HIGH EMISSIVE COATINGS ON TITANIUM ALLOYS

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Abstract

Titanium and its alloys are very interesting materials for space applications due to their low density and high Static and dynamic strength. They have outstanding strength to weight ratio, good fatigue strength and toughness, low elastic modulus, good bio compressibility, corrosion resistance and anti-magnetic properties. However the tribological properties such as low resistance, high suction Coefficient and difficulty to lubricate have a major restriction to their extensive applications.

Micro-arc-oxidation is an advanced anodic oxidation process, with the combination of electrochemical oxidation and high voltage spark treatment. This novel coating technique is capable of disposing dense, hard ceramic composite coatings for the enhancement of tribological properties and the resistance towards corrosion, electrical and their conductivity and chemical actions.

A method for obtaining high micro-hard coating has been discussed.

The present work involves optimization of two important parameters: electrolyte composition and current density in order to get a ceramic like coating on Ti_6Al_4V alloy with required thermos-optical properties. It also involves the study of various other parameters that would affect the thermo-optical property, surface and characterization of the coating.

***Keywords:** Emissivity, Micro arc oxidation, Surface Coating, Thermo-optical property, Electro-chemical oxidation.*

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1. INTRODUCTION

Controlling the level of temperature of equipment, payloads, satellites and launchers is vital during different phases of a space mission. Thermal control allows the maintenance of satellite's temperature within set parameters during its life-time. Physical integrity of the satellites and its effective operation is absolutely essential, because electronic equipment have their optimum performance within a certain temperature range. The satellite's payload will control its operating range by the balance prevailing between incoming external solar, albedo, planet heat fluxes and heat produced internally.

It is desirable for the thermal control subsystems to maintain the overall temperature to an acceptable level and also to obtain the most adequate temperature distribution within the satellite. Proper designing and management of heat distribution within the satellite will be ensured by a thermal engineer. The present work gives the details of development of thermal control coating obtained using Titanium alloy substrate by micro arc oxidation technique.
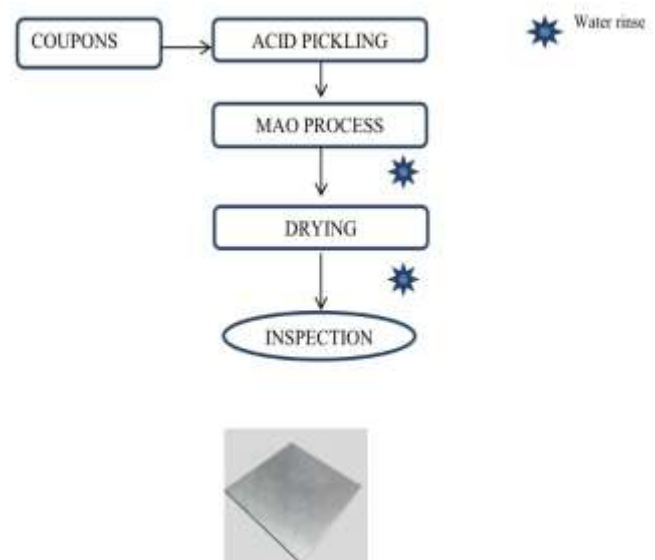
2. OBJECTIVES

The objectives of the project are:
* To provide high emissive oxide coating on titanium alloy using the technique of micro arc oxidation.
* To study the influence of various process parameters on coating-characteristics.
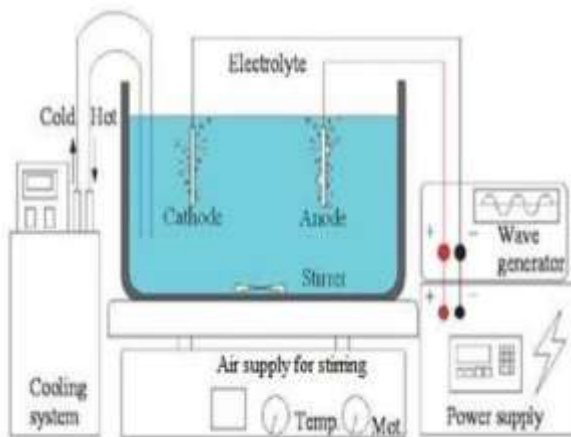* To optimize the process parameters to obtain high emittance coating.

3. MATERIALS AND METHODOLOGY:

PROCESS FLOW DIAGRAM:

Fig 1: Bare sample without coating

A typical treatment unit for MAO processing consists of a processing tank, cooling unit, agitator and a high power electrical source as shown in Fig.2

Fig.2: A schematic of typical treatment unit for MAO processing

A PP processing tank (40cm X 30 cm X 30 cm) having a capacity of 20 liters is connected to a cooling system and high voltage power supply along with an air circulation unit for continuous agitation of the electrolyte. The processing tank is equipped with a stainless steel sheet which acts as cathode during the process of MAO.

