Formation mechanism and surface characterization of ceramic composite coatings on pure titanium prepared by micro-arc oxidation in electrolytes containing nanoparticles

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ABSTRACT

The aim of this work is to study how nanoparticles incorporate into the prepared ceramic composite coatings on titanium by micro-arc oxidation (M.A.O.) technique in electrolytes containing nanoparticles and modify the surface characteristics. In order to achieve this goal, SiC and SiO_2 nanoparticles (as main and auxiliary particles, respectively) were added to aluminate based electrolytes and M.A.O. process was performed under constant voltage regime using a pulsed power supply. Finally, the effect of addition of nanoparticles on current-time responses, surface morphology, thickness, chemical and phase composition of coatings were investigated. The obtained results showed that addition of nanoparticles (7.5 g/l) to the electrolytes, had no effect on the current-time responses and coating thickness of samples. However it caused a reduction in the size of micro-pores and surface roughness of M.A.O. coatings. It was also concluded that nanoparticles incorporate into the coating with the aid of both electrophoretic force and micro-sparks.

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1. Introduction

Many engineering industries such as chemical, marine, aerospace, automotive, biomaterials and aeronautic have considered titanium and its various alloys due to their combination of low density, high specific strength, good biocompatibility and high temperature stability [1–3]. However, their relatively poor tribological properties, such as high friction coefficient, low hardness and severe adhesive wear, are barriers which restrict their use in applications that need wear resistibility [3–5]. In addition, tribological contacts easily damage the thin native surface oxide layer of titanium which enhances the risk of corrosion in aggressive environments [5–7]. Consequently, surface technologies have been developed to improve these properties by fabrication of hard coatings. Most of surface modification techniques, such as physical and chemical vapor deposition, diffusion processes, plasma spray, plasma immersion implantation, laser beam treatments and nitridizing, are expensive, time consuming and may not provide satisfactory adhesion. Therefore, the most accepted technique to resolve the above named problems is oxidation [7–9].

In recent years, micro-arc oxidation (M.A.O.) has been proved to be a very useful technique to form the protective oxide coatings on the surface of valve metals such as Ti, Al, Mg, Zr and their alloys [10–21]. The coatings are prepared by polarizing the metal (anode) to the dielectric breakdown voltage at the sites of micro-discharges in a suitable electrolyte [11,13,22]. These hard oxide coatings in addition to their proper tribological performance have also good corrosion properties [6,11,12,23–28]. This technique also is characterized by economic efficiency and high reproducibility [3]. However, in recent years, significant efforts have been directed toward the improvement of their properties during the M.A.O. process. For this purpose, some investigations have been carried out to densify M.A.O. treated coatings by adding various nanoparticles to coating electrolyte [29–46]. However, only a few of them were concerned about how these particles incorporate into the coatings and mentioned one or more probable formation and incorporation mechanisms, without practical proof in some cases, in their studies. The most cited theories for different types of substrates and nanoparticles listed below:

I) Nanoparticles agglomerate in micro-pores and high current densities and eruption of molten oxide toward the surface of the coating are the major obstacles for the embedding of nanoparticles into the M.A.O. coating [29].

II) Continuous micro-discharges trap nanoparticles inside the molten substrate [37,38,46].

III) Adsorption of nanoparticles into the coating by electrophoretic force [37,40,45].

IV) The high temperature of the micro-discharges evaporates the electrolyte locally, so the nanoparticles stick to coating surface [44].

