

The Effect Of Aluminium Content On Properties Of TiAl Based Binary Alloys[†]

Okti J. P. Manalu¹, Rizal Astrawinata¹, Nurulakmal Mohd. Sharif¹,
Eddy A. Basuki², Toshio Maruyama³

¹School of Materials & Mineral Resources Engineering

Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

²Department of Mining Engineering, Faculty of Earth Sciences and Minerals Technology,
Institut Teknologi Bandung (ITB), Jl. Ganesha 10, Bandung – 40132, Indonesia

³Department of Metallurgy & Ceramic Science, Graduate School of Science & Engineering
Tokyo Institute of Technology (TIT), Japan

email: okti@eng.usm.my; okti_manalu@yahoo.com



Abstract

Four alloys in Ti-Al binary system (Ti-50Al, Ti-53Al, Ti-60Al and Ti-65Al in at.%) have been produced by arc-melting process in a specially-designed and locally-made furnace. The alloy samples were then oxidized in air at 900°C for 50 hours inside a muffle furnace. In this study, microstructures and phases of the alloys have been characterized using XRD and SEM/EDS to link on their properties. It's identified that the present phases of Ti-50Al and Ti-53Al are $\gamma(\text{TiAl}) + \alpha_2(\text{Ti}_3\text{Al})$ and $\gamma(\text{TiAl}) + \text{TiAl}_2$. Some tests such as density and hardness test were also carried out on the samples. Ti-50Al and Ti-53Al alloys have highest hardness value at HVN of 536 and 543 respectively. On the contrary, the lowest hardness was occurred at HVN of 435 and 445 on Ti-65Al and Ti-60Al respectively. While, the lowest density value (3.80 gr/cm³) was reached on Ti-65Al. Meanwhile the highest density value (3.93 gr/cm³) was occurred on Ti-53Al alloy. The oxidation kinetics was also studied by determining the weight gain of the alloy samples during the oxidation process. It's found that the highest oxidation rate belongs to Ti-50Al alloy with a 0.85% weight increase whereas Ti-65Al alloy has the lowest oxidation rate with only 0.65% increased weight for the formation of its oxide scales.

Keywords: binary titanium aluminides; arc-melting furnace; microstructures/phases; oxidation resistance

1. Introduction

TiAl-based alloys are currently being developed for high temperature aircraft and automotive engine applications. This interest is due to their identification of compositions and microstructures which possess both reasonable mechanical properties and some oxidation resistance. Combined with their low density (about 4 gram/cm³) great weight saving is expected from their application [1, 6].

The properties of the alloys are strongly composition and microstructure-dependent. Alloying elements dominate their strengths and hardness of alloys for given microstructures. Al is the most influential element to the alloy hardness and it acts through changing the volume fraction of $\alpha_2(\text{Ti}_3\text{Al})$ phase, which is the hard phase in ($\alpha_2+\gamma$) two-phase alloys. With a decrease in Al concentration the α_2 phase volume fraction is increased and so is the hardness [6].

Binary titanium aluminides alloys can form TiO_2 , $\text{TiO}_2 + \text{Al}_2\text{O}_3$ and Al_2O_3 scales in various proportions depending on Al concentration. The Al_2O_3 scale is protective due to the fact that it is continuous, grows with relatively low kinetics and serves as a barrier layer for the diffusion of interstitial elements. However, with increasing of the Al concentration further usually forms the oxide scale contains greater amounts of Al_2O_3 , interspersed heterogeneously with TiO_2 , and can even form a sub-layer that consists predominantly of Al_2O_3 . In the region with increasing Al of the alloys, phases of TiAl_2 and TiAl_3 which extremely brittle are identified but its oxidation resistance is better than α_2 and γ phase. It's postulated that ($\alpha_2 + \gamma$) alloys have high oxygen permeability which lead to inability of alloys to form a protective alumina scale and internal attack [2, 3].

