Development of Oxidation Resistive Coating for High Temperature Applications

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Abstract

Titanium and its alloys are commercially used in airplanes, missiles, and rockets owing to high mechanical strength, low weight, and prone to oxidation resistance at high temperatures. Aluminide coatings were developed on titanium alloy (Ti-6Al-4V) substrate to protect them from oxidation at high temperature. Coatings were deposited by solid-state diffusion reaction through, chemical vapor deposition (CVD) by adopting halide activated pack cementation (HAPC) technique. The pack consisted of 20 wt% source materials (Al), 10 wt% activator (NH_4Cl) and 70 wt % Al_2O_3 used as a filler. The aluminide coating was carried out for 3 hours at 1000°C. The coated and bare (Ti-6Al-4V) substrates were characterized for structural, microstructural, elemental analysis and thermal stability using X-ray diffraction (XRD), optical microscope (OM) and thermal gravimetric analysis (TGA) respectively. XRD spectra confirm the high concentration of Ti-phase in the Ti-6Al-4V substrate. Aluminum rich phase (Al_3Ti) identified in aluminide coated substrate. Optical micrographs revealed that 60µm aluminide thick coating was developed. TGA results concluded that the (Ti-6Al-4V) bare substrate was not stable and oxidized beyond 600°C in air. The substrate coated with aluminide coating showed good thermal stability up to 1000°C.

Key Words: Ti-6Al-4V alloys, HAPC, oxidation resistance, aluminide coating, deposition

1. Introduction

Refectory metals and their alloys have a high melting point and strong mechanical strength. They are applicable to a variety of industries where we required high operating temperatures. Titanium alloy is one of the refectory metal alloy which have promising properties. Titanium and their alloys are used in aerospace, marine, turbine engine, military, chemical industries and biomedical. Due to their high melting point, light weight, excellent mechanical strength, good corrosion resistance, and biocompatibility [1]. Titanium alloy is particularly used in air frames that compete with other alloy which is particularly less costly. Titanium exist five types of alloy e.g., α-Ti, near α-Ti, α + β phase alloys, β phase alloys and intermetallic Ti compound. TiAl intermetallic is a major interest today. Only this alloy was used in engines due to survive at elevated temperature [2]. Ti-6Al-4V components are replaced subjected to marine aircraft flying load spectrum. The components are suitable fracture toughness replaced when acquiring the high potential [3]. The most famous alloy Ti-6Al-4V which exists in dual phase, α phase and β phase. The production and consumption of these alloys is more than 50% in the overall world due to weight saving [4]**.** The composition of aluminum and vanadium in this alloy reduces the reaction of oxygen at on the Surface [5]. Titanium alloy are good biocompatible used in dental implant, stents and improve the ossecointegration [6]. Titanium alloy Ti-6Al-4V have the excellent mechanical strength and corrosions resistance are used in the manufacturing of aeroplan structural part [7]. Ti-6Al-4V is a high temperature alloy which is used in fan blades, compressors and parts of aircraft engine [1]. Maximum operating temperature of titanium alloy is less than 600°C because titanium base alloys are oxidized at high temperatures [5]. The commercially pure titanium and Ti-6Al-4V alloy are oxidized in both isothermal and dynamically, the resultant is the formation of oxide layer [7]. The oxide layer develop the oxidation diffusion zone and thickness of oxide layer increased with temperature. The oxidation diffusion zone destroyed above the 600°C oxygen penetration to substrate and developed the wide oxidation diffusion zone [8]. When Ti-6Al-4V alloy is exposed in a severe atmosphere the oxygen and titanium both are diffused inward [9].

Improve the oxidation resistance for high temperature application of Ti-6Al-4V alloy by surface modification and alloying element [1]. To develop the coating of Al, Si or Cr on the substrate

