


# The influence of Nano-TiO<sub>2</sub> and Nano-Al<sub>2</sub>O<sub>3</sub> Particles in Silicate Based Electrolytes on Microstructure and Mechanical Properties of Micro Arc Coated Ti6Al4V Alloy

Çağatay Demirbaş<sup>a</sup>, Aysun Ayday<sup>a\*</sup> 

<sup>a</sup>Department of Metallurgical and Materials Engineering, Faculty of Engineering, Sakarya University, Sakarya, 54187, Turkey

Received: February 06, 2018; Revised: April 26, 2018; Accepted: May 20, 2018

Ceramic oxide coatings were fabricated on Ti6Al4V alloy by micro arc oxidation (MAO) in silicate electrolytes, with nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> and without nano-additives. Effects of nano additives on the structural and mechanical properties of the MAO coatings were analysed. The MAO coatings were investigated by scanning electron microscopy (SEM), Energy-Dispersive spectroscopy (EDS) micro-hardness and linear wear test. Results show that the surface morphology and tribological properties of MAO coatings are greatly influenced by nano additives in electrolytes. After the coating treatment the surface hardness values increased from 300 HV<sub>0.1</sub> to 635 HV<sub>0.1</sub>. The hardness tests show that nano-Al<sub>2</sub>O<sub>3</sub> addition coating has higher microhardness values than those without any additives. The results indicated that TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles into the coatings make harder and denser surface and increase the wear resistance. The wear resistance of the nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> additives coatings was enhanced about 5 times than without nano additives coating.

**Keywords:** Oxidation, Ti6Al4V, nano additive, wear.

## 1. Introduction

Micro arc oxidation (MAO) also known as plasma electrolytic oxidation (PEO), or anodic spark deposition (ASD) <sup>1</sup> are the same process assisted by plasma discharges under high voltage for producing oxide ceramic films on surface of light alloys. Titanium, magnesium, tantalum, zirconium, aluminium and their alloys are generally coated by MAO <sup>1-4</sup>, which provide stable oxides in electrolytic solution <sup>2-4</sup>. However, the oxide layer generally have a foam-like structure with high bulk porosity and bad mechanical properties especially poor wear resistance, which limited them from wide technical applications <sup>1,5</sup>. For this reason, researchers have focused their work on the process parameters (electrolyte composition, electrical parameters, coating time and nano-additives etc. in recent years) <sup>2,5-8</sup>. Various researchers have observed that the nano-additives in the electrolyte solution significantly affects the properties of the ceramic coatings <sup>5-8</sup>. Xiang et al. <sup>2</sup>, found that the nanoparticles improved the mechanical properties of Al alloys. Wang et al. <sup>6</sup>, investigated nano-Al<sub>2</sub>O<sub>3</sub> additive on Mg alloy. These reports show that nanoparticles have effect on the MAO process, but there are few scientific articles about the effect of nano additive on the structural and mechanical properties of ceramic coating. The scientific studies shown that nano additives had little effect on the surface phase composition, whereas it influenced on surface morphological feature of the MAO coating. Therefore, the study focus on the influence of nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> additives in silicate based electrolyte on the microstructure and mechanical properties of Ti6Al4V coated by MAO. Effects of nano additives on properties of the MAO coatings were analysed. The phase composition, structure, hardness and wear property

of different coatings were investigated by scanning electron microscopy (SEM), Energy-Dispersive spectroscopy (EDS), micro-hardness and linear wear test, respectively.

## 2. Experimental Details

### 2.1 MAO coating

Ti6Al4V alloy was selected for this study and the composition is ((wt. %) of 6.3 Al, 4.2 V, 0.15 O, 0.11 Fe, 0.03 C, 0.02 N, 0.001 H and Ti balance). The samples with dimensions of 70 mm × 5(Ø) mm cylindrical pieces of titanium alloys were polished with abrasive paper and after cleaned by alcohol and were dried in the warm air blow.