For given compositions the properties of TiAl-based alloys are predominantly affected by the microstructure. Basically the microstructure can be divided into three types: fully lamellar, duplex and equiaxed gamma. The latter two give rise to high strength and some ductility but poor creep resistance, low fatigue strength and low fracture toughness. The fully lamellar microstructure, composed of thin γ and α_2 lamellae, seems to be better than the other two microstructures by offering high strength, high creep resistance, good fatigue strength and high fracture toughness, but generally with somewhat lower ductility than the duplex [6]. Since each of the microstructures type gives different properties, the purpose of the present study is to produce and characterize microstructures on compositional variations of TiAl alloys such as Ti-50Al, Ti-53Al, Ti-60Al, and Ti-65Al alloys (in at.%). Secondly, the other objective of this work is to investigate the effects of aluminum content on microstructures and properties of the alloys.

2. Experimental

TiAl intermetallic alloys used in this present study have been prepared at the School of Materials and Mineral Resources Engineering-USM, Penang, Malaysia. Several necessary steps were taken to produce the alloys. Powders of the required metals were first weighted according to the intended compositional variations (Table-1). The powders were then mixed under inert atmosphere for 5 – 6 hours to obtain a uniform mixture. A Carver compaction equipment was used to make the powder mixture into pellets under 10 tons of loads to ensure the pellet will not splash out during the arc-melting process. Melting the pellets has been carried out using a specially-designed and locally-made arc-melting furnace (Fig.1b) to produce button-shaped alloy samples. To ensure the mechanical homogeneity, each button of the alloy samples has been arc melted for at least 5 (five) times. The buttons were 20 mm in diameter, 5 mm in thickness and about 3.5 – 6 grams in weight. The buttons were then ground to a mirror-like surface with SiC papers up to No. 2000 followed by 0.1 and 0.05 μm alumina powder. Finally, the ground surface of buttons was etched in a modified Kroll's reagent of 10 vol.% HF, 4 vol.% HNO_3 and 86 vol.% H_2O . Each of the alloys has been characterized using a LEO SUPRA 50VP SEM/EDS, a Siemens Diffractometer D5000 XRD, room temperature Vicker's microhardness, and a Micromeritics AccuPyc, Gas Pycnometer 1330 density test. Oxidation processes have been carried out on the coupons of samples in open air under isothermal condition of 900°C for 50 hours inside a muffle furnace. The weight gain of the samples during the oxidation process was determined, and cross-sectional microstructures of the samples have been characterized using SEM/EDS.

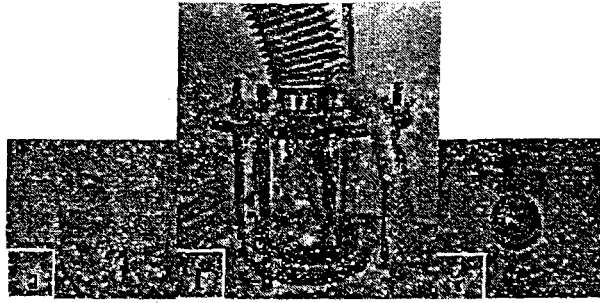


Fig.1. a) a cell of locally-made arc-melting furnace; b) a pellet of metals powder; and c) a button of alloy [8].

Table 1. Some selected compositional variations of alloys in at.%.
 ! Variations

Nominal alloy	Compositional Variations	Titanium (at. %)	Aluminum (at. %)
1	Ti - 50Al	50	50
2	Ti - 53Al	47	53
3	Ti - 60Al	40	60
4	Ti - 65Al	35	65

3. Ti-Al binary phase diagram

The portion of Ti-Al binary phase diagram relevant to solidification is schematically shown in Fig.2.b. The solidification path of binary TiAl alloys can be divided into three categories by McCullough et al. [6]:

$L \rightarrow [\beta] + L \rightarrow [\beta + \alpha] \rightarrow [\alpha] \rightarrow [\alpha_2] \rightarrow [\alpha_2 + \gamma]$ at.% Al	≤ 45
$L \rightarrow [\beta] + L \rightarrow [\beta + \alpha] + L \rightarrow [\beta + \alpha] + \gamma \rightarrow [\alpha] + \gamma \rightarrow [\alpha_2 + \gamma]$ at.% Al	46 - 49
$L \rightarrow [\alpha] + L \rightarrow [\alpha] + \gamma \rightarrow [\alpha_2] + \gamma$ at.% Al	49 - 55
$L \rightarrow [\gamma] + L \rightarrow \gamma \rightarrow [TiAl_2] + \gamma$ at.% Al	55 - 65

