

Plasma electrolytic oxidation of AMCs

R Morgenstern¹, M Sieber¹ and T Lampke¹

¹ Materials and Surface Engineering Group, Institute of Materials Science and Engineering, Technische Universität Chemnitz, 09125 Chemnitz, Germany

roy.morgenstern@mb.tu-chemnitz.de

Abstract. Aluminum Matrix Composites (AMCs) consisting of high-strength alloys and ceramic reinforcement phases exhibit a high potential for security relevant lightweight components due to their high specific mechanical properties. However, their application as tribologically stressed components is limited because of their susceptibility against fatigue wear and delamination wear. Oxide ceramic protective coatings produced by plasma electrolytic oxidation (PEO) can solve these problems and extend the possible applications of AMCs. The substrate material was powder metallurgically processed using alloy EN AW 2017 and SiC or Al₂O₃ particles. The influence of material properties like particle type, size and volume fraction on coating characteristics is clarified within this work. An alkaline silicate electrolyte was used to produce PEO coatings with technically relevant thicknesses under bipolar-pulsed current conditions. Coating properties were evaluated with regard to morphology, chemical composition, hardness and wear resistance. The particle type proved to have the most significant effect on the coating properties. Whereas compactness and thickness are not deteriorated by the incorporation of thermodynamically stable alumina particles, the decomposition of silica particles during the PEO processes causes an increase of the porosity. The higher silica particle content decreases also the coating thickness and hardness, which leads in particular to reduction of the wear resistance of the PEO coatings. Finally, different approaches for the reduction of the coating porosity of silica reinforced AMCs are discussed.

1. Introduction

High strength aluminum alloys are particularly suitable as lightweight materials in vehicle and aircraft engineering. Because of their high specific strength, accelerated masses can be reduced, which enables savings of energy costs and the reduction of CO₂ emissions. A further improvement of material properties can be achieved by the creation of aluminum matrix composites (AMCs). An enhancement of strength, hardness, E modulus and creep resistance can be achieved by ceramic particle reinforcement of aluminum alloys as small particles (below 1 μm) contribute to dispersion hardening and grain refinement during material processing. The resistance of materials against abrasion and adhesive wear generally increases with increasing hardness. Thus, AMCs exhibit superior wear resistance compared with aluminum alloys and cast iron under sliding wear conditions. This enables the implementation of AMCs in automotive applications such as brake discs, drum brakes, calipers and cylinder liners [1] and weight reduction due to the substitution of iron base materials. However, as reviewed by Deuis et al. [2], AMCs consisting of high-strength aluminum alloys and micron or submicron scale particles are susceptible to fatigue wear at higher normal loads. Crack initiation takes place at pores, which arise close to particles due to plastic deformation of the matrix alloy at the



critical depth beneath the surface. Finally, plate-shaped material volumes are delaminated from the surface.

The wear resistance of materials can be improved by surface and coating technology. Especially ceramic coatings provide efficient wear protection due to high abrasion resistance and low adhesion against metallic counter bodies. Compact oxide ceramic coatings can be generated by plasma electrolytic oxidation (PEO) on aluminum alloys. The conversion coatings exhibit excellent adhesion to the substrate and a maximum thickness of more than 100 μm . Due to the nature of the process, PEO coatings consist of an inner compact and an outer porous layer. The inner layer is compacted by several remelting processes in the immediate surroundings of micro-arc discharges and consists predominantly of α alumina (corundum). Hardness values comparable to monolithic alumina ceramics exceeding 10 GPa (about 1500 to 2000 HV) can be measured there [3]. Particularly for tribological applications, the process parameters (e.g. electrolyte composition, pulsed current) are optimized with respect to the proportion of the compact coating. If necessary, the outer porous layer has to be removed by machining.

