Plasma electrolytic oxidation of Titanium Aluminides

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Abstract. Due to their outstanding specific mechanical and high-temperature properties, titanium aluminides exhibit a high potential for lightweight components exposed to high temperatures. However, their application is limited through their low wear resistance and the increasing high-temperature oxidation starting from about 750 °C. By the use of oxide ceramic coatings, these constraints can be set aside and the possible applications of titanium aluminides can be extended. The plasma electrolytic oxidation (PEO) represents a process for the generation of oxide ceramic conversion coatings with high thickness. The current work aims at the clarification of different electrolyte components’ influences on the oxide layer evolution on alloy TNM-B1 (Ti43.5Al4Nb1Mo0.1B) and the creation of compact and wear resistant coatings. Model experiments were applied using a ramp-wise increase of the anodic potential in order to show the influence of electrolyte components on the discharge initiation and the early stage of the oxide layer growth. The production of PEO layers with technically relevant thicknesses close to 100 µm was conducted in alkaline electrolytes with varying amounts of Na2SiO3·5H2O and K4P2O7 under symmetrically pulsed current conditions. Coating properties were evaluated with regard to morphology, chemical composition, hardness and wear resistance. The addition of phosphates and silicates leads to an increasing substrate passivation and the growth of compact oxide layers with higher thicknesses. Optimal electrolyte compositions for maximum coating hardness and thickness were identified by statistical analysis. Under these conditions, a homogeneous inner layer with low porosity can be achieved. The frictional wear behavior of the compact coating layer is superior to a hard anodized layer on aluminum.

1. Introduction
The reduction of moved masses, which can be achieved by the use of modern lightweight materials, leads to high savings of energy and costs in aerospace technology. The application of conventional titanium alloys is limited to about 600 °C. At higher temperatures, nickel-base alloys can be substituted by titanium aluminate alloys, which are based on intermetallic phases in the titanium-aluminum binary phase system. Because of their high creep resistance, low density and comparatively high oxidation resistance, alloys with a chemical composition close to the γ-TiAl phase are viewed as particularly promising. Large research efforts were conducted in order to improve the fracture toughness of these alloys during the last 25 years. This aim was reached by the creation of a homogeneous and fine-grained microstructure through thermomechanical treatments [1, 2].
A further enhancement of the operating temperature of titanium aluminides above 750 °C requires an improvement of the high-temperature oxidation and wear resistance (e.g. against erosion). This cannot be achieved by the variation of the alloy composition without losing the desirable mechanical
properties. Thus, the application of surface technologies is necessary. As already shown by Li et al. [3], protective oxide ceramic coatings can be generated by the plasma electrolytic oxidation (PEO). This technique enables the production of high coating thicknesses over 100 µm, which is a benefit compared to thin PVD or CVD layers that tend to cracking and spallation under high wear stress as the supporting effect of the substrate is not sufficient [4]. Furthermore, the PEO process is typically conducted at room temperature and requires short times, which leads to a higher energy and cost efficiency in comparison with thermal oxidation [5] or thermochemical processes like nitriding or carburizing [6]. Also, there is no thermal modification of substrate microstructure and mechanical properties.

The influence of electrolyte components on the electrochemical passivation or dissolution at anodic potentials during PEO was primarily investigated at aluminum, titanium and magnesium based substrates [7, 8]. Thus, the addition of silicates or phosphates to the electrolyte results in a stronger passivation of aluminum and titanium. The latter is important to avoid strong substrate dissolution at rising anodic potentials. Starting from a certain electric field strength, water vapor is ionized at the anode and the passive layer is broken through by impact and tunnel ionization. Within the discharge channel, substrate material gets molten and anodically oxidized and forms oxide ceramic deposits. During the PEO process, many small discharges or microarcs generate a continuous oxide layer at the substrate surface. Multiple remelting and oxidizing leads to the densification of coating areas close to the substrate and a growing coating thickness. Thus far, the impact of electrolyte components on the initiation of the PEO process as well as on coating microstructure and properties has not been reported in the literature for TiAl substrates.