surface. The aluminide coating is the best choice for high temperature protective layer on titanium base alloys [10]. There are many reliable coating techniques such as Thermal Spray Coating, Warm Spray coating, and Hot Dip. Developed the hard aluminide coating on the Ti-6Al-4V by using Halide Activated Pack Cementation techniques (HAPC). Halide activated pack cementation (HAPC) used due to homogeneous coating, controllable thickness, low operating cost, and also applicable for complex geometry of substrate [11]. The oxidation resistance improved by increasing the Aluminum at the surface which provides the barrier for further oxidation at high temperature [12]. Aluminide coating plays an important role for oxidation resistance of Ti-6Al-4V. The protective coating developed through solid state diffusion mechanisms by using halide activated pack cementation techniques which fulfill our requirements [13]. In pack cementation techniques the mixture of powder which contains halide activator, source materials and filler. The substrate buried in a mixture of powder at high temperature the halide activator reacted with source materials and developed a series of halide vapors. These halide vapors decompose and source material deposits on the surface of substrate. The reaction start between substrate and source material through solid state diffusion process [12]. The partial pressure developed in the crucible depends upon the quantity of halide activator in the pack and deposition temperature [14]**.** The metallic source materials transport through the created gas phase to the substrate surface, inert filler avoids sintering and accumulation of source metallic powder [15]. The strong aluminum activity in powder packs at low temperature, results in a single phase Al_3Ti developed with no other intermetallic compound formed [13]. The crystal structure of coated and bare substrates (Ti-6Al-4V) was investigated by using X-ray diffraction. Model of XRD D8 ADVANCE (BRUKER) via Cu Kα radiation with wavelength λ = (1.54178Å). The sample was scanned in the range of 2θ = (20^o to 85°) with 0.02^o scanning rate, time taken per step 0.3 sec. The dynamically oxidation behavior study by thermogravimetric analysis (TGA) model TGA/DSC 1 STAR^e system (METTLER TOLEDO). Isothermal oxidation analysis in electric muffle furnace model FSMF-140HT. The aluminized coated surface of substrate (Ti-6Al-4V) was characterized by Philips XL-40 Optical microscope**.**

The objective is to develop the aluminide coating on titanium alloy (Ti-6Al-4V) to prevent the oxidation at high temperature application by halide activated pack cementation. The aluminide coating prevent the inward diffusion of oxygen which resist the oxidation. To study the isothermal and dynamically oxidation behavior of Ti-6Al-4V at 1000^{o}C.

2. Experimental procedure

Commercially available titanium alloy (Ti-6Al-4V) bars were purchased from the market. These bars were cut into small pieces of substrates with a wire cutter. The dimension of these substrates are (6×5×2) mm. These substrates were grinded by silicon carbides emery paper and then cleaned ultrasonically. The composing of pack consisted of 20 wt% source materials (Al), 70 wt% Al_2O_3 used as an inert filler and 10 wt% NH_4Cl as an activator. Ammonia chloride use to activate the aluminum at high temperature. Alumina use as inert filler which avoid the sintering and accumulation of source metallic powder. These powder mixed uniformly in mortar pistol and loaded into alumina crucible. Half of the crucible filled with powder mixture and placed the substrates on the surface of the powder. The remaining portion of the crucible filled with powder mixture. High temperature paste of sodium silicate and alumina used to seal the crucible. The sealed crucible loaded into the electric muffle furnace which shown in fig. 1. The furnace heated at 300^{o}C for 30 mints keeping the heating rate10^{o}C/min to dry the composed pack. The aluminizing process is under 1000^{o}C for 3 hour deposition time. The activator ammonium chloride decompose at high temperature into ammonia and chloride. The chloride react with source material and converts into aluminum chloride in the gaseous form. Gaseous aluminum chloride transport through the alumina which provide the connective porosity to the substrate. The pyrolysis of aluminum chloride the high energetic aluminum atoms are deposited on the substrate surface and penetrate.

After the deposition, the furnace cooled down at room temperature. Remove the pack from the muffle furnace. The coated substrate were cleaned by emery paper to remove the residual powder from the surface. The aluminized coated substrate thickness was verified by optical microscope (OM). Thermal stability and phase-structural analysis were ensure by TGA and XRD respectively.

2.1 Diffusion Mechanisms

The aluminized coating successfully developed on (Ti-6Al-4V) alloy with reasonably thickness and smooth morphology. The coating is rather even, with a thickness of around 55±5μm.

