CHARACTERIZATION OF γ-TIAI BASED INTERMETALLIC ALLOY AND IT'S OXIDATION BEHAVIOR ON TI-50Al

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The oxidation behavior of Ti-50Al based intermetallics alloy at 900 °C in air has been investigated inside a muffle furnace for 50 hours. The surface and cross-sectional microstructure of oxidized samples were characterized with XRD and SEM/EDS. It was found that the Ti-50Al exhibited layers of TiO₂ scale on the surface, followed by Al_2O_3 scale between the surface layer and the inner layer of mixed (TiO₂ + Al_2O_3) scale. The thickness of the scales are ~12.5 µm for the TiO₂ surface scale, ~5 µm for the Al_2O_3 inbetween scale and ~40 µm for the TiO₂ and Al_3O_3 mixed inner scale, respectively.

1. INTRODUCTION

Gamma TiAl-based alloy which contains 45 at.% - 50 at.% aluminum is one of the titanium aluminide alloys possessing great potential for high temperature applications, such as jet engine components and exhaust valves in car engines, owing to their specific strength, stiffness, modulus and creep and fatigue resistance at elevated temperatures (750 – 1000 °C). Due to the oxide-forming elements of Ti and Al, an oxide layer containing TiO₂ and Al₂O₃ can easily be formed on the surface of the alloys during service at elevated temperatures. There are two types of the oxide scale at the su alloys, i.e. protective and non-protective. As protective oxide scale, alumina layer can provide protection for the alloys up to a maximum temperature of around 1400 °C. The protective alumina scale formation refers to the establishment of a continuous α -alumina scale over most (> 75%) of the sample surface [1, 2, 13].

However, the practical use of the alloys remains limited to about 750 - 800 °C due to the relatively rapid growth of a non-protective TiO₂ and intermixed Al₂O₃ + TiO₂ scales at higher temperatures. The exact temperature limit depends on the specific alloy composition and the oxidizing conditions. As discussed by Brady, M.P. et al., Ti-49Al based alloys should be viewed as the borderline for forming a protective Al₂O₃ scale. Reinforcing the earlier claim that the transition for TiO/TiO₂ stability to alumina stability occurs at approximately 50 at.% Al, this study also found that the nearly continuous alumina scale was evident on the surface of Ti-50Al alloy specimen [15]. Indeed, improving the oxidation resistance of γ -TiAl based alloys is critical for increasing both their use and their reliability in high-temperature applications. And studying the oxidation behavior on the alloy many contribute to a more systematic understanding of the fundamental aspects in the borderline determination of the protective and non-protective oxide scale formation [3].

Characterization using XRD and SEM/EDS of the as-cast received of Ti-50Al alloy will be provided in this study. The oxidized samples at 900 °C for 50 hours inside a muffle furnace were also analyzed and SEM/EDS results from the cross-sectional microstructures of the oxidized alloy surface will be presented.

2. EXPERIMENTAL

Ti-50Al intermetallic based alloys used in this present study has been prepared at the School of Materials and Mineral Resources Engineering-USM, Penang, Malaysia. Several necessary steps were

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taken to produce the alloys. Powders of the required metals were first weighted according to the intended compositional variation of Ti-50Al. The powders were then mixed under inert atmosphere for 5-6 hours to obtain a uniform mixture/distribution. Carver compaction equipment was used to make the powder mixture into pellets under 10 tons of loads to ensure the pellets with 10 mm in diameter (Fig.1a) will not splash out during the arc-melting process. Melting the pellets has been performed using a specially-designed and locally-made arc-melting fumace (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 (Fig.1c) were 20 mm in diameter, 5 mm in thickness and about 4 - 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. % HNO3 and 86 vol. % H2O. Each of the alloys has been characterized using LEO SUPRA 50VP SEM/EDS and Siemens Diffractometer D5000 XRD. Oxidation processes have been carried out on the coupons of samples inside a muffle furnace open to room air under isothermal condition of 900°C for 50 hours. And the cross-sectional microstructures of the samples resulted by the oxidation process have been characterized using SEM/EDS.



Fig. 1. (a) A pellet of metals powder; (b) A cell of locally-made arc-melting furnace; and (c) A button of alloy [4].

3. SOLIDIFICATION AND MICROSTRUCTURAL TYPES

The portion of Ti-Al binary phase diagram relevant to solidification is schematically shown in Figure 2. The solidification path of binary TiAl alloys has been divided into 3 categories by Mccullough et al. [5, 6]:



Fig. 2. (a) Ti – Al binary system of phase diagram [7]; and (b) The central portion of Ti-Al phase diagram showing solidification and $\alpha \rightarrow \gamma$ phase transformation processes of alloy with stoichiometric composition [10].