2. Material and methods

The general effect of single electrolyte components was investigated in a small electrolyte volume of 200 ml at a circular surface of 0.79 cm² using TNM-B1 (Ti43.5Al4Nb1Mo0.1B) gamma titanium aluminide alloy. The samples were polarized as anode against a stainless steel cathode. The current-potential characteristic was recorded with an electrochemical workstation (IM6+CVB120, Zahner, Germany) with the potential increasing from 0 V to 80 V at a rate of 1 V/s. Afterwards, the potential was kept constant at 80 V for 120 s in order to observe the discharge phenomena and passivation effects. The experiments were conducted in an alkaline solution containing 70 (50) g/l of potassium hydroxide (KOH, Merck, purity: for analysis) and varying amounts of sodium metasilicate (Na$_2$SiO$_3$·5H$_2$O, Aldrich, purity: for analysis), sodium metaphosphate (Na(PO$_3$)$_n$, Carl Roth, purity: for analysis), potassium pyrophosphate (K$_4$P$_2$O$_7$, chemPUR, purity: for analysis), citric acid (C$_6$H$_8$O$_7$, VWR BDH Prolabo, purity: for analysis) and deionized water.

In order to produce PEO coatings with high thicknesses up to 100 µm, cylindrical samples of TNM-B1 alloy were embedded in epoxy resin and electrically connected by an aluminum wire. One circular surface with a diameter of 25 mm was exposed to the electrolyte. The plasma anodized coatings were produced in an alkaline electrolyte consisting of 10 g/l KOH. Contents of Na$_2$SiO$_3$·5H$_2$O and K$_4$P$_2$O$_7$ were varied according to a design of experiments between 10–20 g/l and 0–10 g/l respectively in aqueous solution. The coating process was carried out under a symmetrical rectangular bipolar pulse current regime with a pulse amplitude of 2 A and a pulse length of 10 ms in both anodic and cathodic half-cycle. The temperature of the electrolyte was kept constant at 20 °C during the process. The principal arrangement of the laboratory plant for the plasma anodizing process is shown elsewhere [9]. Reference samples for wear testing with the same dimensions consisting of Al 99.5 material were hard anodized in 10 vol% H$_2$SO$_4$ aqueous solution at 5 °C, 2 A/dm² for 1 h.

For scanning electron microscopy (SEM), cross sections were prepared by cutting, hot mounting in electrically conductive resin, diamond grinding, polishing and finally polishing with a silica oxide polishing suspension. Carbon coating was used to avoid sample charging. Secondary electron (SE) and backscattered electron (BSE) images were obtained at SEM LEO 1455VP using 25 kV excitation voltage. The elemental composition was simultaneously recorded by EDS data collection (EDAX Genesis). The X-Ray diffraction (XRD) phase analyses were performed using an X-ray diffractometer.
D 5000 (Siemens) with Co anode. The phase identification was done with the help of the PDF-2 2010 database (International Centre for Diffraction Data).

Hardness values HM0.25/30/30 were obtained by registering hardness measurement with Fischerscope HM2000 XYm at the cross-section of the coating. A Vickers diamond was used as the indenter. Per sample, a series of 5 measurements over the coating thickness was conducted. Oscillating dry sliding wear behavior was evaluated by a ball-on-disc arrangement (SRV, Optimol Instruments) at room temperature using a frequency of 20 Hz, 10 N normal force, WC-Co-ball with a diameter of 10 mm and an oscillation amplitude of 1 mm.

3. Results and discussion

3.1 Modell experiments on the influence of electrolyte components

The influence of electrolyte components on the discharge initiation was determined in the potential range of 0–80 V in highly concentrated KOH solutions. In many cases, a current peak can be observed at the passivation potential. Within the subsequent passivation region, the current density stays at a low level. The discharge is initiated at the breakthrough potential, which is characterized by a sudden increase in current density. Above the initiation potential, a stable discharge process is marked by a constantly high current density. In that state, thin oxide ceramic layers consisting of an adherent base layer and an easily removable outer layer develop on the substrate. If the sample surface is completely covered by a dense oxide layer, the discharges might temporarily or permanently break down, which is characterized by a constantly low current density. An increase of the KOH concentration leads to lower discharge initiation potentials and higher discharge current densities. By using an aqueous solution of 70 g/l KOH, the discharge initiation potential amounts to 50 V, which enables the observation of potential shifts due to the addition of passivating electrolyte components within the regarded potential range. While retaining the KOH concentration, the other electrolyte components were added in the concentrations of 5, 50 and 100 g/l.