The ceramic oxide coating was fabricated using a 5 kW MAO unit, which consists of an electrolyte bath, a thermometer, a stirrer, and a high-voltage DC power supply with approximate 1000 V of the maximum voltage amplitude. A piece of stainless steel cylinder was used as the cathode and titanium substrate as the anode. During the MAO coating, the applied voltage, treatment time and cooling systems were fixed at 400V, 15 min and 30±5 °C, respectively. The base electrolyte was prepared from Na<sub>2</sub>SiO<sub>3</sub> (8,75 g/l), NaOH (1,25 g/l) and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (0,6 g/l) in distilled water. The MAO processes for non-additives MAO-Ti (called MAO-Na) sample were carried out in the base electrolyte. Then in the base electrolyte, 3,75 g/l nano-Al<sub>2</sub>O<sub>3</sub> (average size of 300 nm) or 3,75 g/l nano-TiO<sub>2</sub> (average size of 32 nm) powders were added and the MAO treatment for MAO-Al<sub>2</sub>O<sub>3</sub> and MAO-TiO<sub>2</sub> samples respectively were carried out. The coating parameters were given in Table 1.

\*e-mail: aayday@sakarya.edu.tr

**Table 1.** MAO coated samples and characteristics of their coating electrolyte

Sample codes	Electrolyte components (g/l)	Nano- $\text{Al}_2\text{O}_3$ (g/l)	Nano- $\text{TiO}_2$ (g/l)	Electrolyte (pH)	Electrolyte conductivity (ms/cm)	Micro Hardness ( $\text{HV}_{0.1}$ )
Non Additive (MAO-Na)	(8,75) $\text{Na}_2\text{SiO}_3$ / (1,25) $\text{NaOH}$ / (0,6) $\text{Na}_2\text{B}_4\text{O}_7$	-	-	12±0.1	11,5	520±10
MAO- $\text{TiO}_2$	(8,75) $\text{Na}_2\text{SiO}_3$ / (1,25) $\text{NaOH}$ / (0,6) $\text{Na}_2\text{B}_4\text{O}_7$	-	(3,75)	12,3±0.1	14	580±10
MAO- $\text{Al}_2\text{O}_3$	(8,75) $\text{Na}_2\text{SiO}_3$ / (1,25) $\text{NaOH}$ / (0,6) $\text{Na}_2\text{B}_4\text{O}_7$	(3,75)	-	12,3±0.1	14	635±10

## 2.2 Specimen examination

The microstructural characteristics of coating, elemental distribution were investigated by scanning electron microscopy (SEM, JEOL) and EDS. Table 1 shows the components, pH, and conductivity of the electrolytes and the surface microhardness of the coated samples. The hardness of uncoated Ti6Al4V and coated samples were measured using an FUTURE TECH-CORP.FM-700 microhardness tester at a load of 100 g for loading time of 8 s. The average of three repeat measurements was reported. The friction and wear behaviour of MAO coated with/without nano- $\text{TiO}_2$  and nano- $\text{Al}_2\text{O}_3$  additives samples were evaluated by a computer controlled linear ball-on-disk (CSM tribometer) friction and wear-test machine. The counterpart was an  $\text{Al}_2\text{O}_3$  ball ( $\Phi=6$  mm) according to DIN 50 324 and ASTM G 99-95a. The tests were performed with a nominal load of 2 N and a sliding speed of 0.10 m/s for the total sliding distance of 50 m. After the test, the loss of weight was measured by electronic balance.  $\text{Al}_2\text{O}_3$  wear ball was harder than coated samples and had excellent wear resistance, there was no damages and measurable wear loss found in the experiment. The worn surface of oxidized Ti6Al4V alloy has also been examined by scanning electron microscopy.