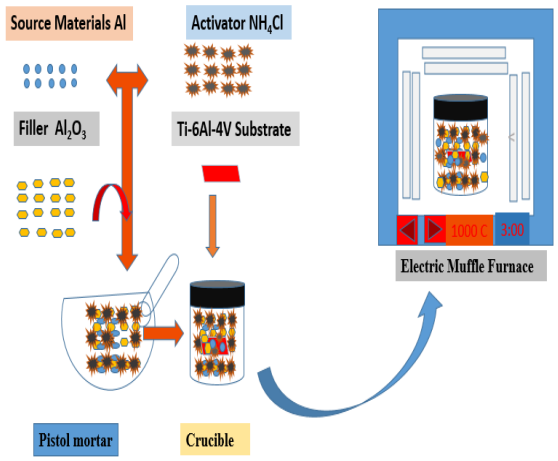

Fig. 1: Show the experimental procedure of Aluminide coating on Ti-6Al-4V alloy by Halide Activated Pack Cementation (HAPC)

The developed aluminide layer show the parabolic behavior, was synchronized by element diffusion. During the heating up period, the activator NH_4Cl, decompose at roundabout 500°C, as shown in following reaction:

$$NH4Cl \leftrightarrow NH_3+HCl \quad (1)$$

Ti might have a significant reaction with oxygen at temperature. The released gases from the activator during the decomposition may not be enough to produce aluminide.

The following reaction occurs in the alumina crucible during the heating up process:

$$2Al+6HCl \leftrightarrow 2AlCl3+3H2 \quad (2)$$

The gaseous form of $AlCl_3$ would transport to the surface of the sample. The full dissociation of oxides at 1000°C generates the surroundings for the reaction occurred in below:

$$2AlCl3 \leftrightarrow 2Al+3Cl2 \quad (3)$$

The Al react with Cl anions produced in the pack which contribute to the aluminizing process. Resulting in titanium (Ti) activity decreased at the substrate surface and further reaction is continued shown in Eq. (3) which increased the Al activity at substrate surface. Ti would appear to move outwards and developed the AlTi layer, shown in following reaction:

$$Al + Ti \leftrightarrow AlTi \quad (4)$$

The following reaction happens when the Al concentration increases and the outward migration of Ti from the substrate decrease:

$$2Al+Ti \leftrightarrow Al_2Ti \quad (5)$$

The aluminum rich (Al_3Ti) layer developed on the substrate surface. The outward transport of Ti from the substrate begins to regulate the coating development.

$$3Al+Ti \leftrightarrow Al3Ti \quad (6)$$

3. Crystal Structure Characterization

Fig. 2 show the XRD pattern of aluminide coated and bare substrates (Ti-6Al-4V). The XRD spectrum of bare substrate (S1) confirms the high concentration of titanium which is allocated by JCPDS card (00-001-1198).

Ti-6Al-4V substrate is coated at 1000°C for 3 hours. XRD pattern with the presence of residual powder illustrated in spectrum (S2). In XRD patterns Al_3Ti dominant phase was confirmed in coating. Al_3Ti shows the rich aluminum concentration on the surface. It is observed that major peaks confirmed the aluminum rich phase Al_3Ti. The Al_2Ti and Al_2O_3 phases exist which is from the residual powder in the pack mixture confirmed in the aluminide coating. These phases are allocated by JCPDS card number (00-002-1121) and (00-042-1136) respectively. The movement of Ti atoms are outward and Al atoms inwards which attribute the formation of Al_3Ti coating [17]. The XRD pattern of aluminide coating without presence of residual pack is illustrated in spectrum (S3). Which confirm the single aluminum rich phase (Al_3Ti) which is allocated by JCPDS card (00-026-0039). (S4) show the XRD pattern of oxidized aluminide coated substrate in the presence of air atmosphere. The XRD pattern after oxidation confirmed the evidence of rich aluminide (Al_3Ti) phase in coating. The aluminum oxide layer (Al_2O_3) and Al_3Ti phases are exist in XRD spectra. Which is confirmed by the XRD pattern of JCPDS card (00-031-0026) and (00-002-1121) correspondingly. The oxide layer developed during the testing of oxidation behavior at high temperature. The source of the aluminum oxide layer is the oxygen taken from air and aluminum from the aluminide coating. The oxide layer is favorable for the resistance to inward diffusion of oxygen.