Generally, the effect of the investigated additions increases with higher concentrations. For a clearer presentation of the effects, only the curves for 100 g/l additive concentration are displayed in figure 1. It can be seen that the discharge initiation potential is shifted towards about 60 V and the discharge current density is slightly decreased by the addition of 100 g/l K₄P₂O₇. No remarkable change of the current-density time behavior was observed at K₄P₂O₇ concentrations of 50 g/l and below. The components Na(PO₃)ₙ and Na₂SiO₃·5H₂O contribute to the development of a thin and compact passive layer with the result that the discharge is temporarily interrupted or permanently prevented. Also the discharge initiation potential was shifted towards higher values by silicate addition (70 V at 100 g/l Na₂SiO₃·5H₂O). A significantly stronger passivation is achieved by the addition of 50 or 100 g/l citric acid. This electrolyte component seems to be unsuitable as discharges are completely prevented within the examined potential range.
3.2 Properties of PEO coatings with industrially relevant thickness

The production of PEO coatings with industrially relevant thickness of up to 100 µm was conducted at constant KOH concentration of 10 g/l and temperature under pulsed current conditions. As shown by the model experiments, phosphates and silicates are suitable additives for influencing the discharge initiation and the PEO process itself. As Na$_2$SiO$_3$ and K$_4$P$_2$O$_7$ showed the strongest and weakest effect, respectively, both components were varied according to a statistical design of experiments. Coating thickness and hardness served as dependent variables. Also the process time has to be adjusted according to the process parameters in order to generate homogeneous coatings. Due to a local concentration of the electric field lines, the discharges were first initiated at the edge of the circular samples and continued towards the center. In case of compact PEO layers, the process ended as soon as the sample surface was completely covered. Otherwise, in case of a higher coating porosity, the process was aborted, when larger discharges started to destroy the PEO coating locally. The average hardness is related to the average coating porosity, whereas the standard deviations of coating thickness and hardness correlate with the structural homogeneity of PEO layers.

An overview of electrolyte compositions, process times and coating properties is provided by table 1. The analysis of variance reveals that both the pyrophosphate and the metasilicate concentration exert a significant influence on the coating thickness as shown by figures 2a and b. The error probability for considering the effect of the former and the latter on the coating thickness as significant is smaller than 2 % and 1 %, respectively. However, it cannot be excluded that the maximum thickness at 5 g/l K$_4$P$_2$O$_7$ and 15 g/l Na$_2$SiO$_3$ is also affiliated to the high process time of 240 minutes. Meanwhile, as displayed by figures 3a and b, the hardness is not significantly affected by the electrolyte composition. The error probability for considering the effect of pyrophosphate and metasilicate concentration as significant is 44 % and 48 % respectively. This is caused by the high deviation of the hardness because of the considerable amount of flaws in the coatings.

Figure 1. Influence of electrolyte component addition (100 g/l) on the current density time behavior at discharge initiation between 0 and 80 V (sweep rate 1 V/s) and early oxide coating growth at 80 V of a 70 g/l aqueous NaOH solution.
Table 1. Process time, coating thickness and hardness obtained for different concentrations of potassium pyrophosphate and sodium silicate

| No. | c(KOH)/g/l | c(K₄P₂O₇)/g/l | c(Na₂SiO₃)/g/l | Process time /min | Coating thickness /µm | Coating hardness /Nmm⁻² |
|-----|------------|----------------|----------------|-------------------|-----------------------|-------------------------|
| 1   | 10         | 5              | 15             | 240               | 103±25               | 3100±1100               |
| 2   | 10         | 0              | 10             | 230               | 30±4                 | 2500±1200               |
| 3   | 10         | 10             | 10             | 90                | 82±22                | 3700±1000               |
| 4   | 10         | 10             | 20             | 90                | 92±29                | 2900±500                |
| 5   | 10         | 0              | 20             | 90                | 95±10                | 3600±1300               |

Figure 2. Influence of a) K₄P₂O₇ and b) Na₂SiO₃ concentrations on the coating thickness

Figure 3. Influence of a) K₄P₂O₇ and b) Na₂SiO₃ concentrations on the coating thickness