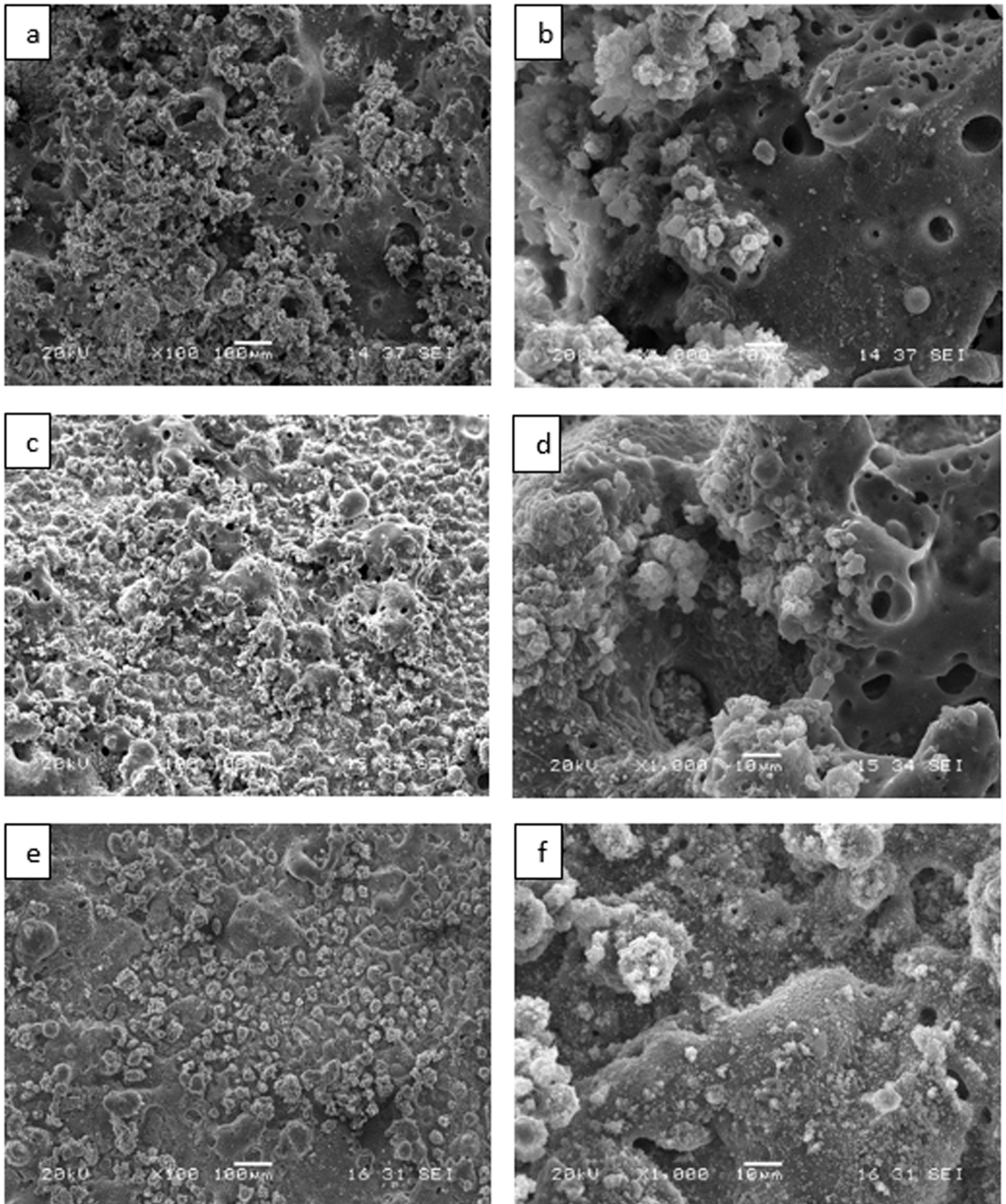
## 3. Results and Discussion

Fig. 1 shows the surface morphologies of the MAO coatings prepared under different conditions. The MAO coatings prepared under Si based electrolytes without nano additive (Fig. 1(a)–(b)) presented different images among them. The surface images of MAO coatings with nano additive  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  are shown in Fig. 1(c)–(d) and Fig. 1 (e)–(f), respectively. As shown in Fig. 1(b), the surface of the coating without nano additive (MAO-Na) showed several micropores like a pancake. It can be seen that the MAO-Na coating included large micropores ( $\sim 10\mu\text{m}$ ) compared than with coated nano additives. This indicated that nanoparticles introduced into electrolyte could embed into the MAO discharge channels by diffusion during the MAO process<sup>5</sup>. It can be seen that addition of nano powder plays an important role in producing ceramic coatings with a lower porosity. There were some differences between the