The maximum Al concentration in binary TiAl in beta titanium is 44.8% as shown in the phase diagram (Fig.2a). Alloys with 44.8% (or lower) Al solidifies as the primary beta phase. Alloys with Al above 44.8% solidify as beta phase first but at the peritectic temperature solidification to the beta phase stops and the remaining liquid reacts with the beta solid to form the peritectic alpha₂ phase. The Al concentration thus affects the beta phase volume fraction which decreases with increasing Al concentration. In alloys with 49 % Al or higher all the liquid solidifies through the alpha phase and goes to alpha₂ and gamma. For alloys with 55% to 65% all liquids solidifies through the gamma phase and goes to TiAl₂ and gamma phases.

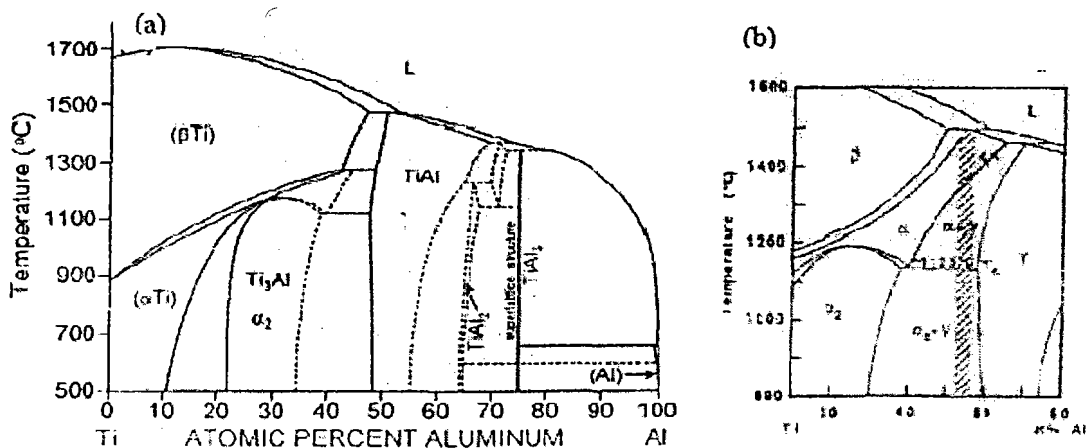


Fig.2. (a) Ti – Al binary system of phase diagram; (b) Schematic illustration of the central part of Ti-Al binary phase diagram with range 25 – 60 at.% Al [5, 7]

4. Results and Discussion

4.1 Alloys Phase Compositions and Microstructures

In this present study the compositional variations of alloys is divided into 2 ranges: 45 – 55 at.% Al and 55 – 65 at.% Al alloys. The binary titanium aluminides alloys are Ti-50Al, Ti-53Al, Ti-60Al and Ti-65Al alloy. The composition range of 45 – 55 at.% Al is called as γ -titanium aluminides alloy which consist of two-phase ($\gamma + \alpha_2$) and single-phase γ alloy. Then, Ti-50Al and Ti-53Al alloys are included in the phase region. While Ti-60Al and Ti-65Al alloys are grouped in 55 – 65 at.% Al with γ and TiAl₂ of present phases.

The microstructures of Ti-50Al and Ti-53Al alloys show fully lamellar and nearly lamellar respectively which Ti-50Al alloy shows grains size ~ 40 – 70 μ m coarser than ~ 20 – 30 μ m in Ti-53Al alloy (see Fig.3a and Fig.3b). The grains in Ti-50Al are γ/α_2 while in Ti-53Al alloy are $\gamma + \alpha_2$. Then, Ti-60Al alloy shows γ as matrix and TiAl₂ as precipitates as well as in Ti-65Al alloy (Fig.3c and Fig.3d). However, TiAl₂ grains in Ti-65Al alloy are much more than Ti-60Al alloy. This is agreement with binary phase diagram of Ti-Al whereas TiAl₂ phase developed in region around of Ti-65Al. Much more Al in Ti-60Al and Ti-65Al alloy than in Ti-50Al and Ti-53Al has been used to form many alumina scales possibly.