The incorporation or dissolution of ceramic particles influences microstructure and properties of PEO coatings. Wang et al. [4] describe that the growth rate of PEO coatings on AMCs is generally lower compared with the unreinforced matrix alloy due to the high electrical resistivity of the particles. Thermodynamically stable and electrochemically inert alumina (Al_2O_3) particles are incorporated in the coating without restraining the coating hardness, whereas higher porosity is caused by the presence of silicon carbide (SiC) particles. According to Wang et al. [4], a higher number of cracks and pores develops due to internal stress and the formation of Al_4C_3 plates at the substrate-coating interface. However, this correlation is not clear as the authors simultaneously varied the matrix alloys and observed that alloy composition also strongly affects coating thickness and porosity. In contrast, according to the model of Xue [5], SiC particles are dissolved in several steps in the vicinity of microarc discharges without causing pores or cracks. Furthermore, no comparable studies dealing with the influence of particle properties on the wear behavior of PEO coatings exist. However, separate studies on SiC and Al_2O_3 reinforced materials give evidence that sliding wear resistance of AMCs against steel counter bodies can be improved by PEO [6, 7].

The aim of the work is to investigate the influence of particle type, size and volume fraction on coating thickness, microstructure, hardness and sliding wear resistance and to give some indications of the particle incorporation or dissolution mechanism.

2. Material and methods

The AMC materials were produced by a powder metallurgical process. A gas-atomized alloy AlCu4MgMn powder was used as metallic matrix. The chemical composition was determined by inductively coupled plasma optical emission spectroscopy (ICPOES) in wt%: 3.8 % Cu, 1.2 % Mg, 0.6 % Mn, 0.4 % Pb, 0.2 % Fe, 0.2 % Zn. Cubic silicon carbide (SiC, Plasmachem GmbH) and α alumina (Al_2O_3 , Plasmachem GmbH) each with different particle sizes 300 nm and 3 μm at maximum were used as ceramic reinforcement. Alloy powder and different particle volume fractions (5, 10, 15 vol%) were mixed by high-energy ball-milling (HEM, Zoz GmbH Simoloyer). The composite powder was encapsulated in a cylinder of commercially pure aluminum, hot degassed, hot isostatically pressed (HIP, 450 $^\circ\text{C}$, 1100 bar, 3 h) and extruded (370 $^\circ\text{C}$) to a cross section of 15 x 15 cm^2 . Subsequently, a T4 temper (solution annealing, natural aging) of the composite was carried out. The process conditions, the microstructure formation of the powder after HEM processing and the material after the extrusion are described in detail in [8].

Samples with a thickness of 5 mm were cut perpendicular to the extrusion direction. The aluminum encapsulation was removed and the front surfaces were grinded until grain size of 600. Samples were electrically bonded by an aluminum wire. All rectangular surfaces were exposed to the electrolyte. The plasma anodized coatings were produced in the alkaline electrolyte consisting of 5 g/l KOH, 3 g/l $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and 0.5 g/l Na_2HPO_4 . The coating process was carried out under a symmetrical rectangular bipolar-pulsed current regime with pulse amplitude of 50 A/dm² 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 [3]. The time-dependent behavior of pulsed current and voltage was recorded with a transient recorder Yokogawa DL850 at a sampling rate of 200 kHz.

The coating thickness was measured at the coating cross section by optical microscopy. Cross sections for optical and scanning electron microscopy (SEM) were prepared by cutting, hot mounting in electrically conductive resin, diamond grinding and polishing. SEM samples were finally polished with a silica oxide polishing suspension and carbon coating was used to avoid sample charging. Backscattered electron (BSE) images were obtained at SEM LEO 1455VP using 25 kV excitation voltage. Secondary electron (SE) images as well as Energy and angle selective BSE (ESB) images were obtained at FE-SEM Zeiss NEON40EsB. Hardness values were obtained by hardness measurement at 100 mN testing force with Fischerscope HM2000 XYm at the cross-section of the coatings. A Vickers diamond was used as the indenter. Oscillating dry sliding wear behavior was evaluated by a ball-on-disc arrangement (Tetra) at room temperature using a rotational speed of 90 min⁻¹, turning radius of 3 mm, 15 N normal force and a 100Cr6 ball with a diameter of 6 mm as the counter body. The cross section profiles of wear traces were measured by contact stylus instrument Hommelwerke T 4000.