3.1 Dynamic Oxidation behavior

Fig. 3 which shows the dynamic behavior of coated and uncoated substrate. The analysis was carried out at 1000°C by using thermogravimetric analysis (TGA). The analysis was done under dynamic flow of air at heating rate 10°C/min with flow rate 30 ml/mint. In the case of uncoated substrate, the sharp weight gain observed at high temperature. temperature. The result shows that

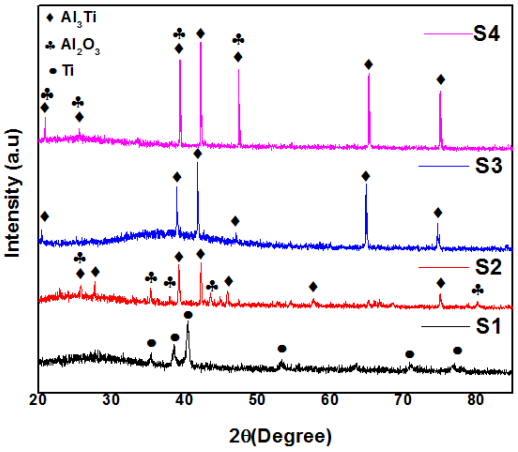

Fig. 2: XRD Analysis of TI-6Al-4V alloy pack Aluminide (S1) Bare substrate (S2) Aluminide coating with residual powder for 3 hours (S3) Aluminide coating without residual powder for 3 hours (S4) Aluminide coating isothermal oxidized

initially there is no significant increase in weight up to 700°C. When the temperature exceeds 800°C weight gain sharply increases due to oxidation phenomena. Maximum weight gain was observed in the range of 850°C to 1000°C temperature. In the case of aluminide coated substrate there are no substantial oxidation occurred. There was no significance wait gain observed with the same parameter. The coated substrate survives at 1000°C. Al_3Ti layer resist the oxidation than titanium alloy Ti-6Al-4V particularly at high temperature. Aluminum oxide scale and Al_3Ti both play an important role in oxidation resistance. The uncoated and Aluminide coated substrate had mass

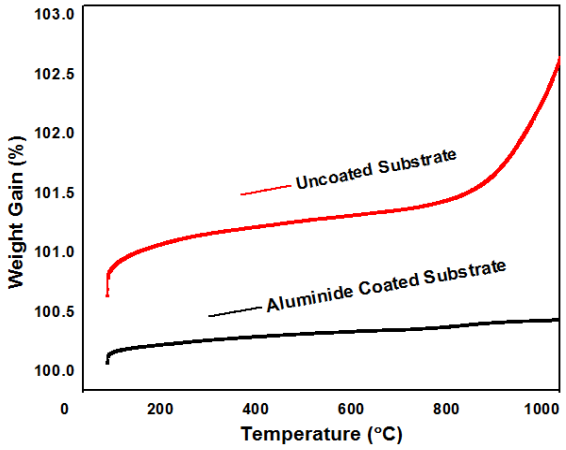

Fig. 3: Dynamic oxidation behavior of aluminide coating on titanium alloy (Ti-6Al-4V) for 3 hours

gain 2.5% and 0.3% Correspondingly, suggesting the Al_3Ti coated samples are not oxidized. Because oxide scales prevent oxidation and lower the substrate's oxidation. Oxidation resistance behavior obey the parabolic law, whereas the linear law comes from the formation of a non-protective oxidized substrate.

3.2 Isothermal Oxidation

Isothermal oxidation resistance of coated substrate carried out at 1000°C in an electric muffle furnace in the presence of static air. The measured the weight of the substrate which we oxidized before placing it in the muffle furnace. The 1st interval of oxidation time 10 mint then measured the weight of the oxidized sample. The duration of each interval consists of 10 minutes. Fig. 4 shows the results of an isothermal oxidation behavior. The coated sample show there is no oxidation occurred initially**.** The oxidation investigation data recorded only six different intervals of time at the same temperature. The recorded data of change in mass is tremendously low which demonstrate the excellent oxidation resistance of aluminide coated sample. The variation of recorded values in the range of 0.3 mg/cm^2 to 0.4 mg/cm^2 at 1000°C. Which confirmed that the protective oxide layer reduced the oxidation. Conclusion of this study, significantly oxidation resistance improved by Al_3Ti coating at high temperature.