nano additive  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  containing MAO coatings. The MAO- $\text{Al}_2\text{O}_3$  coating was smoother and only a few micro pores.  $\text{Al}_2\text{O}_3$  nanoparticles could embed into the micro arc discharge channels through the diffusion during MAO, so the coating surface became denser and smoother. The MAO- $\text{TiO}_2$  coating was more roughness compared with other two coatings. This caused that the nano additives adhesion is strong and the discharge channels are coated by the nanoparticles and making a better surface morphology<sup>9,10</sup>.

Fig. 2 shows the elemental distribution of the MAO coatings prepared under different conditions. The EDS analyses were obtained to determine how nanoparticles dispersed on the coating surface. The EDS maps show that the main element oxygen, titanium and aluminium existed in all coatings but the distribution was changed (Fig2.a-c). From Figs. 2(b), it can be seen that the  $\text{TiO}_2$  nanoparticles were dispersed all over the coatings surface. The similar transformation was shown in Fig.2(c), the nano- $\text{Al}_2\text{O}_3$  additive coating contained more aluminium than other coatings and dispersed all over the surface. It can be indicated that aluminium element was oxidized to form alumina ( $\text{Al}_2\text{O}_3$ ) during the MAO process.

Linear ball-on-disk (alumina ball) sliding wear tests under a constant load of 2 N were applied to the MAO coatings with/without nano additives samples. Fig. 3 shows the friction coefficients and the wear rate of the coated samples. It was observed that the friction coefficient (Fig.3a) of the MAO coatings with nano- $\text{TiO}_2$  additive was lower than the formed coating in the absence of nanoparticles. Probably, less and smaller micropores, more coating density and reduction of the surface roughness which are caused by the addition of the  $\text{TiO}_2$  nanoparticles are the main reason for this behaviour<sup>2,4</sup>. Thus, the low coefficient of friction for MAO treated samples is thought to be associated with the topography of the surfaces<sup>8</sup>. On the otherhand nano- $\text{Al}_2\text{O}_3$  was highest friction coefficient than the other coatings. This caused from the nano- $\text{Al}_2\text{O}_3$  additive coating hardness which was the hardest ceramic layer. The tribological behaviour confirmed by the coefficient of friction can be mostly explained by the surface morphology (roughness) or hardness of the MAO layers,<sup>11,12</sup>. The wear rates of three specimens of MAO-Na, MAO- $\text{TiO}_2$ , MAO- $\text{Al}_2\text{O}_3$  are  $7.5 \times 10^{-7}$ ,  $1.7 \times 10^{-7}$  and  $0.8 \times 10^{-7}$  kg/(Nm), respectively. All the nano additive improve the wear rate nearly 5