The chemical composition and microstructure of phases affect some properties of alloys including oxidation resistance strongly. The two phase γ (TiAl) + α_2 (Ti₃Al) classes of titanium aluminides beside offers good mechanical properties also superior oxidation resistance compared to the single α_2 -phase alloy. But both of phases have poor oxidation resistance as compared to TiAl₃ and TiAl₂ phases however they are extremely brittle.

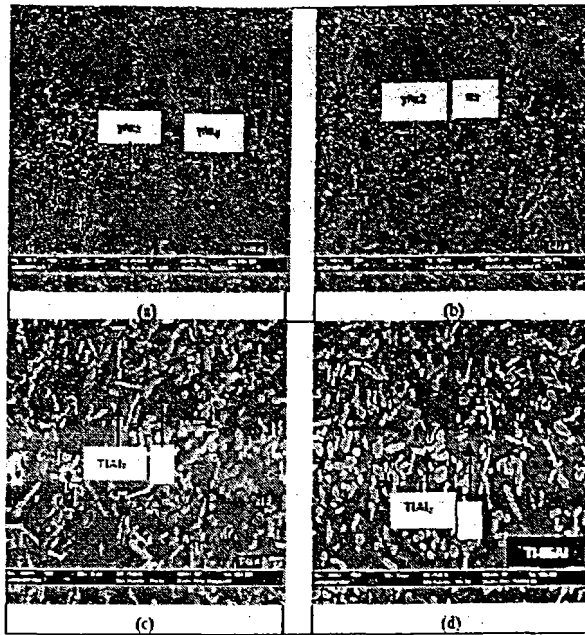


Fig.3. SEM image showing microstructure of: (a) Ti-50Al; (b) Ti-53Al; (c) Ti-60Al; (d) Ti-65Al alloy

4.2 Density and Hardness Analysis

Hardness test was carried out using Vickers Hardness Tester with loads of 10 kgf and density test was done using Micromeritics AccuPyc 1330, Gas Pycnometer. It can be seen from the Fig.4b that the average hardness value increases with the decrease of aluminium content which raising α_2 -Ti₃Al phase. It is in a good agreement with other reported investigators as D. Hu [6]. The higher hardness value was reached on Ti-53Al and Ti-50Al at HVN of 543 and 536 respectively. On the contrary, the lower hardness was occurred at HVN of 435 and 445 on Ti-65Al and Ti-60Al respectively.

Fig.4a shows the relationship between density and compositional variations of alloys. Value of density of alloys increases with decreasing Al content of alloys. That is postulated that due to decreasing Al content, means increasing Ti content, in alloys whereas density of Ti element is 4.5 gr/cm³ greater than Al element is 2.7 gr/cm³.

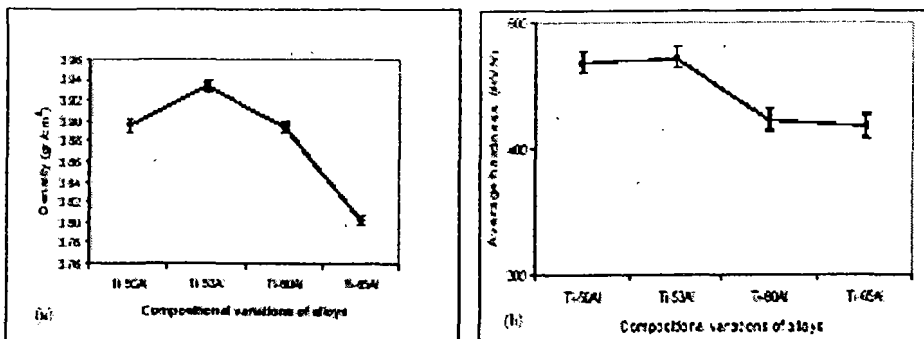


Fig.4. (a) Density values of some TiAl based alloys; (b) Room temperature average hardness values of some TiAl based alloys

