High Temperature Oxidation Behaviour of Substitution Vanadium with Iron in Ti-6Al-4V Metal Alloy: A Review

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Abstract

Ti-6Al-4V which is known as the workhorse of the aerospace industries has been widely used for structural body frame and engine components specifically in fan blade due to its capabilities to withstand the harsh environment of the workplace with properties of high in strength to weight ratio, high in tensile and fatigue strength, and high in corrosion resistance. By substituting vanadium with Iron in Ti-6Al-4V, it is economically beneficial as a low-cost material alloy composition. Since iron is closely related to rusting, the effect of substitution vanadium to iron should be consider. This paper reviews on various mechanical properties of a newly formed alloy of Ti-6Al-xFe. All such properties are then compared with Ti-6Al-4V as a reference alloy.

Keywords: *High Temperature Oxidation, Oxidation behaviour, Ti-6Al-4V, Ti-6Al-Fe, Titanium alloys.*

1. Introduction

Titanium alloys become staple in engineering for industries such as aerospace, marine, chemical, constructions, and medical sector for its biocompatibility properties [1,2]. Ti-6Al-4V alloy composition is the most commonly used titanium alloy in many industries due to its ability to withstand the harsh working environment with its high in strength to weight ratio, high in tensile and fatigue strength and high in corrosion resistance properties. It is also known as the workhorse of the aerospace industries [3]. The main justification of using titanium in aerospace industries as a replacement of steel is it properties of high in strength to weight ratio with 60% low in density compared to steel [4,5]. For Ti-6Al-4V, it is mainly use as body frame and engine part especially as a fan blade since it has low service temperature of 200˚C-400˚C [6,7].

The operation cost of aerospace industries is relying on the performance of the flight and one of it is regarding on interaction between weight of the aircraft with fuel consumption [8]. Initially titanium alloys higher cost of production can be balanced by cost savings in the life and durability of the component corresponding to a reduction in the repair and maintenance frequency of the components. [7]. Furthermore, since titanium alloys usually undergo a series of complexity working processes to become a finished product increases the cost of the alloys [9]. As

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such, low cost titanium alloys composition has been developed and the method use is by substituting the expensive material with much lower material. In Case of Ti-6Al-4V, the vanadium is substitute with iron which is a much cheaper material [9-14]. Since iron are widely known to have the capabilities of producing ill-defined material call rust which are iron oxides product namely wüstite (FeO), hematite (Fe_2O_3) and magnetite (Fe_3O_4). These oxides are worst to present on the surface of the application [15].

2. Titanium Alloy

Titanium are known to have high in strength to weight ratio, high in tensile and fatigue strength, lightweight and high in corrosion resistance properties. These properties depend on a number of alloy composition and reinforcement mechanisms done to the alloy such as its solid solution phase, grain size and hardening of precipitation [2]. All these mechanisms can be adjusted by various processing steps that lead to specific microstructures. Combinations of some working processes and heat treatment resulting in microstructure modifications and improvements in the mechanical properties. The microstructure and properties of the composition of the titanium alloy can also be modified by adding additional elements depending on the phase of the alloy to be dominant. [16].

Commercially pure titanium belongs to the group of allotropic metals which can exist in two different equilibrium lattice modifications. There are three categories of Titanium alloy according to the predominant phases in their structures which is alpha (α) phase, alpha-beta (α+β) phase and beta (β) phase. The α+β phase alloys are most commonly utilized titanium alloys due to have balanced mechanical properties offered by both phase alloys. In room temperature, titanium alloy can have both crystallize structure, body centered cubic (BCC) and in a hexagonal close packed structure (HCP) [17]. These crystallographic variations can be subjected to manipulation through adding or substitute of alloying elements and/or heat treating to obtain an extended diversity of alloys and properties [18].

The physical and mechanical properties of alloy is unique depending on its element composition. Certain properties were needed in certain application that has in that particular binary alloy composition but there will have a certain limit that the binary alloy composition can perform. The mechanical properties of binary alloys depend heavily on the composition of its constituent elements. [19]. From an atomic point of view, the enhancement of the observed mechanical properties seems most likely to be due primarily to the structure of the ternary alloy component atoms in the binary alloy crystal lattice location in the sub-micro volume [20].

3. Substitution of vanadium with iron in Ti-6Al-4V (Ti-6Al-xFe)

Since Ti-6Al-4V is an α+β phase alloy, the alloy is flexible to manipulate its composition and in this cases vanadium which is an expensive material can be replaced with much low-cost material such as iron. Most β stabilizing elements used in titanium alloys, such as vanadium, molybdenum and niobium are called isomorphous are very expensive. To reduce costs, researchers had replaced isomorphous elements with eutectoid β stabilizers such as iron, chromium, and nickel. The aluminum as α stabilizer in Ti-6Al-4V should be remained in the composition at certain wt% to prevent embrittlement of the α alloys [11].