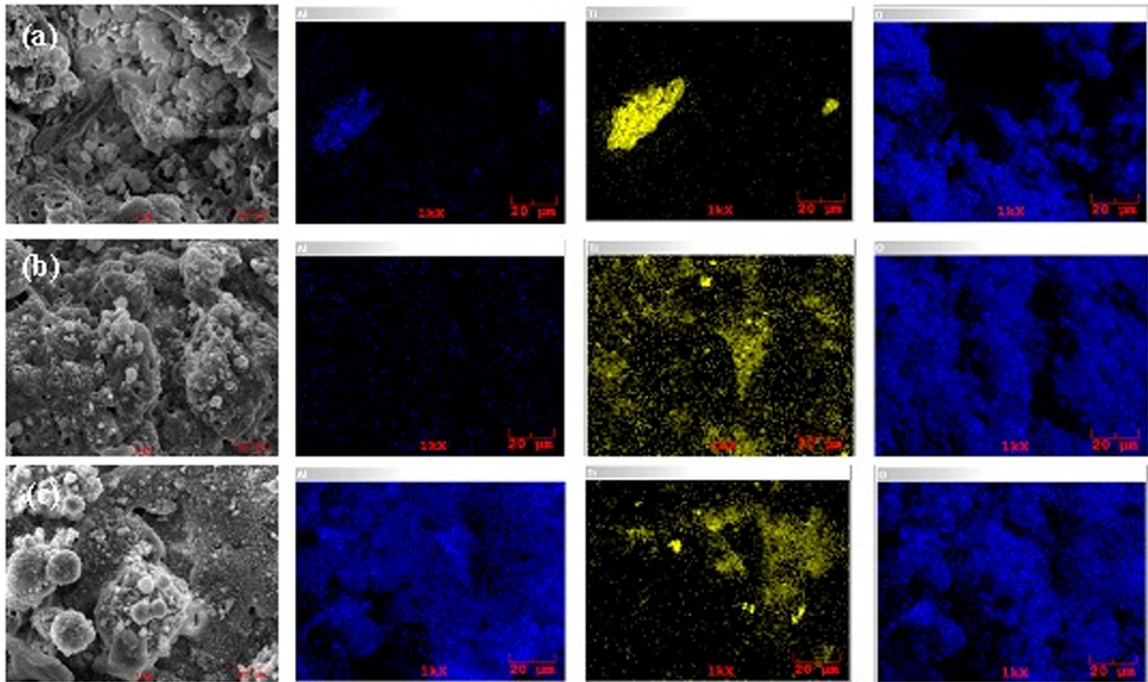


**Figure 1.** Surface Morphologies of MAO coatings of (a-b) MAO-Na, (c-d) MAO-TiO<sub>2</sub>, (e-f) MAO-Al<sub>2</sub>O<sub>3</sub>

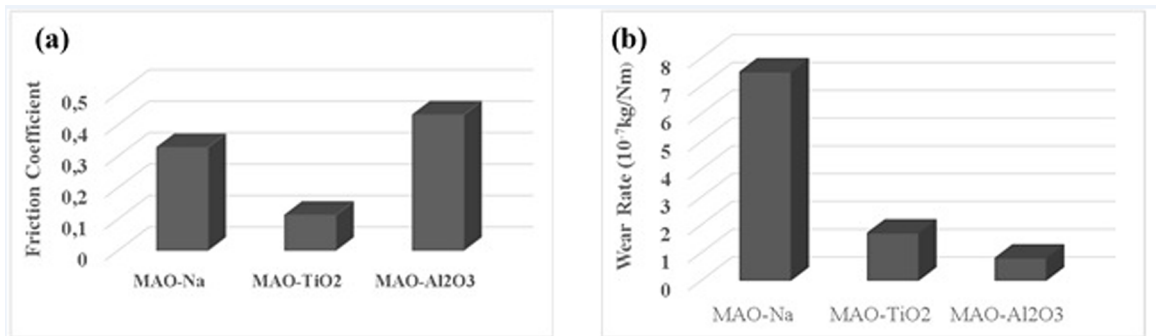
times (Fig.3b). The micro arc oxidization coating is structured with a porous layer and increasing the nano additive made the oxide layer denser. As is well known that the MAO coatings often possess porous structure on the sample surfaces<sup>13,14</sup>, nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> particles introduced into the electrolyte could embed in the micro arc discharge channels by diffusion and electrophoresis during MAO process. Therefore, a

denser and less porous MAO ceramic coating structure was composed. The dense layer and hard phases in the MAO coatings play an important role for the wear mechanisms<sup>10</sup>. The base materials hardness was 300±10 HV<sub>0.1</sub>. After the coating the hardness was increase two times (shown in Table 1).