3. Results and discussion

3.1 Energy efficiency

For many tribological applications, a PEO coating thickness of about 100 µm is pursued in order to provide sufficient supporting effect and long-term wear protection. From an economical point of view, this should be achieved in a minimum time and with the lowest possible energy consumption. As the PEO process is conducted with constant current density and process time, the total energy consumption grows with increasing process voltage. It is known from conventional electrolytic anodizing of AMCs that the process voltage increases especially with the presence of electrically insulating and chemically inert Al₂O₃ particles [9]. However, as evident from figure 1, the height of voltage amplitudes is not significantly influenced by particle reinforcement during PEO process with the pulsed current. The positive voltage amplitude increase at the beginning of the process, which can be observed for Al₂O₃ reinforced and unreinforced material, can be explained by the increasing electrical resistance during the growth of a continuous compact oxide layer. After approximately 1200 s, the curves converge to a similar voltage height for all investigated materials. At this stadium, multiple microarc discharges remelt the continuous primary oxide layer at points of lower coating thickness. This leads to a macroscopic uniform coating growth and the compaction of the inner layer. It can be concluded that the electrical energy requirement is similar for matrix alloy and AMCs.

Despite the similar energy consumption, the coating thickness depends strongly on the particle type as can be seen from figure 2. In general, the total coating thickness is not deteriorated by the incorporation of Al₂O₃ particles except from slightly lower thickness values at 10 vol% particle content. Furthermore, there is a tendency that the thickness of the porous layer (empty bars in figure 2) grows with increasing particle size. In contrast to this, significantly lower coating thicknesses can be observed on SiC reinforced AMCs. Moreover, a higher portion of the total coating thickness can be attributed to the outer porous layer and there are higher standard deviations with regard to the coating thickness. The SiC particle volume content does not influence the coating thickness significantly. However, total coating thickness and the thickness of the inner compact layer are slightly reduced by increasing particle size.

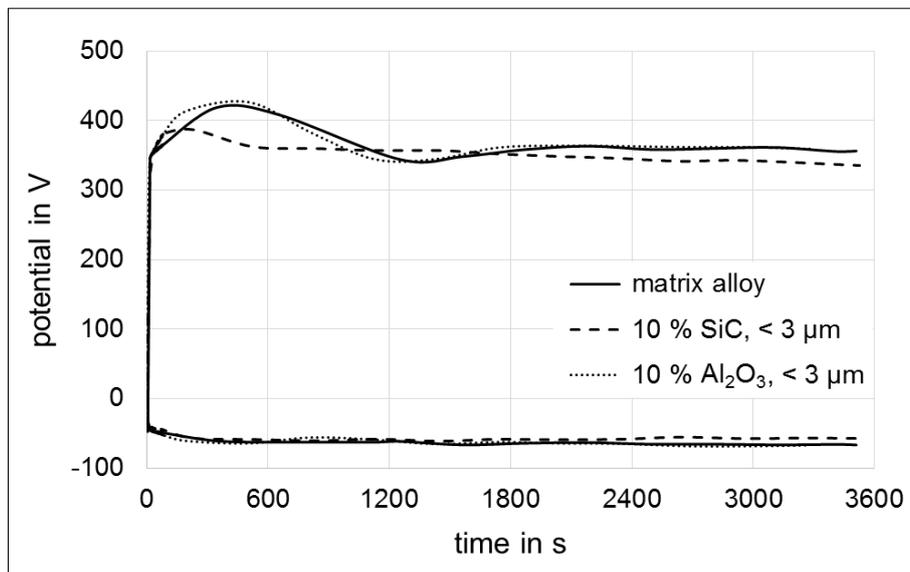


Figure 1. Envelopes of positive and negative potential amplitudes as a function of time during PEO process with pulsed current.