There are several researches that had been done by substitute vanadium with iron in Ti-6Al-4V composition. The newly formed composition had showed a different in mechanical properties compared to the original composition which is Ti-6Al-4V. As in 2002, Fujii and Takahashi [11] developed a Ti-5.5Al-1Fe composition of titanium alloy. Ti-5.5Al-1Fe exhibited such unique properties as a high in fatigue strength to ductility relationship after the composition had been treating and annealing [11]. Yoon et al. (2011) was developed a composition of Ti-6Al-1Fe and Ti-6Al-4Fe. Both compositions showed a higher oxidation resistance at 700˚C and 800˚C for 96 hours [12]. Simsek and Ozyurek (2019) also showed a higher oxidation resistance with their Ti-5Al-2.5Fe composition alloy [21]. Kim et al. (2013) was developed a composition of Ti-6Al-4Fe. As for comparison after been expose to high temperature of 700˚C, the grain size of the alloys had higher volume fraction of its β phase [22]. Lu et al. (2016) was developed a composition of Ti-6Al-1Fe alloy, Ti-6Al-2Fe alloy and Ti-6Al-4Fe alloy. Electrochemical corrosion testing of the alloys showed that when dissolved in the electrolyte, TiO, Ti_2O_3 and TiO_2 form faster on the surface with iron addition. [23]. Abdala et al. (2017) was developed a composition of Ti-6Al-1Fe alloy, Ti-6Al-2Fe alloy and Ti-6Al-3Fe alloy. These alloys undergo heat treatment process and showed that the hardness of the alloys hardness gradually increased with an increase of iron content [10]. Same with Bondurin et al. (2018) when his Ti-6Al-4Fe alloy showed much more hardness compared to Ti-6Al-4V composition [15].

4. Oxidation Behaviour of Metal

Chemical reaction between metal and oxygen is called oxidation, which is a type of corrosion that involves a number of processes that occur sequentially and simultaneously with oxidant adsorption, and when ion species are involved in the growth, dissociation and diffusion of oxides, either on cations and anions through the growing scale. Oxygen enters the subsurface area of metal alloys at high temperatures, resulting in some adverse effects. Scale thickness of oxidation formed and increased by internal oxygen diffusion. The diffusion of oxide defects controls the transport of cations and anions, except where gasses were chemically involved. [24].

The rate of oxidation for metals and alloys is crucial because the rate of oxidation of many metals and alloys determines the lifespan of the element. The oxidation rate is usually measured and expressed as a function of time in terms of weight per unit area. As for oxidation rate, it follows three basic kinetic laws which is parabolic rate law, logarithmic rate law and Linear rate law [25]. When oxidation occur and oxide-scale formed at very thin condition on the surface, diffusion through the oxide scale will be rapid. Hence, establishing virtual equilibrium with the metal at the gas-scale interface. During this time, the metal behavior will be sustained at a high value, initially close to unity and through rapid diffusion within the oxide scale [26].

4.1 Mechanism of Oxide-Scale Formation

The formation of an oxide-scale on the metal surface consists of four steps, starting with the surface oxygen adsorption, the formation of an oxide nucleation, the lateral growth of the nuclei and therefore the formation of a compact oxide-scale on the metal surface. After the lateral growth of the nuclei has been established, a measure consisting of an oxide material surrounds the metal surface and is therefore isolated from the gaseous atmosphere if the metal layer is completely covered. The characteristics of the scale oxide, which is completely covered on the surface, have an effect on the oxidation resistance [6]. Some oxide scales reduce the bonding force between the substrate and the oxidation scale and cause the substrate to break out of the oxidation scale. These phases are brittle scale layers which form on the surface of the substrate, resulting in distortion of the lattice and reduction of the substrate mechanical properties. Under such conditions, the alloy is susceptible to enhanced oxidation, which may impair its lifespan if the protective oxide layer cracks, when the activity within the alloy at the oxide scale metal interface falls below equilibrium [27].