SEM photographs of worn tracks of MAO coatings without nano additive, with nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub>



**Figure 2.** The elemental distribution of MAO coatings of (a) MAO-Na, (b) MAO-Ti<sub>2</sub>, (c) MAO-Al<sub>2</sub>O<sub>3</sub>



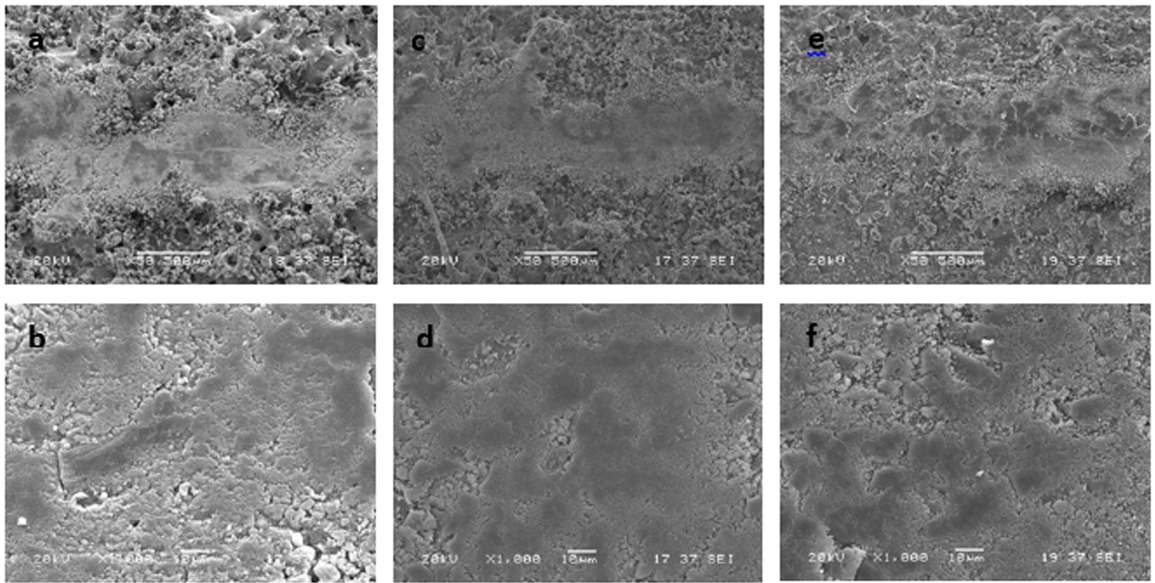
**Figure 3.** MAO-Na, MAO-Ti<sub>2</sub>, MAO-Al<sub>2</sub>O<sub>3</sub> samples of (a) Friction coefficient (b) Mass wear rate

additive prepared in silicate electrolytes can be seen in Fig. 4 (a-f). The wear trace on MAO coatings without nano additive (Fig. 4 (a)) is obviously wider than that of coated by nano additives (Fig. 4(c,e)). This result is dependable with the weight loss of coated without nano additive.. Plastic shearing, scratches and many cracks occurred on the worn trace, can be seen in Fig.4 (b). These are typical features of the abrasive wear and plastic deformation, which usually results in a high wear rate. On the other hand, nanoparticles in the coatings play a pinning and second phase strengthening role which improve the hardness of the oxide coating. Therefore, strengthening by the nano additives decreases the ploughing effect which causes decline weight loss. Small micro cracks and some abrasive occurred on the worn traces, can be seen in Fig.4 (d), (f). It is also correlated with dense surface and high hardness of oxide layer coated by MAO.

## 4. Conclusions

The ceramic oxide coatings were prepared on the surface of Ti-6Al-4V alloy in silicate electrolyte with/without nano additives by micro-arc oxidation. The coating without nano additives are a typical MAO porous structure. The nano additive coatings have different morphologies compared with the non-additives and improved the mechanical properties. The structure became denser with nano-TiO<sub>2</sub> and nano-Al<sub>2</sub>O<sub>3</sub> additives in silicate solution. The MAO-Al<sub>2</sub>O<sub>3</sub> coating have smooth surface and only a few micro pores. The average microhardness values of the ceramic coatings increased with adding nano-additives. The wear rate of MAO coating by adding nano-Al<sub>2</sub>O<sub>3</sub> additives enhance the wear resistance about 5 times. The MAO- Al<sub>2</sub>O<sub>3</sub> coatings shows the best microhardness and the nano coatings have good wear resistance.