Most γ TiAl-based alloys of technical interest contain 40 – 55 at% Al. A key point illustrated in the diagram is that the solidification and solid-state equilibria of γ -TiAl based alloys are complex and sensitive to the Al concentration. For example, γ is quite stable in Al-rich compositions. In Al-lean compositions, α -Ti can form as a result of solidification or heat treatment process. The maximum Al concentration in binary TiAl in β -Ti is 44.8% as shown in the phase diagram. Alloys with 44.8% (or lower) Al solidifies as the primary β phase. Alloys with Al above 44.8% solidify as the β phase first but at the peritectic temperature solidification to the β phase stops and the remaining liquid reacts with the β solid to form the peritectic α 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 α phase [5, 6, 8].

With the aid of the phase diagram in Fig. 2a and 2b above, it can be described various microstructures obtainable in TiAl-based materials. The classification here is primarily based on phase equilibria as a function of temperature and alloy composition. The microstructural size scale is also a function of heat treatment time and cooling schedule, and typical values are given below for comparison in Figure 3. They are single phase γ (equiaxed γ), duplex (bimodal) and fully lamellar [8].

As a result of the solid-state phase equilibria shown in Fig. 2, three distinctly different types of microstructures can be obtained by annealing as mentioned before as be shown in Fig. 3. Alloys 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 (Fig. 3a). The grains are equiaxed and about 0.04 mm in diameter. For alloys between 46 and 50 at.% Al, heat treatment in the ($\alpha + \gamma$) phase field results in a two-phase structure upon cooling (Fig. 3.b). 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 a result of transformation from the primary α during cooling to room temperature. The grains are typically 0.01 - 0.02 mm in diameter, and the lamellar plates are 0.04 - 0.08 mm thick. This structure is referred to as the duplex structure. Finally, alloys below 48 at % Al that are heat treated in the single-phase α field can form the fully lamellar structure, as shown in Fig. 3c. The grains are typically greater than 0.12 mm in diameter, which reflects the rapid coarsening rate of the disordered α [8].



Fig. 3. Typical as-cast microstructures of γ-TiAl based alloys: (a) single-phase γ, (b) duplex of γ and lamellar, and (c) fully lamellar [8].

For a lamellar structure, the grain size, i.e. lamellar spacing (λ) and diameter (d) are very important to determine the properties of the alloys such as mechanical, physical and oxidation resistance. The fully lamellar microstructure seems to be better than the other two microstructures (single phase gamma and duplex) by offering high strength, high creep resistance, good fatigue strength and high fracture

toughness, but generally with somewhat lower ductility than the duplex. Fig. 4 shows schematically of grain size for polycrystalline lamellar materials [8, 9].



Fig. 4. Grain size (d) and lamellar width (λ) for polycrystalline lamellar materials [9].

4. RESULTS AND DISCUSSION

4.1 Alloys Phase Compositions and Microstructures Of Ti-50Al

Fig. 5a and 5b show the microstructure of the as-cast received of arc-melted Ti-50Al alloy sample. Many grains exhibited a columnar morphology with a colony width of ~ 50 μ m and a length > 80 μ m. Within the colony grains, the microstructure consisted of alternating lamellae of α_2 -Ti₃Al (D0₁₉) and γ -TiAl (L1₀) plates. The microstructure of colony shows that a grain of the γ phase as matrix within which distributed α_2 laths can be found.

Microanalytic study has shown that the regions free of lamellar microstructure or those in the form of thick lamellae have an increased Al content (above 50 at. %), which shows that it is the γ -TiAl phase. The Al content in the lamellar structure regions consisting of fine lamellae is lower than its average content in the alloy. Thus, the predominating component in the lamellar structure is the α_2 -Ti₃Al phase poor in Al, whereas the lamellar structure, according to the equilibrium system, is composed of a mixture of alternating ($\alpha_2 + \gamma$) lamellae [9].

The lamellar microstructure is obtained from solidification route of $L \rightarrow [\beta] + L \rightarrow [\alpha] + L \rightarrow [\alpha] + \gamma \rightarrow [\alpha_2] + \gamma$. During cooling, the primary β reacts with the remaining liquid resulting in the formation of peritectic α at the β/l interface. And further cooling of the alloy through the $(\alpha + \gamma)$ phase field results in the formation of lamellar (α_2/γ) lath structure as observed in the room temperature microstructure of this alloy. EDS results show that the composition of Ti-50Al alloy with Ti ranging from 53.63 to 53.99 at.% and Al from 46.01 to 46.37 at.%. Additional TEM (Transmission Electron Microscopy) test is necessary to accurately determine which γ or α phase is present in the Ti-50Al alloy.

4.2 X-Ray Diffractometer (XRD) Analysis

X-ray diffraction spectra are given for the alloy in Fig. 6 while the complementary XRD pattern with dspacing and relativity intensity is provided in Table-1. XRD test using XRD Siemens Diffractometer D5000has been carried out to confirm the phases present in the Ti-50Al alloy. The phases in alloys were analyzed by PC-APD for Windows Ver. 4.0g manufactured by Philips Electronics N.V. 1999 and identified to Jabatan Penyiasatan Kajibumi-Malaysia Semenanjung. The result indicated that γ -TiAl and α_2 -Ti₃Al phases are present in Ti-50Al. It is in agreement with observed results of the previous Secondary Electron Microscopy (SEM) and Electron Dispersive Spectroscopy (EDS) in this study.



