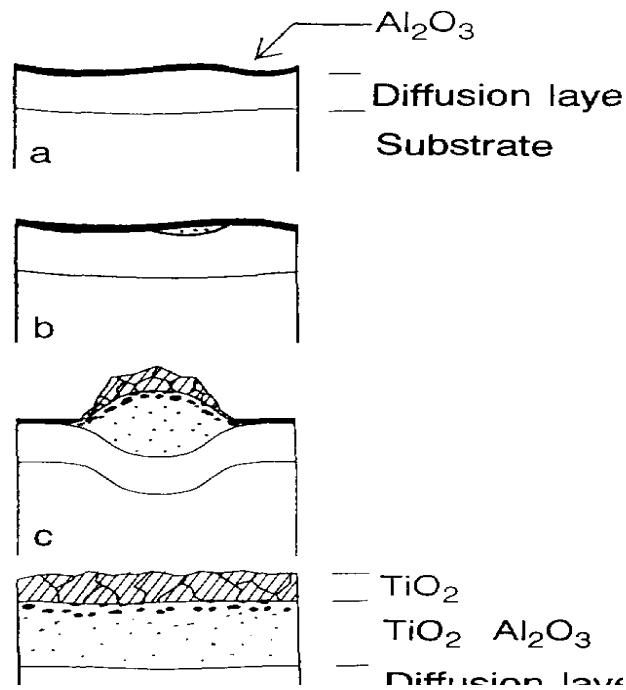


Figure 2.6: A model for the transition from stage I to stage II (Taniguchi and Shibata, 1995).

2.3.4 Protective Oxide Scale Formation

During elevated-temperature exposure in air, almost all metals react to form oxides. The conversion of a structural component from metal to oxide can culminate in failure due to dissolution of oxygen into metal (Okafor and Reddy, 1999). Metallic materials are protected against high temperature oxidation by formation of protective

oxide scales such as Cr_2O_3 , SiO_2 or Al_2O_3 which acquire sufficiently low growth rates to prevent rapid component degradation (Tang et al., 2003).

The oxidation product of Ti during exposure to air is TiO_2 which has a tetragonal rutile crystal structure. This oxide layer is often called scale and is an n-type anion-defective oxide, through which the oxygen ions can diffuse. The reaction front is at the metal/oxide interface and the scale grows into the Ti base material. The formation of an oxide scale is directly influenced by thermodynamics, such as the stabilities of TiO_2 and Al_2O_3 , and kinetic aspects such as the high growth rate of TiO_2 relative to Al_2O_3 . Figure 2.7 shows schematic cross section through the oxide layers and the oxygen interdiffusion zone of Ti-based alloys with Al contents exposed to identical thermal condition. The scale of Y axis shows percentage of X/X_{Ti} which is referring to concentration of Al and Ti. The schematic in Figure 2.7 does not describe the arrangement of oxide scales of particular alloys in a universally valid way. However, it provides a clue about principle differences. Oxide scale formation in isolated cases depends on number of parameters such as alloys chemistry, exposure temperature and time, as well as oxidizing atmosphere. The structure of oxide scale on multi component alloys systems can be far more complex than shown in Figure 2.7 (Leyen and Peter, 2003). The improvement of the oxidation resistance of Ti-Al, such as Ti_3Al or $\gamma\text{-TiAl}$ based alloys, resulted from increasing of volume fraction of Al_2O_3 in the scale. The amount of Al_2O_3 increases with concentration of Al and the Al_2O_3 layer becomes continuous at around 40 at.% Al. The oxide scale typically has a multilayer microstructure consisting of a heterogeneous mixture of TiO_2 and Al_2O_3 in varying proportions and of a TiO_2 top layer. Addition of more Al leads to a reduction of oxide scale thickness, e.g the oxidation resistance of the oxide scale is generally

improved (Lutjering and Williams, 2003; Leyen and Peters, 2003). At high temperature, layers of mixed oxide grow by competitive oxidation of the Ti and Al alloying elements, which prevents the formation of a continuous alumina layer that would provide an effective oxidation barrier (Maurice et al., 2007).