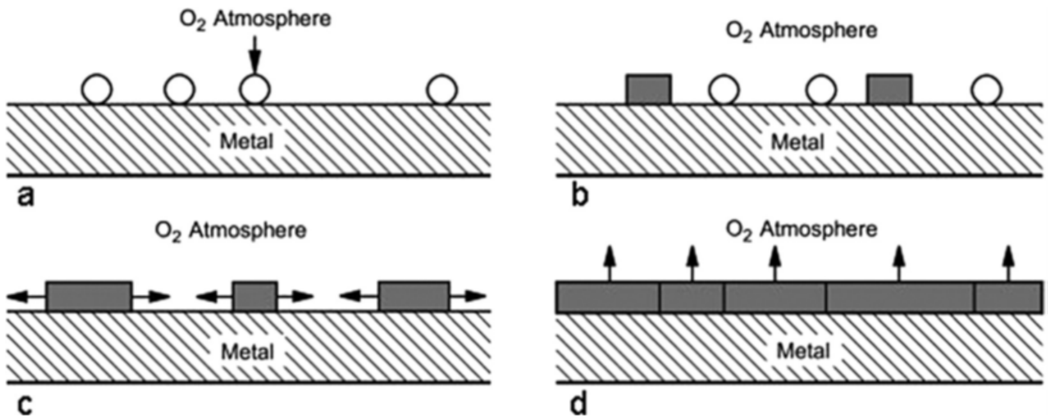

Figure 1. Model of oxide scale formation on pure metal surface. (a) Oxygen absorption at the surface; (b) formation of nuclei; (c) lateral growth of nuclei; (d) growth of the oxide-scale [6].

4.2. Oxidation Resistance Alloy

The ability to construct a protective oxide scale across the surface of the material is the main concern of all high temperature metallic materials against high temperature oxidation. The protective oxide scales should meet certain criteria depending on the operating conditions, including high thermodynamic stability in the oxidation setting, low oxide vapor stress, low oxide scale elements inter-diffusion, crack healing capability, thermomechanical metal compatibility and good metal adhesion. [28].

In this situation, some methods of modification needed to be developed, the most effective oxide layer to be chosen is Al_2O_3, as it is a protective oxide layer with its low growth rate properties, excellent compactness and better adhesion. Therefore, the most effective alloy element for improving the resistance of titanium alloys to high temperature oxidation is certainly aluminum. The ratio of

Al_2O_3 to the oxide scale increases at high temperatures, resulting in an increase in the aluminum content of titanium alloys. At a certain point, high concentration aluminum can be deliberately oxidized to a single layer of aluminum scale that can effectively prevent the diffusion of titanium with oxygen and increase the sensitivity of titanium alloys at high temperatures. In addition, incorporating aluminum will decrease the alloy's total density, enhance the atomic binding force in the solid solution and improve the alloy's high temperature strength. Furthermore, titanium alloy corrosion resistance can be increased efficiently. This also refers to elements other than aluminum that effectively increase the oxidation of titanium alloys when alloy elements are added to titanium alloys simultaneously as aluminum. Therefore, the alloying elements, other than aluminum referred to as the third elements [6].

5. Oxidation of Titanium Alloy

In the case of pure titanium, oxidation at lower temperatures in the atmosphere can result in a compact of TiO_2 oxide scale produced by the reaction of titanium to oxygen, which can completely cover the surface of the alloy and therefore separate the alloy from the gaseous environment. TiO_2 scale oxidize on the surface provides an excellent isolation barrier between the metal and the gaseous environment which provides resistance to corrosion and contamination at temperature below 535˚C. While at above 535˚C, the oxide scale breaks down and microscopic molecules, such as carbon, oxygen and hydrogen will embrittle the titanium [29]. This state will comply with the parabolic law of oxidation kinetics due to low operation and lower diffusion rate of oxygen. However, the layer of TiO_2 oxide scale will becomes loose and brittle due to high temperatures. As a consequence, activity and diffusion rate of oxygen on the surface are getting stronger. The oxygen atoms then penetrate the metal and titanium atoms and diffuse to the surface from the cores and cracks of the oxide scales. This will cause the oxide scales thicker, making the bonding strength between the oxide scales and the metal weaker. [28]. Hence, titanium properties of excellent corrosion resistance arise when the adhesive binds.

The most common constituent elements for titanium alloys are titanium and aluminum. As the aluminum content of the composition increases, the plastic deformation of titanium alloys will deteriorate. On this account, the aluminum content in titanium alloys composition should not exceed a maximum of 6 wt %. It is possible to precipitate phase such as Ti_3Al and TiAl from titanium alloys. For Al_2O_3, the phase form when there is a low activity of aluminum interacts with specific oxidation of aluminum. For titanium alloy, TiO_2 is the main phase precipitate at high temperature. Since the structure of these oxide scales has poor oxidation resistance, there is limited use in certain maximum operating temperature ranges only [6].