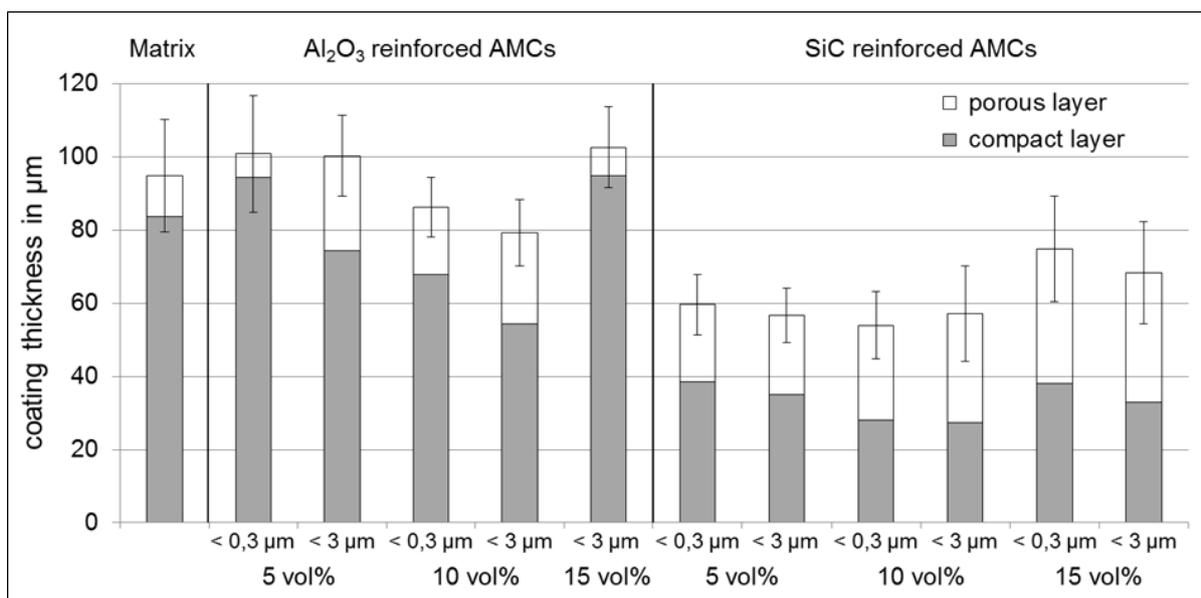


Figure 2. Comparison of total thickness, thickness of porous layer and compact layer for PEO coatings on matrix alloy as well as SiC and Al₂O₃ reinforced AMCs with varying particle sizes and particle volume contents

3.2 Coating properties

The observation of Wang et al. [4] that PEO coatings on SiC reinforced AMCs exhibit higher porosity than those on Al₂O₃ reinforced material can be approved by SEM investigations (figures 3a and 4a). It can be seen from high magnification images that both materials show microscale porosity in close vicinity to the substrate coating interface (figures 3b and 4b) which is a typical phenomenon in PEO processes. Fine submicron scale porosity (highlighted in figure 3b) with a similar size as copper containing precipitates (highlighted in figure 4b) can be observed in the PEO coatings on both AMC

substrates. It might be concluded that some of those pores evolved due to the dissolution of the intermetallic phases (IMP). In accordance with the literature, it can be assumed that Al_2O_3 particles are incorporated into the PEO coating without any chemical interactions. However, they can hardly be differentiated from the Al_2O_3 matrix and, therefore, are not detectable within the PEO coating by SEM investigations. PEO coatings on SiC reinforced AMCs exhibit larger pores additionally to the submicron scale porosity. As indicated in figure 3b, silicon rich particles can be detected qualitatively within these pores by EDS spot measurements. In accordance with the theory of Xue et al. [5], SiC particles are gradually transformed into oxide phases and finally dissolved. However, it has to be emphasized that conversion and dissolution of SiC particles cause the increasing coating porosity. As SiC particles are not electrically insulating like Al_2O_3 particles, the particle dissolution might be accompanied by oxygen evolution and, therefore, pore formation. The side process of gas evolution consumes the electrical charge, which means that less electrical energy is available for coating growth. This would be an explanation for the lower thickness of PEO coatings on SiC reinforced AMCs.