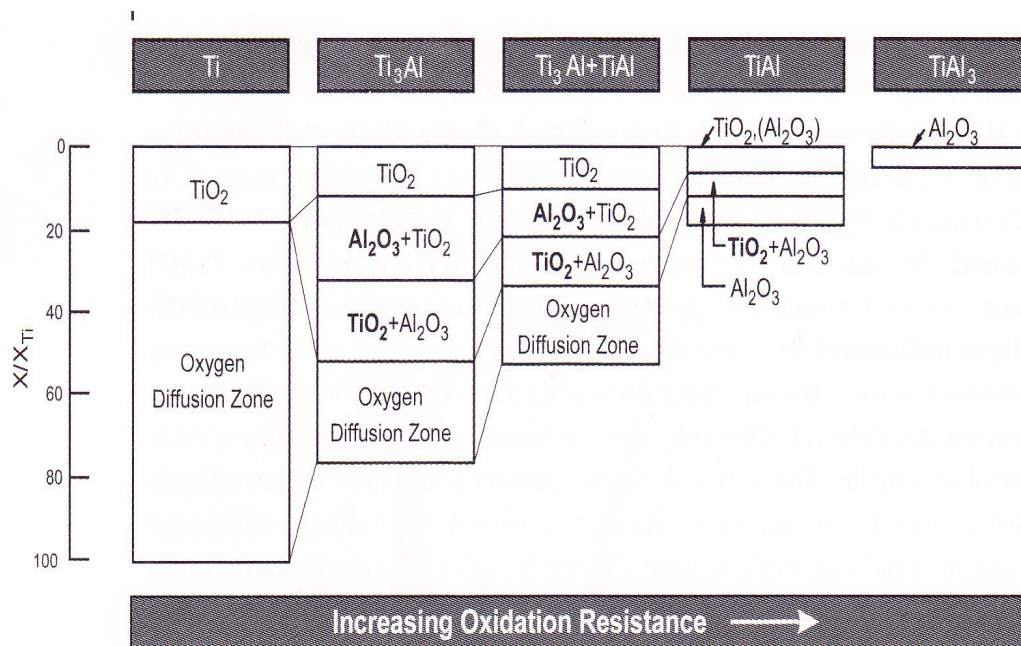


Figure 2.7: Schematic cross sections through the oxide layers and the oxygen diffusion zone in Ti and Ti-Al (Leyen and Peter, 2003).

2.3.4.1 Structure of the oxide scale

In general, oxide scales of Ti-Al alloys have been noted to consist of three layers. Typically, rutile (TiO_2) is observed on the outer scale surface followed by a discontinuous Al_2O_3 layer and intermixed porous inner layer $\text{TiO}_2/\text{Al}_2\text{O}_3$ region. Figure 2.8 shows a structure model for oxide scale and the substrate near the

scale/substrate interface (Taniguchi and Shibata, 1995). The inner layer contains many small pores and there are several voids near the interface between outer layer and Al_2O_3 layer. After longer oxidation exposure, small crack will appear near the interface due to the formation of Al_2O_3 platelet that will induce stress. These small cracks then allow diffusion of oxygen through to substrate and caused failure in oxidation protection.

At high temperature, layers of mixed oxides grow by competitive oxidation of Ti and Al which presents the formation of a continuous and dense Al_2O_3 layer that would provide an effective barrier (Maurice et al., 2007; Dudziak et al. (2009). Investigation on oxidation environment at high temperature reported that the affinity of Ti and Al for oxygen leads to formation of an outer layer of TiO_2 . The development of TiO_2 layers leads to the depletion of Ti and increasing Al activities beneath the TiO_2 layer promote the formation of Al_2O_3 layer by the ingress of oxygen species through the TiO_2 .

Despite their high Al content, Ti-Al based intermetallics do not form long lasting protective Al_2O_3 scale. This is because of the thermodynamic stability of TiO_2 is similar to Al_2O_3 . After longer exposure time, the scale initially rich in Al_2O_3 deteriorate and complex scales are formed containing a high amount of TiO_2 thus having high growth rate similar to that of pure TiO_2 (Sunderkotter et al., 1997).

However, oxidation resistance may be improved by addition of alloying element as discussed in section 2.4. The effect of the alloying element was attributed to the formation of a barrier layer as shown in Figure 2.8 (b). As an example, the