3.1 Sample Preparation

Ti_4Al_4V sheet was cut into square pieces of dimension 4 cm X 4cm X 1mm. 2 holes of diameter 1mm were drilled at the edges of the sample. The irregular spurs along the cut edges and drilled holes of the square pieces were eliminated by abrasive equipment. The samples were jigged using aluminum wire.

Pre-treatment techniques: Although pre-treatments are not necessary for the substrate, degreasing and/or acid cleaning were done to ensure a clean and active surface to start with. Degreasing: The samples were degreased using Methyl-ethyl ketone in an ultra-sonicatorfor 5-10 minutes at a temperature of 25±50C

Acid picklingSolution:

Nitric acid (70%) – 262.5 ml/l   Hydrofluoric acid (40%) – 225 ml/l

The substrate was cleaned in the above solution for 1 to 2 minutes at a temperature of 25±50C. After cleaning, the sample was rinsed thoroughly with fresh water followed by D M water.

3.2 MAO Process

All the samples were connected as anodes and a stainless steel plate was used as cathode to complete the circuit. Appropriate electrolytes were used for the process. A detailed explanation of electrolyte selection is given under

Results and Discussion. Air sparger was used to agitate the electrolyte by bubbling air through 20 liters of electrolyte to maintain uniform composition throughout. The electrolyte bath was maintained at 25±50C with cooling circulation bath. MAO of the specimen was carried out at constant current mode. The sample was immersed in the solution and the firm electrical connections were made to AC power supply. The processing parameters like duty cycle, current density, frequency, on time and off time were selected. The process was performed until the set processingtime is reached, after which, it was removed from the solution and rinsed with demineralized water. The sample was again dried using hot air gun.

TESTS: The evaluation of the coatings was done using thickness meter, emissometer and reflectometer.

Thickness meter   Emissometer

Reflectometer

Thickness meter: The thickness measurement was done by using FISHCER ISOSCOPE THICKNESS METER. This thickness meter works on the eddy current principle and measures the non conducting/ oxide coating thickness.

Emissometer:

The emissometer works on the law of radiation.

$$q = \varepsilon\sigma T^4$$

Where ε is emissivity corresponding to temperature T , q is the heat transfer per unit area and σ=Stefan-Boltzmann's constant = 5.670 x 10-8 W/m^2-K^4

Reflectometer: The reflectometer is designed using Beer-Lambert's law.

$A = -log\,T = -log(I/Io)$. Where, I is the light intensity after it passes through the sample, Io is the initial

light intensity, T is the transmittance and A is the absorbance. The reflectometer determines the reflectance of the coating and the term (1-reflectace) would give the value of absorbance.

4. RESULTS AND DISCUSSION

The project pre-dominantly involves determination of two important parameters: electrolyte composition and current density

4.1 Electrolyte Selection

Several electrolytes picked up randomly from literature were utilized for the development of oxide layer on titanium alloy. The thickness, emissivity and absorptivity of the resultant coatings were analyzed. The selection of the appropriate electrolyte was not only based on the higher value of emittance but also on the appearance and uniformity of the coating.

General process parameters employed for the present study are as follows:

Frequency: 50 Hz
On-time (+ve): 700 µs
Average current density (+ve): 15, 25 and 50 ASF (Ampere per sq. feet)
Processing time: 15, 30, 45, 60 min
Temperature: 25±50C

4.2 Solution1

Initially, a silicate and phosphate based aqueous electrolyte was selected for the process.

The process was done at an average current density of 50 ASF for 15 min. The solution composition and thermos-optical properties obtained for the corresponding coating is consolidated in Table 1.

With increase in concentration of phosphate in the electrolyte the thickness of the coating was increasing and there was a corresponding increase in the emissivity. The coating obtained with 15 g/l of phosphate gave a high emittance value of 0.83. However, the coating roughness was high and the coating obtained was non uniform and patchy, especially at the edges. Hence, this electrolyte was not considered for further studies.

Table 1: Solution composition and corresponding thickness and thermo-optical properties

Sample No	SS	NaOH	TSOP	Thickness	Absorptivity	Emissivity
	g/l	g/l	g/l	µm	α	ε
1	15	2	0	6	0.826	0.8
2	15	2	5	7	0.823	0.81
3	15	2	10	13	0.829	0.82
4	15	2	15	20	0.832	0.83

4.3 Solution2

In the second set of trials, again a silicate-phosphate electrolyte was chosen in which the concentration of tri-sodium orthophosphate remained constant while the concentration of sodium silicate was increased in steps of 5g/l. The process was done at an average current density of 50 ASF for 15 min. The solution composition and thermos-optical properties obtained for the corresponding coating is consolidated in Table2.