The subsequent BSD images illustrate the influence of the electrolyte components on the coating microstructure. Low coating thickness of about 30 µm and high porosity are obtained in electrolyte 2 containing 10 g/l KOH and 10 g/l Na₂SiO₃ (figure 4a). A significant enhancement of coating thickness (figure 4b) is achieved by raising the Na₂SiO₃ concentration to 15 g/l and adding 5 g/l K₄P₂O₇ (electrolyte 1). Under these conditions, a compact inner coating area with low porosity can be generated (figure 4c). As shown by the results of EDS measurements in table 2, almost no constituents of the electrolyte (e.g. Si) are incorporated within the inner compact layer (area 3). However, higher concentrations of Si and K are detected within the outer porous layer (area 4) or PEO layers with a generally higher porosity (areas 1 and 2). This correlates to the less intense remelting and compaction.
of these areas. XRD measurements generally proved the existence of crystalline phases of TiO$_2$ (rutile, anatase, monoclinic) in PEO coatings on titanium aluminides. There is no clear evidence for the existence of Al$_2$TiO$_5$ as many characteristic reflection peaks are superimposed by those of TiO$_2$ phases. In case of higher Si contents in the outer porous layer (area 4) or porous PEO coatings (areas 1 and 2), significant fractions of unknown amorphous phases have to be expected. Generally, the thin porous PEO coating in figure 4a exhibits a lower Ti and higher Si content compared with the thicker and more compact coating in figure 4b. This might be explained by the presence of amorphous aluminum silicates. In both cases, an undisturbed interface between oxide and substrate can be observed. Cracks that proceed near the substrate-coating interface can be attributed to the materialographic preparation.

![BSD images of PEO coatings generated from electrolytes a) 2 and b) 1; c) shows the framed detail of b) at higher magnification](image1)

**Figure 4.** BSD images of PEO coatings generated from electrolytes a) 2 and b) 1; c) shows the framed detail of b) at higher magnification

| No. | Ti  | Al  | O   | Si  | K  |
|-----|-----|-----|-----|-----|----|
| 1   | 13,7| 14,2| 64,4| 6,4 | 0,4|
| 2   | 6,7 | 6,1 | 67,3| 19  | 0,5|
| 3   | 18,6| 14,9| 65  | 0   | 0,3|
| 4   | 13,9| 10,7| 61,1| 4,7 | 6,5|

**Table 2.** Results of EDS measurements at different areas of figure 4; chemical composition is given in at%

As shown in figure 5a, PEO coatings with high thickness and low porosity can also be created without K$_4$P$_2$O$_7$ addition at a Na$_2$SiO$_3$ concentration of 20 g/l (electrolyte 5) at a significantly lower process time. However, in comparison with figure 4b, the coating appears to be more heterogeneous with respect to phase distribution and microstructure. A remarkable Si content of 4.5 at% is already detected within the inner compact layer. Thus, the presence of amorphous phases is to be expected. Areas with a significantly higher Si and K contents directly border to the inner compact layer. Those appear darker in figure 5a and continue towards the outer areas of the coating. The further addition of 10 g/l K$_4$P$_2$O$_7$ (electrolyte 4) leads to higher porosity and heterogeneity of coating microstructure and coating thickness, as can be seen at Fig. 5b. This correlates to a lower average hardness and a higher standard deviation of coating thickness in table 1. Also the coating appears to be less adherent to the substrate and more brittle as a higher number of larger cracks can be seen. The EDS measurements 4 to 6 show a more gradual increase in Si and K contents with increasing distance from the substrate compared to measurements 1 to 3 at figure 5a. Furthermore, higher amounts of Na and P were detected within the coating. Unexpectedly, the Na content is generally about twice the P content.
although the $K_2P_2O_7$ concentration in the electrolyte was raised. As indicated by XRD measurements, small amounts of the crystalline phase NaAlSi$_3$O$_8$ might be present within the PEO coating. Due to the substrate alloy composition, a small quantity (about 1 at%) of Nb was incorporated into all coatings. Generally, the Nb content decreases with increasing distance from the coating-substrate interface. Thus, no influence of the process parameters on the Nb content could be observed and no statement can be made, whether the Nb content influences the coating properties.

**Figure 5.** BSD images of PEO coatings generated from electrolytes a) 5 and b) 4

**Table 3.** Results of EDS measurements at different areas of figure 5; chemical composition is given in at%

| o.  | Ti | Al | O   | Si | K   | Na+P |
|-----|----|----|-----|----|-----|------|
| 1   | 14 | 13 | 66,6 | 4,5 | 0,9 | 0    |
| 2   | 9,1| 10,7| 59,7 | 9,3 | 8,5 | 0    |
| 3   | 8,4| 8   | 60,9 | 9,4 | 9,4 | 0    |
| 4   | 16 | 11,5| 67,3 | 1,8 | 1,5 | 0,8  |
| 5   | 10,2| 10,6| 61,8 | 7,9 | 6,5 | 2,3  |
| 6   | 6,4| 7,7 | 60,9 | 10,2| 11,2| 3,3  |