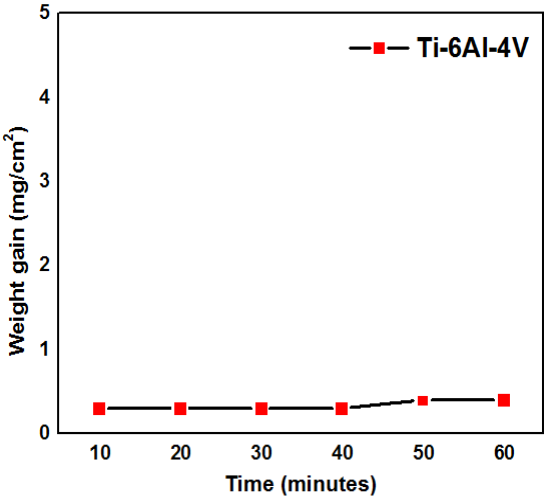

Fig. 4: Isothermal Oxidation of aluminide coated of titanium alloy (Ti-6Al-4V) for 3 hours

3.3 Optical Microscope

Fig. 5(a) the cross-sectional optical micrograph of aluminide coating developed on titanium alloy (Ti-6Al-4V). On the titanium alloy surface, the coating was effectively produced. The surface of the coated substrate is smooth and uniform. The thickness of the coating is approximately 55±5µm with a uniform layer. The

micrographs show that Al_3Ti exists in the inter-diffusion region. The inter-metallic layer developed at the interface which resists the oxidation of titanium alloy. Surface of coating with free of intensive cracks. Fig 5(b) shows the surface morphology of coated samples after oxidation at 1000°C. The isothermal oxidation was carried out for 1 hour keeping the interval of 10 minutes. Coating of substrate is survive with less and more about 50±5µm thick layer. Optical micrographs show that the side walls of the coatings are not smooth and observed cracks during the oxidation test because of the sharp edges of the substrate.

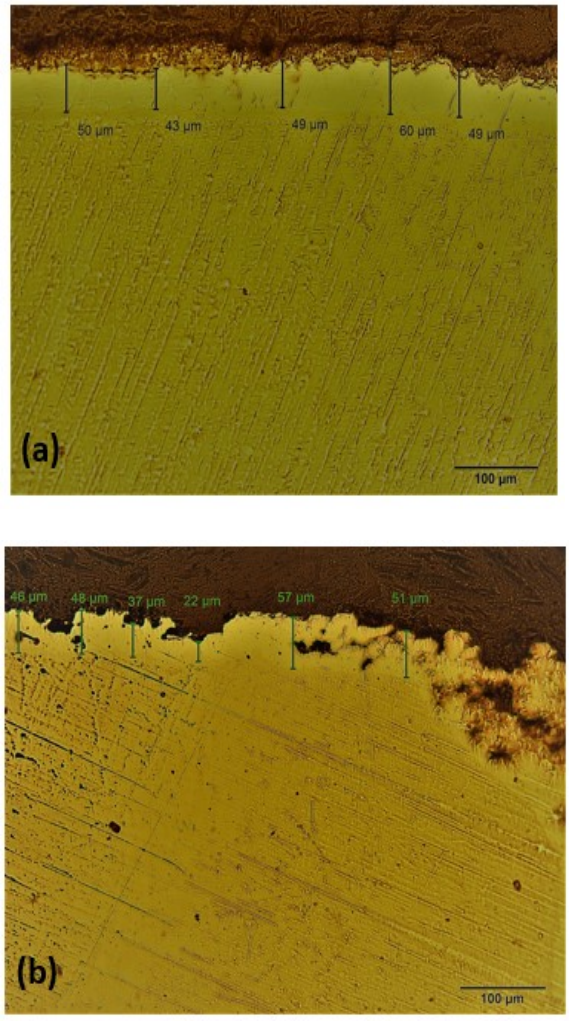

Fig. 5: The cross-sectional optical micrograph of aluminide coatings on titanium alloy Ti-6Al-4V for 3 hours (a) coated substrate (b) after oxidation

4. Conclusions

The commercially available titanium alloy (Ti-6Al-4V) was aluminized by halide activated pack cementation technique, followings are conclusions.

- We have successfully developed, dense and smooth aluminide coating on Ti-6Al-4V alloy.
- Optical microscope reveals that film have good interface with substrate.
- It is observed that Al_3Ti coating with thickness 55±5µm.
- XRD spectrum confirmed the Al_3Ti, Ti and Al_2O_3 phases.
- The single aluminum rich phase coating was developed.
- The coated substrate survive at 1000°C, which resist the oxidation.
- Bare substrate pile out beyond the 600°C.
- Weight gain observed in coated substrate is 0.3% and without coating substrate is 2.5% after isothermal oxidation.

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