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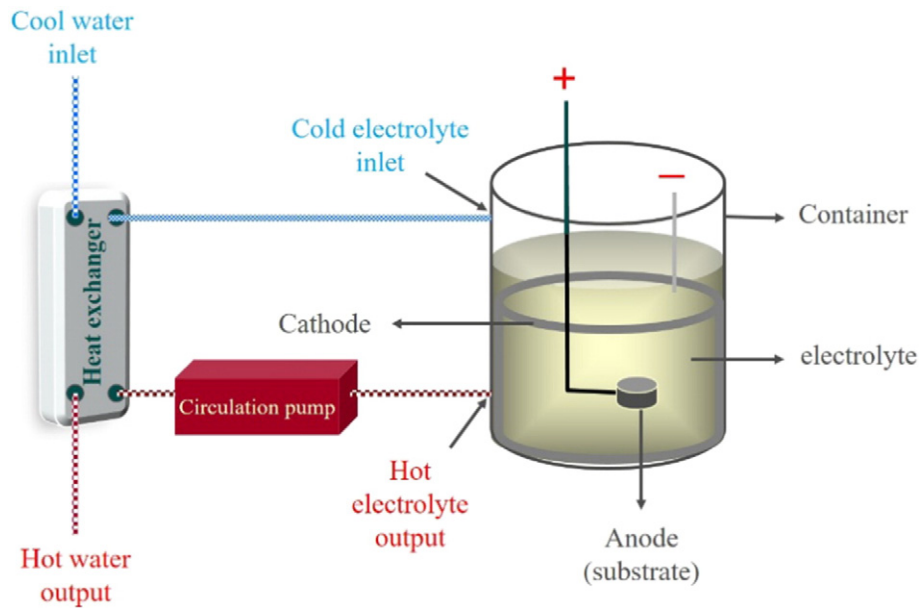   *E-mail address:* akaram@ut.ac.ir (S.R. Allahkaram).

Fig. 1. Schematic of M.A.O. processing cell.

V) The high temperature of the micro-discharges melt nanoparticles and the melted particles, which may react with substrate oxide to form new phases, cover micro-channels and seal them [45,46].

In the authors' previous works the influence of electrolyte composition on the properties of the M.A.O. coated titanium were concerned and the produced coatings in the sodium aluminate electrolyte showed the best performance in comparison to the others [47,48]. In the present research, further to the previous works, SiC nanoparticles were added to an aluminate based electrolyte to find out which of the above mentioned theories is a dominant phenomenon during the M.A.O. composite coating process of titanium. In other words, how these particles incorporate into the coating and affect its surface characteristics and what is the formation mechanism of these composite coatings. Moreover, whenever further investigations were needed to complete the experiments results with practical evidences and reach an accurate conclusion about formation mechanism of the M.A.O. composite coatings, additional studies were done on two other samples. One of these samples has been coated in electrolytes containing SiO_2 nanoparticles, the same way as before, and the other one by different coating regime an electrolytes containing SiC nanoparticles.

2. Experimental details

2.1. Substrate preparation

The used substrate in this study was commercially pure titanium whose chemical composition determined by optical emission spectroscopy is as follows: Fe 0.61 wt.%, V 0.29 wt.%, C 0.05 wt.%, Mo 0.04 wt.%, Al 0.03 wt.%, Cu 0.02 wt.%, Zr 0.01 wt.%, and Ti balance. The samples were cut in discs with 30 mm diameter and 5 mm thickness. First the discs were polished with SiC abrasive paper (60-2000#) and then washed with distilled water and acetone.

2.2. M.A.O. process

A pulsed DC potentiostatic power supply was employed to fabricate ceramic composite coatings on the Ti surface. The growth rate of the coatings in constant voltage process is lower than constant current process, because of the decaying current during the process. By the way, using the constant voltage regime causes coatings with much smoother surfaces and better adherence to substrate. The applied voltage, duty cycle, frequency were designated to be 400 V, 60% and 2000 Hz,

Table 1
Coated samples and characteristics of their coating electrolyte.

Sample code		Electrolyte components (g/l)	Particles (g/l) - (~nm)	Electrolyte conductivity (ms/cm)	Electrolyte pH	Particles zeta potential (mV)	Breakdown voltage (~V)
M.A.O		NaAlO$_2$: 10 KOH: 4	–	19.2	13	–	340
M.A.O + SiC		NaAlO$_2$: 10 KOH: 4	SiC (7.5)–(40)	19.1	13.1	−23.5	340
M.A.O + SiO$_2$		NaAlO$_2$: 10 KOH: 4	SiO$_2$ (7.5)–(25)	19.1	13	−15.5	340
M.A.O + E.Ph + SiC	Step 1	NaAlO$_2$: 10 KOH: 4	–	19.3	12.9	–	340
	Step 2	NaAlO$_2$: 10 KOH: 4	SiC (7.5)–(40)	19.3	12.9	−23	–