4.3 Oxidation of Alloys

Fig.5a. presents the oxidation results on Ti-50Al alloy. The microstructures of the alloy are still fully lamellar as the initial alloy. While the grains have become finer after the oxidation process, its chemical composition remained unaltered. Three types of oxide scales have been produced as the results of the oxidation process TiO_2 , $(TiO_2 + Al_2O_3)$ and Al_2O_3 . The thickness of the TiO_2 scale is $\sim 10 \mu m$ and $(TiO_2 + Al_2O_3)$ mixed scale is $\sim 37.5 \mu m$ while the alumina scale at interface of both scales is $\sim 5 \mu m$ thick. The existence of a protective alumina scale in the Ti-50Al alloy is contrary to the previous investigation which claimed that approximately 60 – 70% at.% Al is needed for binary Ti-Al alloys to form a protective alumina scale in air according to Perkins and Meier [2, 3].

Fig.5b. shows the oxidation products on Ti-53Al alloy. After the oxidation process, the grains become finer and microstructures type of the alloy are still fully lamellar. Oxide scales have been resulted as the products of the oxidation process such as TiO_2 , $(TiO_2 + Al_2O_3)$ and Al_2O_3 . The thickness of the TiO_2 scale is $\sim 5 \mu m$ as outer scale while the alumina scale beneath the scale is $\sim 3 - 5 \mu m$ thick. $(TiO_2 + Al_2O_3)$ mixed scale inner scale is $\sim 15 \mu m$. The existence of a protective alumina scale in the Ti-53Al alloy is also contrary to the previous investigation which claimed that approximately 60 – 70% at.% Al is needed for binary Ti-Al alloys to form a protective alumina scale in air based to Perkins and Meier's investigation [2, 3].

For Ti-60Al alloy, however, the surface layer of the oxide scale is made of $\sim 5 \mu m$ thick TiO_2 scale sitting on top of the alumina layer with thickness of $\sim 3 - 4 \mu m$ (Fig.5c). The $(TiO_2 + Al_2O_3)$ scale of $\sim 25 \mu m$ thick is also present beneath the previously mentioned outer scale. And for Ti-65Al alloy, TiO_2 scale is not dense layer but it's only grains with sizes $\sim 3 - 4 \mu m$. Alumina is sitting on beneath of the scale with thickness of $\sim 2 - 3 \mu m$ while $(TiO_2 + Al_2O_3)$ mixed scale is $10 - 20 \mu m$ thick.

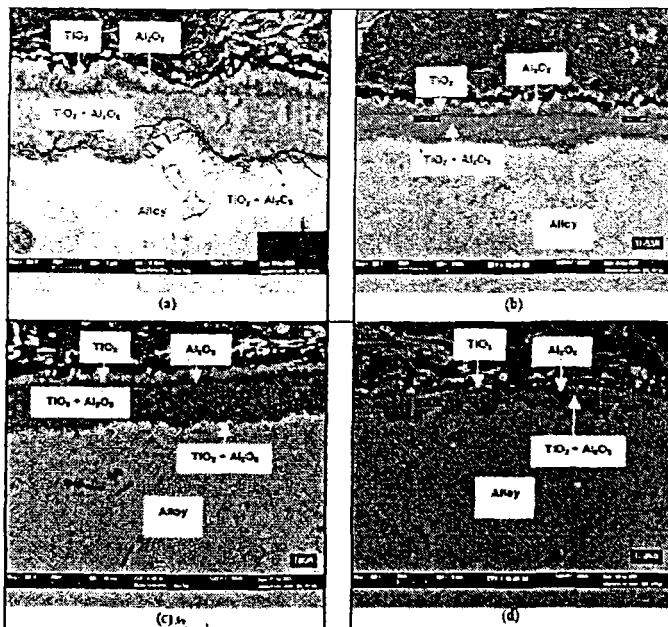


Fig.5. Cross-sectional microstructures after oxidation in air at 1173K for 50 hours of : a) Ti-50Al; b) Ti-53Al; c) Ti-60Al and d) Ti-65Al alloy

From the observed weight-gain experienced by the alloys, Ti-65Al alloy has the lowest oxidation rate with only 0.65% increased weight for the formation of its oxide scales whereas the highest oxidation rate belongs to Ti-50Al alloy with a 0.85% weight increase. In the intermediate range, Ti-60Al and Ti-53Al alloys exhibit increased weight of 0.67% and 0.74%, respectively. It is agreement with Fig.5 that in Ti-65Al, the oxide scale formed is thinner and not dense. It means more slightly oxygen gases diffuse and form the oxide scale on the surface of alloys.