With regard to high coating thickness and reasonable process time, PEO coatings of electrolytes 4 and 5 are promising candidates for practical application. Thus, they were chosen for oscillating dry sliding wear investigations. As shown in figure 6, both PEO coatings reveal high wear rates at the beginning of the test. This can be explained by the fast wear of the brittle outer porous coating areas. Due to high frequency and relative motion, a crack network is formed between pores and coating material is removed. As PEO coatings generated from electrolyte 4 are characterized by higher heterogeneity and porosity, higher initial wear and a high variation of the wear depths can be observed. When the outer porous layer is removed and the inner compact layer is reached, the wear rate is significantly reduced to a comparable low constant value for both PEO coatings. This can be attributed to the higher hardness of the crystalline phases and the fine cracks and pores that dissipate fatigue cracks. At this stage, three-body abrasion and fatigue wear are the dominating wear mechanisms. In comparison, a hard-anodized Al 99.5 sample with a comparable coating hardness of approximately 3000 MPa shows lower initial wear because of lower surface roughness and a more homogeneous porosity across the coating thickness. As the diameter of the ordered pore structure slightly decreases from the outer surface towards the substrate coating interface, the wear rate is also slightly decreasing during the wear process. However, the wear rate of the hard anodized coating remains higher than those of the
compact inner layers of the PEO coatings on titanium aluminides. The wear tests on the hard anodized coating were aborted as soon as the coating thickness of approximately 50 µm was reached. Because of the higher wear stock and the lower wear rate of the inner compact layer, PEO coatings are more suitable as a long-term wear protection.

![Figure 6](image_url)

**Figure 6.** Progress of wear depth for PEO coatings generated from electrolytes 4 and 5 and hard anodized reference coating during oscillating dry sliding wear tests

4. Conclusions
It was the aim of the work to identify the influences of different electrolyte components on the plasma electrolytic oxidation of titanium aluminide alloy TNM-B1. Therefore, model experiments were conducted primarily in order to simulate the discharge initiation. It became apparent that an increasing KOH concentration leads to the reduction of the initiation potential and an increase of the discharge current density. The substrate passivation was slightly increased by the addition of K₄P₂O₇, whereas high concentrations of Na₃(PO₄)₃ and especially Na₂SiO₃ led to a strong passivation. This resulted in a significant enhancement of the discharge initiation potential and interruptions or the termination of the discharges after short times. Furthermore, C₆H₈O₇ was proved to be an unsuitable additive due to strong passivation and the suppression of discharges. Hence, the applicability of the newly developed model process was demonstrated.

Based on the findings of the model experiments, PEO coatings with an industrially relevant thickness of about 100 µm were produced successfully. The statistical analysis of the experimental results showed that the coating thickness is significantly enhanced by the addition of both K₄P₂O₇ and Na₂SiO₃. The most homogeneous coating with the lowest porosity was obtained for 10 g/l KOH (supporting electrolyte) and the addition of 5 g/l K₄P₂O₇ and 15 g/l Na₂SiO₃ at a high process time of 240 min. Similar coating hardness and thickness can be achieved by the addition of 20 g/l Na₂SiO₃ without K₄P₂O₇ at a significantly lower process time of 90 min accompanied by a higher heterogeneity. Both parameter sets can be seen as optima regarding coating hardness, thickness and homogeneity due to a suitable combination of coating growth promotion and low incorporation of elements from the electrolyte. A reduction of the Na₂SiO₃ content to 10 g/l and the omission of K₄P₂O₇ leads to porous coatings with a significantly reduced thickness without a pronounced inner compact layer. On the other hand, the incorporation of elements from the electrolyte increases at 20 g/l Na₂SiO₃ and 10 g/l K₄P₂O₇. This leads to a higher portion of amorphous phases, higher porosity and brittleness
of the coatings and a disturbed substrate-coating interface. Furthermore, oscillating dry sliding wear tests showed that the initial wear increases with increasing thickness of the outer porous layer. As soon as the outer porous layer is removed and the inner compact layer is reached, the wear rate is significantly reduced. The wear resistance of the inner compact layer proved to be superior in comparison with a hard anodized reference coating.

It is to be expected that the total wear volume of PEO coatings on titanium aluminides can be reduced by removing the outer porous layer. However, it has to be taken into account that the inner coating layer is not damaged by the machining of the porous layer. A further reduction of the coating porosity and an enhancement of the coating hardness can be achieved by increasing the alumina content of the PEO coating. This might be achieved by applying aluminum layers on the surface or the incorporation of alumina particles from the electrolyte. Furthermore, high-temperature properties of PEO coatings have to be investigated as titanium aluminides are predominantly used at high temperatures. These include coating adhesion and thermal shock resistance as well as high temperature oxidation and wear resistance.

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