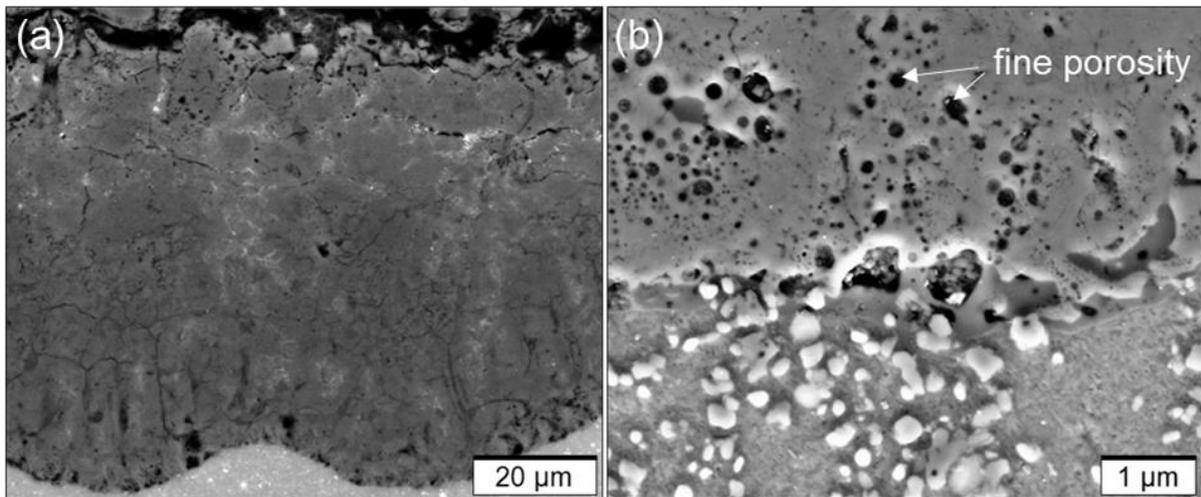


Figure 3. Microstructure of PEO coatings on AMCs with 10 vol% Al_2O_3 particles $< 3 \mu\text{m}$: a) BSD overview image, b) SE close-up image of the substrate-coating interface

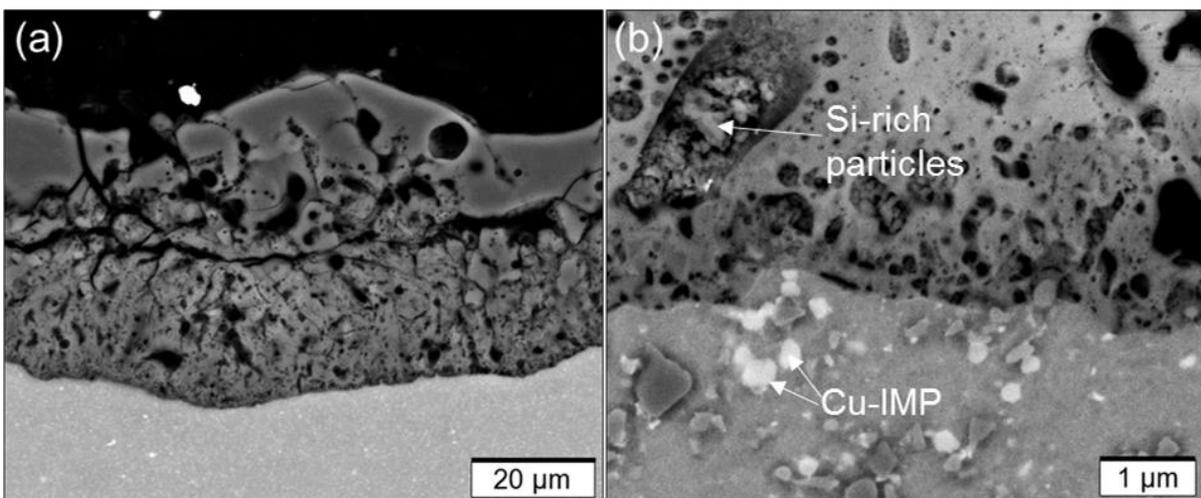


Figure 4. Microstructure of PEO coatings on AMCs with 10 vol% SiC particles $< 3 \mu\text{m}$: a) BSD overview image, b) ESB close-up image of the substrate-coating interface

Generally, the coating hardness decreases with increasing distance to the substrate/coating interface within the inner compact layer due to the growing amount of amorphous phases and slightly increasing porosity. It can be seen from figure 5a, that PEO coatings on SiC reinforced AMC exhibit significantly lower hardness values in comparison to those on the matrix alloy. More precisely, the hardness of PEO coatings decreases with increasing SiC particle content as a higher particle density in the AMC enhances the formation of pores. Furthermore, coating hardness is decreasing with increasing particle size at constant particle content because large particles leave large pores after dissolution. In contrast to this, the coating hardness is slightly improved by the presence of small Al_2O_3 particles (filled symbols in figure 5b) compared with PEO coatings on the unreinforced matrix alloy (dotted line in figure 5b). Larger Al_2O_3 particles (unfilled symbols in figure 5b) do not influence the coating hardness significantly. Furthermore, there is no considerable correlation between coating hardness and particle volume fraction.