Oxidation resistance in the alloys is related to the extent to which they form continuous and protective alumina (Al_2O_3) scales [4]. The fours of alloys can form alumina protective oxide scale in oxidation process at 900°C for 50 hours inside muffle furnace with almost same thickness $\sim 3 - 5 \mu m$. Ti-50Al alloy with (α/γ) phase has the highest oxidation rate due to the phases of alloy have high oxygen permeability which lead to inability of alloys to form a protective alumina scale and internal attack. Meanwhile, the lowest oxidation rate was occurred on Ti-65Al alloy with $\gamma + TiAl_2$ phases because of more content Al to form alumina protective oxide scale.

4.4 X-Ray Diffractometer (XRD) Analysis

X-ray diffraction spectra are given for each of alloys in Fig.6. XRD test has been carried out to confirm the present phases in titanium aluminides alloys using XRD Siemens Diffractometer D5000. The present phases in alloys were analyzed by PC-APD for Windows Ver. 4.0g manufactured by Philips Electronics N.V. 1999 and licensed to Jabatan Penyiataan Kajibumi-Malaysia Semenanjung.

From analyzed XRD in Ti-50Al, γ -TiAl and α_2 -Ti₃Al phases have been identified as well as in Ti-53Al. While in Ti-60Al and Ti-65Al, γ -TiAl and TiAl₂ are present phases.

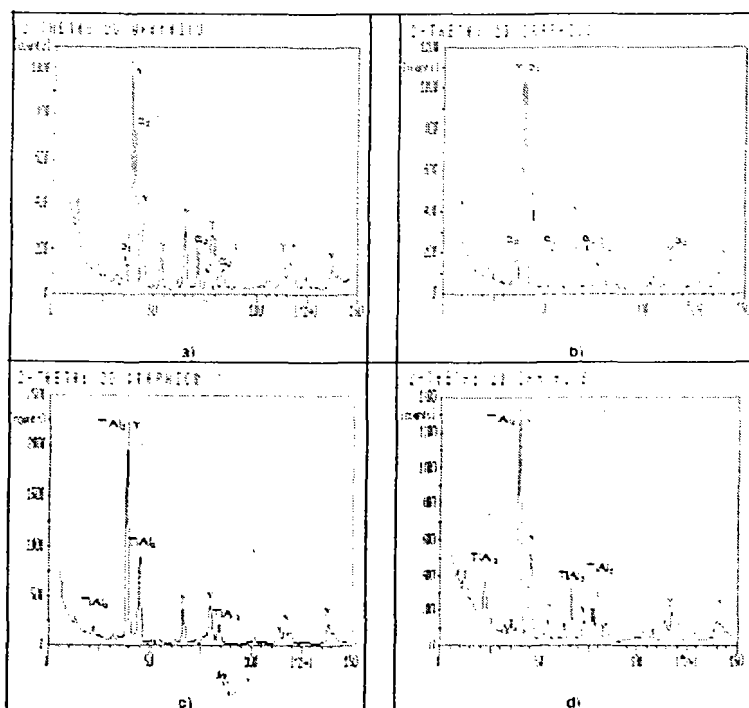


Fig.6. XRD patterns of Ti – Al system for (a) Ti – 50Al, (b) Ti – 53Al, (c) Ti – 60Al and (d) Ti – 65Al

5. Conclusions

Alloy phases composition and microstructures can affect the properties of alloys. In binary titanium aluminides alloys, Al content is the most influential element to the alloy hardness, density and oxidation resistance. It acts through changing the volume fraction of phases, which is the hard phase in $\alpha_2(\text{Ti}_3\text{Al})$ while the lightest alloy and good oxidation resistance are related to TiAl_2 of present phase.

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