Fig. 5. Typical lamellar grains observed from the Ti-50Al by SEM micrograph (a) in the econdary electron mode (b) in the back-scattered electron mode.



Fig. 6. X-ray Diffraction patterns of Ti –50Al alloy with γ -TiAl and α_2 -Ti₃Al phases.

d-Spacing,A	R.Intensity (%)	Phases
4.0571	6.9	Gamma
3.3828	3.4	alpha 2
2.8269	4.2	alpha 2
2.5998	3.8	alpha 2
2.4907	8.9	alpha 2
2.3153	71.8	gamma
2.2568	25.3	alpha 2
2.1911	44.6	gamma
2.0380	15.6	gamma
1.9988	17.6	gamma
1.6964	5.6	alpha 2
1.4259	7.8	gamma
1.3108	6.2	alpha 2
1.2515	2.9	gamma
1.2229	5.6	gamma
1.2059	6.0	alpha 2

Table I. d-spacing, relativity intensity and phases of Ti-50Al

4.3 Oxidation of Alloys

The oxidation of γ -TiAl based titanium aluminides proceeds in four characteristic modes dependent upon oxidation temperature, as illustrated in Fig. 7. Mode I occurs at ambient temperatures with the formation of a thin titanium oxide that quickly passivates the surface. Some alumina has also been observed to form at these low temperatures. Mode II occurs at higher temperatures up to approximately 800 - 950 °C (threshold increase with AI content in the alloy) with the formation of an alumina scale and some rutile-phase. The alumina offers complete coverage and rapid passivation with minimum loss of subsurface alloy. At higher temperatures up to approximately 1100 °C the oxidation rate constants increase by several orders of magnitude and mode III occurs with the formation of a tri-layer scale. An outward-growing TiO₂: layer borders an inward-growing two-phase TiO₂/Al₂O₃ layer, with an often observed stationary Al₂O₃ layer at their interface. Passivation is tenuous at best, and breakaway oxidation often results. Finally, above about 1100 °C, mode IV occurs with internal oxidation adding to even more rapid deterioration of the alloy [11].

Fig. 8 presents the isothermal oxidation results on Ti-50Al alloy after 50 hours in opened air at 900 °C. The microstructures of the bulk alloy are still lamellar as the initial alloy. While the grains have become finer after the oxidation process, its chemical composition altered. Its chemical composition is deficient in Al (suggesting preferential Al oxidation) and rich in α_2 -Ti₃Al. The initial composition of Ti-50Al is approximately 46.01 – 46.37 % Al and 53.63 – 53.99 % Ti then in oxidized of the bulk alloy is ~ 38.44 % Al and ~ 47.51% Ti. Deficiency of aluminum and titanium in the bulk alloy were due to form oxides scale on the surface of the alloy.



Fig. 7. Schematic of the four oxidation modes of y-TiAl based titanium aluminides [11].

Three types of oxide scales have been produced as the results of the oxidation process at 900 °C for 50 hours TiO_2 , $(TiO_2 + Al_2O_3)$ and Al_2O_3 . The thickness of the TiO_2 scale is ~ 10 µm and $(TiO_2 + Al_2O_3)$ mixed scale is ~ 25 µm while the alumina scale at interface of both scales is ~ 5 µm thick. The TiO_2 and $(TiO_2 + Al_2O_3)$ scales are not non-protective and not expected to form in the oxidation process due to the scales cannot fulfill the following requirements for protective oxide scales: high thermodynamic stability in the respective operating environment, low interdiffusion of the oxide scale-forming elements (low oxide scale growth rate), low vapor pressure of the oxide, crack healing ability, good adhesion with the metal, and thermomechanical compatibility with the metal [12]. Although the intermixed TiO_2/Al_2O_3 scale formed by Ti-50Al alloy provided adequate oxidation resistance, it may not be an effective barrier to oxygen/nitrogen (hot gases) dissolution during oxidation into the bulk of alloy.

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 [13, 14]. In this study, it was found that a thin nearly continuous and protective alumina scale on the surface of the alloy. The inability to form a true protective alumina scale is also potentially troublesome [15]. It indicates that there is approximately ~14.05% carbon in bulk of alloy. It is postulated the carbon interact with titanium to form TiC (titanium carbide).



Fig. 8. SEM image showing cross-sectional microstructure of as-cast received of oxidized Ti-50Al alloy with Maginification of 500x.

4. CONCLUSIONS

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Characterization of Ti-50Al shows that microstructure consisted of alternating lamellae of α_2 -Ti₃Al (D0₁₉) laths and γ -TiAl (L1₀) plates. The composition of the phases are 46.01 – 46.37 % Al and 53.63 – 53.99 % Ti. The decreasing aluminum and titanium content in bulk alloy after isothermal oxidation process at 900 °C for 50 hours is due to the formation of TiO₂, (TiO₂+Al₂O₃), and Al₂O₃ scales. The Al₂O₃ scale formed is nearly continuous and protective oxide scale.

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