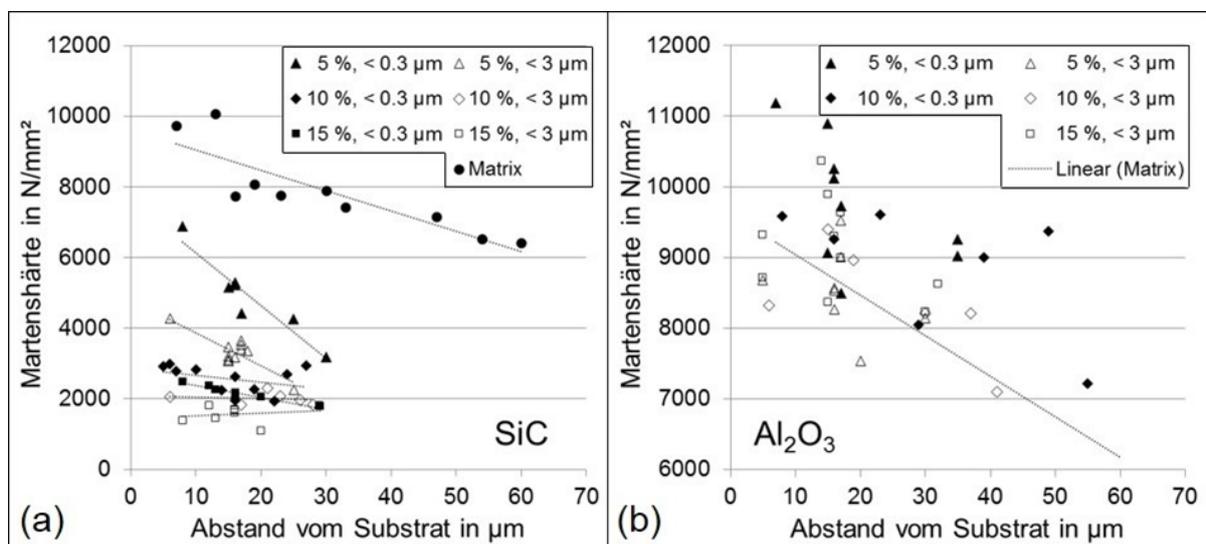


Figure 5. Hardness profiles of PEO coatings on a) SiC and b) Al_2O_3 reinforced AMCs with different particle volume fractions and particle sizes

Sliding wear behavior of uncoated SiC and Al_2O_3 reinforced AMCs with 10 vol% particle content and particle size $< 3 \mu\text{m}$ was investigated as a reference for the wear resistance of PEO coatings. Both types of AMCs exhibit a comparable wear behavior. As numerous cracks and flat pittings can be observed within the wear tracks by SEM investigations, it can be verified that fatigue and delamination wear are the dominating wear mechanisms. In many cases the edges of pittings were overlapped by plastic deformation of the surrounding material. Wear depths and cross section profiles of wear traces are also similar for both uncoated AMCs, thus, only one profile for Al_2O_3 reinforced material is displayed in figure 6a. It can be seen from this profile that wear depth was about $10 \mu\text{m}$ and material accumulation took place at the edges of the wear trace due to plastic deformation. However, the porous PEO coatings on SiC reinforced AMCs exhibit distinct wear traces with depths of 20 to $30 \mu\text{m}$ (figure 6a) and significantly higher wear volumes compared with the untreated material (figure 6b). Furthermore, it can be seen from the BSD cross section image (figure 7a) and the cross section profile (figure 6a) that there is a sharp transition between unworn surface and wear trace. The outer porous layer is removed quickly; however, the inner compact layer withstands sliding wear. Fatigue cracks are stopped by fine pores within the compact layer and do not reach the substrate surface. Moreover, the steel counter body is worn when it gets in contact with the hard inner layer. The adherent layer of compacted fine-grained debris from PEO coating and counter body consisting of iron rich and alumina particles with sizes below $2 \mu\text{m}$ can occasionally be observed at the worn PEO

surface. In contrast to this, no significant wear of PEO coatings on Al₂O₃ reinforced AMCs can be observed. However, due to the high hardness of the PEO coating, the steel counter body is severely worn during sliding wear tests. Thus, wear traces are almost completely covered by a layer of compacted wear debris, which also consists of fine iron-rich and alumina particles. This accumulated debris can be suggested by the cross sectional profile of the wear trace in figure 6a and can be seen as a bright layer on top of the PEO coating in BSE image figure 7b.