**Figure 4.** Worn surface morphologies of MAO coatings of (a-b) MAO-Na, (c-d) MAO-TiO<sub>2</sub>, (e-f) MAO-Al<sub>2</sub>O<sub>3</sub>

## 5. Acknowledgements

This work is financially supported by Sakarya University, Scientific Research Projects for master (project no. 2017-50-01-049) and Scientific Research Project (project no. 2016-01-08-018) Fund.

## 6. References

- Li Q, Yang W, Liu C, Wang D, Liang J. Correlations between the growth mechanism and properties of micro-arc oxidation coatings on titanium alloy: Effects of electrolytes. *Surface and Coatings Technology*. 2017;316:162-170.
- Xiang N, Song R, Zhao J, Li H, Wang C, Wang Z. Microstructure and mechanical properties of ceramic coatings formed on 6063 aluminium alloy by micro-arc oxidation. *Transactions of Nonferrous Metals Society of China*. 2015;25(10):3323-3328.
- Wang P, Wu T, Peng H, Guo XY. Effect of NaAlO<sub>2</sub> concentrations on the properties of micro-arc oxidation coatings on pure titanium. *Materials Letters*. 2016;170:171-174.
- Erfanifar E, Aliofkhaezai M, Nabavi HF, Rouhaghdam AS. Growth kinetics and morphology of micro arc oxidation coating on titanium. *Surface and Coatings Technology*. 2017;315:567-576.
- Li H, Song R, Ji Z. Effects of nano-additive TiO<sub>2</sub> on performance of micro-arc oxidation coatings formed on 6063 aluminium alloy. *Transactions of Nonferrous Metals Society of China*. 2013;23(2):406-411.
- Wang Y, Wei D, Yu J, Di S. Effects of Al<sub>2</sub>O<sub>3</sub> Nano-additive on Performance of Micro-arc Oxidation Coatings Formed on AZ91D Mg Alloy. *Journal of Materials Science & Technology*. 2014;30(10):984-990.
- Daroonparvar M, Yajid MAM, Yusof NM, Bakhsheshi-Rad HR. Preparation and corrosion resistance of a nanocomposite plasma electrolytic oxidation coating on Mg-1%Ca alloy formed in aluminate electrolyte containing titania nano-additives. *Journal of Alloys and Compounds*. 2016;688(Pt A):841-857.
- Wu X, Xie F, Hu Z, Wang L. Effects of additives on corrosion and wear resistance of micro-arc oxidation coatings on TiAl alloy. *Transactions of Nonferrous Metals Society of China*. 2010;20(6):1032-1036.
- Zhao D, Lu Y, Wang Z, Zeng X, Liu S, Wang T. Antifouling properties of micro arc oxidation coatings containing Cu<sub>2</sub>O/ZnO nanoparticles on Ti6Al4V. *International Journal of Refractory Metals and Hard Materials*. 2016;54:417-421.
- Mandelli A, Bestetti M, Da Forno A, Lecis N, Trasatti SP, Trueba M. A composite coating for corrosion protection of AM60B magnesium alloy. *Surface and Coatings Technology*. 2011;205(19):4459-4465.
- Shokouhfar M, Allahkaram SR. Effect of incorporation of nanoparticles with different composition on wear and corrosion behaviour of ceramic coatings developed on pure titanium by micro arc oxidation. *Surface and Coatings Technology*. 2017;309:767-778.
- Li H, Sun Y, Zhang J. Effect of ZrO<sub>2</sub> particle on the performance of micro-arc oxidation coatings on Ti6Al4V. *Applied Surface Science*. 2015;342:183-190.
- Yang Y, Wu H. Effects of Current Frequency on the Microstructure and Wear Resistance of Ceramic Coatings Embedded with SiC Nano-particles Produced by Micro-arc Oxidation on AZ91D Magnesium Alloy. *Journal of Materials Science & Technology*. 2010;26(10):865-871.
- Wang P, Wu T, Xiao YT, Zhang L, Pu J, Cao WJ, et al. Characterization of micro-arc oxidation coatings on aluminum drillpipes at different current density. *Vacuum*. 2017;142:21-28.