5.1 Oxidation of Ti-6Al-4V

Usage of titanium alloys are often restricted to the temperatures under 550˚C as the oxide layer expands as temperatures are above this mark and the subsequent oxide transition becomes more active and non-protective. Of all the applications for the composition of titanium alloys, Ti-6Al-4V accounts for almost 60% of the titanium produced [30]. The Ti-6Al-4V which is an $\alpha+\beta$ phase is the commonly used because of its high in specific strength, high in corrosion resistance and metallurgical stability rather than its pure titanium form.

Guleryuz and Cimenoglu (2009) stated that corrosion resistance of Ti-6Al-4V alloy improved greatly after the alloys undergoes oxidation treatment at 600˚C for 60 hours [31]. The surface oxidized Ti-6Al-4V alloy shows the formation of a thin layer of oxide starting at 500°C and growing thicker in time to completely cover the surface. [32]. The growth of the oxide scale follows the parabolic law when the air environment oxidizes the Ti-6Al-4V alloy and The oxidation rate rises quickly above 650˚C [33]. In other research, the oxidation rate follows parabolic kinetics in the range of 600˚C and 700˚C and provides a dense and adhesive oxide layer. Then, a brittle and crumbly oxide layer formed over the surface of the alloys above 700˚C and the oxidation rate fitted linear kinetics [31].

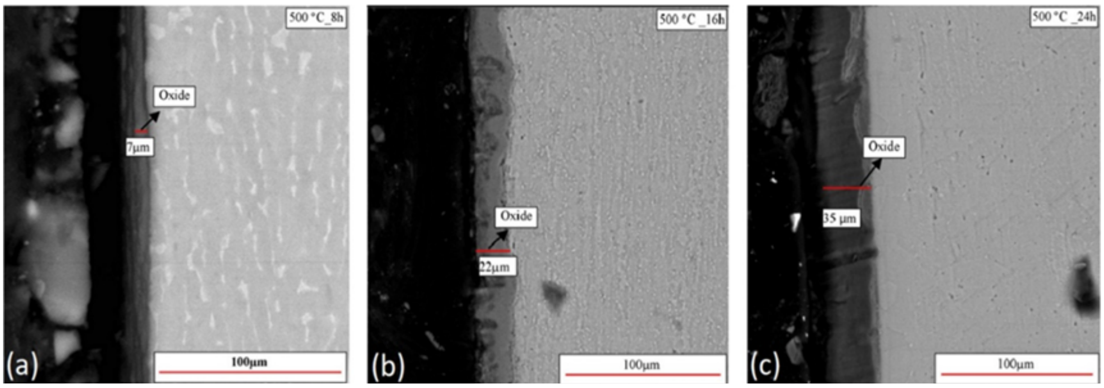

Figure 2 : Ti-6Al-4V cross-sectional scanning electron micrographs of thermally oxidized samples at 500°C temperature for durations of 8-hour, 16-hour and 24-hour in air [32].

5.2 Oxidation of Ti-6Al-xFe

Since Iron are widely known to have the capacity to produce an ill-defined material called rust which are iron oxides product namely a few as Wüstite (FeO), Hematite (Fe_2O_3) and Magnetite (Fe_3O_4). These oxides are the worst to be present on the surface of the application [15]. As for Ti-6Al-xFe, TiFe formation has been reported to have a negative effect on the mechanical and corrosion properties of titanium alloys. According to Lu et al. (2016), The passive current density of Ti-xFe alloys was increased when the TiFe component was developed, resulting in poor corrosion resistance [13].

As in previous research, formation of TiFe precipitate was observed when the high temperature oxidation of Ti-5.5Al-1Fe was performed at 450˚C for 100 hours [11]. As for Ti-6Al-4Fe has higher oxidation resistance compare to Ti-6Al-1Fe [12]. Other research has shown that the Ti-6Al-xFe form oxide scale consists of three layers (TiO, Ti2O3 and TiO2), that are much faster on the surface with the addition of iron when dissolved in the electrolyte [14].

6. Conclusion

Ti-6Al-4V is a staple alloy that widely used in many areas. It also known as workhorse of the aerospace industries. Since the composition itself is an expensive alloy, researchers had come out a solution of substituting expensive element in the composition which is Vanadium with much lower cost element which is Iron. Several researches had been conducted to the newly formed alloy of Ti-6Al-xFe and the result shows an improvement compared from certain point of view to the original composition. As for its oxidation behaviour, formation of Ti-Fe precipitate was observed. For this to conclude the characteristic of the newly formed alloy is not enough. More of the study focusing on oxidation behaviour of the substituting composition alloy of Ti-6Al-xFe need to be done.

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