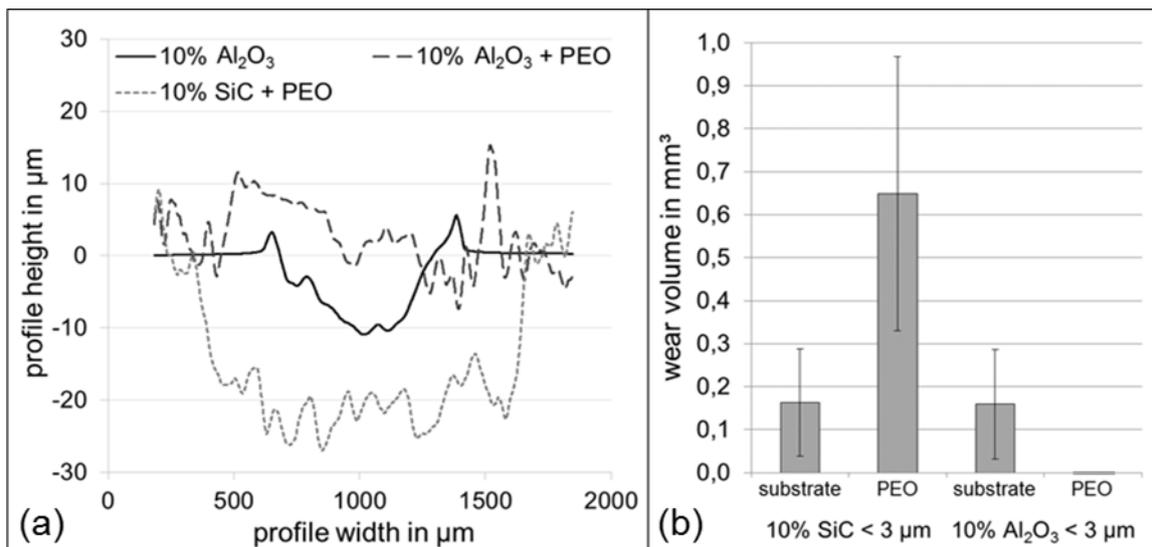


Figure 6. a) Elevation profile and b) wear volume of wear tracks on uncoated and PEO treated AMCs s

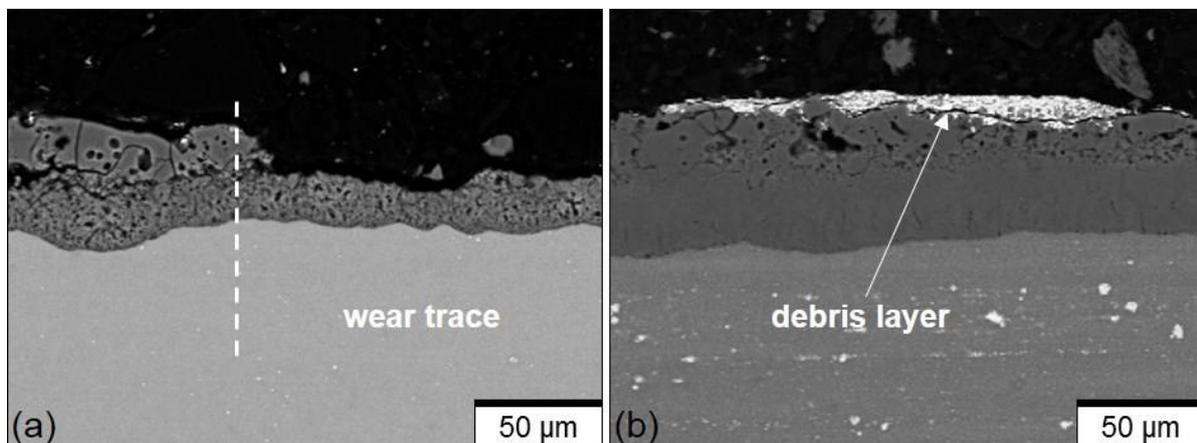


Figure 7. Cross sections of wear traces of PEO coatings on AMCs reinforced with 10 vol%, < 3 μm a) SiC and b) Al₂O₃ particles (BSD images)