This electrolyte gave well finished and uniform coating on the substrate, while the thickness and roughness increased in proportion to the concentration of aluminates. Also, the emissivity did not increase significantly with the thickness. Thus, this solution was excluded from further studies.

Table 2: Solution composition and corresponding thickness and thermo-optical properties

Sample No	SS	NaOH	TSOP	Thickness	Absorptivity	Emissivity
	g/l	g/l	g/l	µm	α	ε
1	15	2	15	20	0.831	0.82
2	20	2	15	25	0.832	0.82
3	25	2	15	30	0.85	0.83
4	30	2	15	30	0.876	0.83

4.4 Solution3

The effect of concentration of phosphate on the roughness was studied by adding Tri-sodium orthophosphate to a solution having high concentration of silicate (30 g/l) and a very low concentration of sodium hydroxide (2 g/l) in increments of 5g/l. The process was carried out for 15minutes using an average current density of 15ASF. The solution composition and thermo optical properties obtained for the corresponding coating is consolidated in Table 3.

A similar effect was observed i.e. roughness increased with the concentration of phosphate. Thus, the electrolyte was rejected.

Table 3: Solution composition and corresponding thickness and thermo-optical properties

Sample No	SS	NaOH	TSOP	Thickness	Absorptivity	Emissivity
	g/l	g/l	g/l	μm	α	ε
1	30	2	0	10	0.841	0.77
2	30	2	5	9	0.835	0.78
3	30	2	10	15	0.852	0.79
4	30	2	15	27	0.876	0.83

4.5 Solution4

Introduction of small quantity of potassium fluoride to the electrolytic solution decreases the roughness of the surface of coating. So, to evaluate the effect of KF, the process was carried out for a processing time of 15 minutes at an average current density of 15 ASF. The solution composition and thermo optical properties obtained for the corresponding coating is consolidated in Table 4.

Table 4: Solution composition and corresponding thickness and thermo-optical properties

Sample No	SS	TSOP	KF	Thickness	Absorptivity	Emissivity
	g/l	g/l	g/l	μm	α	E
1	30	0	0	6	0.825	0.76
2	30	0	1	8	0.824	0.77
3	30	5	1	10	0.835	0.79
4	30	10	1	15	0.836	0.81

The addition of potassium fluoride to the solution did not vary the surface characteristics of the coatings, greatly. It can also be observed that the addition of potassium fluoride has decreased the coating rate, thickness and emissivity. Considering the above negative impacts on the coating, the solution was omitted from further studies. The above silicate-phosphate based solution did not provide the desired coating characteristics on the substrate. Thus, the electrolytic solution constituents were changed.

4.6 Solution5

An Aluminate and phosphate based aqueous electrolyte was chosen to study its effect on the coating. The concentrations of both aluminate and phosphate were varied simultaneously during the process carried at an average current density of 15 ASF for 60 minutes. The solution composition and thermo optical properties obtained for the corresponding coating is consolidated in Table 5.

Table 5: Solution composition and corresponding thickness and thermo-optical properties

Sample No	TSOP	S A	Thickness	Absorptivity	Emissivity
	g/l	g/l	μm	α	ε
1	5	5	4	0.64	0.66
2	5	10	4	0.642	0.66
3	5	15	5	0.653	0.67
4	10	15	7	0.668	0.7
5	15	15	8	0.673	0.71
6	25	15	10	0.713	0.73
7	25	25	12	0.731	0.75
8	35	25	15	0.757	0.77
9	35	35	17	0.77	0.78
10	45	35	22	0.798	0.81
11	45	45	30	0.826	0.84
12	50	45	35	0.818	0.85

It can be observed from Table 5 that the concentration of electrolyte has direct influence on the thickness and emissivity of the coatings. Also, from visual observation, it was noticed that the samples were grey-colored, uniform and smooth. It had developed uneven edges and the coating was not uniform.

The sample treated in an electrolyte having composition 45g/l Sodium Aluminate and 50g/l Tri-sodium orthophosphate at a current density of 15 ASF gave desirable parameters like:
Thickness: 35μm;
Emissivity: 0.85;
Appearance: smooth, well finished and uniform.
Thus, the electrolyte composition was finalized.

CONCLUSION

1. The emissivity of the coating is influenced by coating thickness, current density, frequency, voltage applied, processing time, additives and temperature of the electrolyte.

2. A sample treated at room temperature (25±50C) using 45 g/l Sodium aluminate, 50 g/l Tri-sodium orthophosphate and 2 g/l Cobalt acetate (additive) at an average current density of 15 ASF for 60 minutes gave a high emissivity value of 0.85 and absorbance of 0.818.

For a coating, any value of Emissivity>0.8 is desirable for application in spacecraft.

3. The coatings have excellent interfacial adhesion.

ACKNOWLEDGEMENT

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