One possibility of improving the wear resistance of porous PEO layers on SiC reinforced AMCs could be the infiltration of pores by sol-gels or nanoparticle reinforced polymers. Similar process combinations were recently applied to porous PEO coatings on magnesium alloys in order to improve their corrosion and wear resistance [10]. Furthermore, the application of an aluminum layer by thermal spraying enables the formation of compact wear resistant coatings on numerous substrates that are not well suited for PEO treatment [11].

4. Conclusions

The influence of different particle types, sizes and volume contents on the PEO process as well as on the microstructure evolution and the properties of PEO coatings on AMCs were investigated. It is apparent that the coating thickness and hardness are not significantly deteriorated by the incorporation of Al₂O₃ particles. A slight increase in coating hardness can be observed when small Al₂O₃ particles (< 0.3 μm) are present in the AMC. As a consequence of high hardness and low porosity, PEO coatings on Al₂O₃ reinforced AMCs do not show any wear damage after sliding wear tests. In contrast to this, PEO coatings with significantly lower coating thickness and higher porosity develop on SiC reinforced AMCs at the same electrical charge quantity and similar electrical energy consumption. Furthermore, porosity increases with increasing particle volume fraction and particle size, because the gradual dissolution of SiC particles in the vicinity of microarc discharges causes pores within the coating. As SiC particles exhibit a significantly lower electrical resistivity than the alumina rich PEO layer, oxygen might evolve during the electrochemical particle dissolution. This could also be a reason for higher porosity and lower coating growth efficiency. Despite protecting the substrate material from wear, the porous outer layer of PEO coatings on SiC reinforced AMCs was severely worn during sliding wear tests.

Because of the severe wear of steel counter bodies against compact PEO coatings, it became evident that the implementation of PEO treated AMCs in sliding contacts also necessitates the development of appropriate counter body materials. This might also be achieved by the use of surface and coating technologies.

Acknowledgement

The authors gratefully acknowledge funding by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) within the framework of the Collaborative Research Centre 692 (SFB HALS 692). The technical assistance of C. Cai, D. Spieler, Dr. D. Dietrich, K. Muhr and C. Gläser is also gratefully acknowledged.

5. References

- [1] Prasad S V and Asthana R 2004 *Tribol. Lett.* **17** 445
- [2] Deuis R L, Subramanian C, Yellup J M 1997 *Compos. Sci. Technol.* **57** 415
- [3] Sieber M, Mehner T, Dietrich D, Alisch G, Nickel D, Meyer D, Scharf I and Lampke T 2014 *Surf. Coat. Technol.* **240** 96
- [4] Wang Y K, Sheng L and Xiong R Z, Li B S 1999 *Surf. Eng.* **15** 112
- [5] Xue W 2006 *Appl. Surf. Sci.* **252** 6195
- [6] Cui S, Han J, Du Y and Li W 2007 *Surf. Coat. Technol.* **201** 5306
- [7] Ceschini L, Martini L, Sambogna G and Tarterini F 2011 *Mater. Sci. Forum* **678** 61
- [8] Podlesak H, Siebeck S, Mücklich S, Hockauf M, Meyer L W, Wielage B and Weber D 2009 *Materialwiss. Werkstofftech.* **40** 500
- [9] Morgenstern R, Nickel D, Dietrich D, Scharf I and Lampke T 2015 *Mater. Sci. Forum* **825-826** 636
- [10] Castellanos A, Altube A, Vega J M, García-Lecina E, Díez J A and Grande H J 2015 *Surf. Coat. Technol.* **278** 99
- [11] Wielage B, Meyer D, Pokhmurska H, Alisch, G and Grund T 2008 *Materialwiss. Werkstofftech.* **39** 920